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THÈSE EN COTUTELLE PRÉSENTÉE

POUR OBTENIR LE GRADE DE

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SPÉCIALITÉ BIOGÉOCHIMIE ET ÉCOSYSTEMES

Par **Pablo RAGUET**

**Long-term mineralization of organic phosphorus in
agricultural soils: evaluation and control factors**

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Résumé

La disponibilité du phosphore (P) du sol pour les plantes cultivées (phytodisponibilité) est au centre d'enjeux agronomiques (production agricole, raisonnement de la fertilisation) et environnementaux (eutrophisation, pénurie des réserves mondiales) importants. Le phosphore (P) total du sol est à 30-40% sous forme de composés organiques (POS) dans la couche labourée. La minéralisation du POS est peu connue, alors même que ce processus pourrait contribuer à la phytodisponibilité du P du sol et ainsi à la nutrition phosphatée des plantes cultivées.

L'objectif de cette thèse est de chiffrer la minéralisation à long-terme du POS dans les conditions du champ et d'en identifier les facteurs de contrôle (e.g. spéciation du POS, propriétés du sol, conditions climatiques).

Pour répondre à ces questions, quatre dispositifs expérimentaux de longue durée (LTFE) ont été utilisés, deux appartenant au réseau des LTFE de l'INRAE sur la fertilisation minérale et les deux autres à l'observatoire de recherche en environnement sur les produits résiduels organiques (SOERE-PRO). Ils ont été sélectionnés pour couvrir une diversité de situations agropédoclimatiques. L'hypothèse sous-jacente associée est que la nature (superphosphate, composts urbains, boues de STEP, fumier de vache) et la dose (entre 0 et 112 kg P ha⁻¹ an⁻¹) des apports d'engrais, la gestion des résidus de culture, le type de sols, les conditions climatiques, la succession culturale, pourraient affecter la vitesse de minéralisation du POS (Vm-POS). De plus, les bases de données des séries chronologiques de mesures sur les cultures et les sols de ces essais sont complètes, et les échantillons de terre régulièrement échantillonnés ont été stockés. Cela a permis de déterminer les évolutions des teneurs en POS et en P inorganique du sol (PIS) pendant plusieurs décennies, ainsi que le cumul du budget phosphaté des parcelles ($B_{cum} = \sum (P \text{ apporté} - P \text{ exporté dans les récoltes})$). Vm-POS a été calculée à l'aide du modèle bi-compartimental de Hénin and Dupuis (1945). Ce modèle décrit l'évolution annuelle du stock de POS en fonction de sa minéralisation et de l'incorporation de P au POS par la décomposition des résidus de culture et des PRO. Dans deux des quatre LTFE, la spéciation du POS et du PIS a été déterminée par résonance magnétique nucléaire du P dans des solutions NaOH-EDTA (RMN-P).

Le stock initial de POS varie considérablement entre les essais de 368 à 1145 kg ha⁻¹. En moyenne des essais et traitements, 3.2 kg P ha⁻¹ an⁻¹ de résidus aériens et racinaires post-récolte ont été incorporés au stock de POS pour 10.9 kg P ha⁻¹an⁻¹ libérés dans la solution du sol. Pour les PRO, l'apport de P varie considérablement de 24 à 112 kg P ha⁻¹an⁻¹ (moyenne 32.4) selon le mode de raisonnement (soit 2 t C-PRO ha⁻¹ an⁻¹, soit 170 kg N-PRO ha⁻¹ tous les deux ans) et du rapport C/P et N/P. En moyenne, 5.5 kg P ha⁻¹an⁻¹ ont été incorporés au POS et 26.9 kg P ha⁻¹an⁻¹ libérés dans la solution de sol.

Vm-POS est comprise entre 1.7 et 11.2 kg P ha⁻¹ an⁻¹ (5.1 en moyenne soit 0.8% du stock de POS) avec un temps de résidence compris entre 56 et 227 ans. Les résultats de RMN-P indique que le POS est majoritairement sous forme d'orthophosphate monoesters, les inositolhexakisphosphates (IHP) y étant prédominants. Les faibles valeurs de Vm-POS pourraient être expliquées par la présence des IHP, connus pour s'associer fortement avec la phase solide du sol, et par une concentration élevée d'ions phosphates en solution, qui pourrait inhiber la catalyse enzymatique des IHP. Malgré des valeurs de Bcum très différentes (de -724 à +1830 kg P ha⁻¹ pour l'un des essais), le stock de POS est invariant dans tous les LTFE, alors que, au contraire, le stock de PIS change strictement en fonction des valeurs de Bcum.

En conclusion, ce travail de thèse indique que Vm-POS est faible, bien que variable entre les quatre LTFE. Elle varie proportionnellement au stock de POS mais les déterminants de ce stock et du coefficient de minéralisation n'ont pu être clairement identifiés, probablement par manque de situations analysées. Ce flux contribue à alimenter marginalement le compartiment de P phytodisponible du sol, par rapport au processus de diffusion des ions phosphate à l'interface solide-solution.

Mots-clés : Phosphore organique du sol, Agrosystèmes, Cycle biogéochimique, Fertilisation, Phytodisponibilité, Essai agronomique de longue durée.

Abstract

Total phosphorus (P) in the plough layer of cropped soils is at 30-40% in the form of organic compounds (SOP). Little is known about SOP mineralization, even though this process may significantly contribute to the soil plant-available P and therefore to the P nutrition of cropped plants.

The objective of this thesis is to quantify the long-term mineralization of SOP under field conditions and to identify its driving factors (SOP speciation, soil properties, climatic conditions).

To answer these questions, four long-term field experiment (LTFE) were selected, two belonging to the INRAE LTFE network on mineral fertilization and the other two to the Observatory of Environmental Research on Organic Waste Products, i.e. OWP (SOERE-PRO). They were selected to cover a diversity of agropedoclimatic situations. The underlying hypothesis is that the nature (superphosphate, urban composts, urban sewage sludge, cattle manure) and the fertilization P dose (between 0 and 112 kg P ha⁻¹ yr⁻¹), crop residue management, soil classification, climatic conditions, and crop succession, affect the SOP mineralization rate. In addition, the time-series databases of crop and soil measurements from these trials are complete, and the soil were regularly sampled and stored. This allowed determining changes in soil SOP and inorganic P (SIP) levels over several decades, as well as the plot cumulative P budget ($B_{cum} = \sum(P_{supplied} - P_{exported\ in\ crops})$). The SOP mineralization rate was calculated using the bi-compartmental model of Hénin and Dupuis (1945). This model describes the annual evolution of the SOP stock as a function of its mineralization and the incorporation of P into the SOP through the decomposition of crop residues and OWP. In two of the four LTFE, the speciation of SOP and SIP was determined by nuclear magnetic resonance of P in NaOH-EDTA solutions (P-NMR).

The initial SOP stock varied considerably among the trials from 368 to 1145 kg ha⁻¹. On average across trials and treatments, 3.2 kg P ha⁻¹yr⁻¹ of post-harvest aerial and root residues were incorporated into the SOP stock for 10.9 kg P ha⁻¹yr⁻¹ released into the soil solution. For OWP, P input varied considerably from 24 to 112 kg P ha⁻¹yr⁻¹ (mean 32.4) depending on the reasoning (i.e. 2 t C-OWP ha⁻¹yr⁻¹ or 170 kg N-OWP ha⁻¹ every two years) and the C/P and N/P ratio. On average, 5.5 kg P ha⁻¹yr⁻¹ was incorporated into the

SOP and $26.9 \text{ kg P ha}^{-1}\text{yr}^{-1}$ was released into the soil solution.

The SOP mineralization rates ranged from 1.7 to $11.2 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ (5.1 on average or 0.8% of the SOP stock) with a residence time ranging from 56 to 227 yrs. The P-NMR results indicate that the SOP is predominantly in the form of orthophosphate monoesters, in which inositolhexakisphosphates (IHP) are the main compounds. The low SOP mineralization values could be explained by the presence of IHP, which are known strongly interact with the soil solid phase, and by a high concentration of phosphate ions in soil solution, which could inhibit the enzymatic catalysis of IHP. Despite very different B_{cum} values (between -724 and $+1830 \text{ kg P ha}^{-1}$ for one of the trials), the SOP stock is constant in all LTFE while, on the contrary, the SIP stock changes strictly according to B_{cum} values.

In conclusion, this thesis indicates that SOP mineralization is low, although variable among the four LTFE. It varies proportionally to the SOP stock but the drivers of this stock and of the mineralization coefficient could not be clearly identified, probably due to the scarcity of analyzed situations. This mineralization flux contributes marginally to the soil plant-available P, compared to the diffusion mechanism of phosphate ions at the solid-to-solution interface.

Keywords: Soil organic phosphorus, Agrosystems, Biogeochemical cycle, Fertilization, Plant-availability, Long-term field experiment.

Résumé substantiel

La gestion du phosphore (P) dans les sols agricoles est au centre d'enjeux agronomiques (production agricole, raisonnement de la fertilisation) et environnementaux (eutrophisation, pénurie des réserves mondiales) majeurs. Les méthodes d'extraction chimique utilisées pour évaluer la disponibilité du P du sol pour les plantes cultivées (phytodisponibilité) se sont révélées insatisfaisantes. Il est donc impératif d'adopter une approche plus efficace qui implique l'analyse, la compréhension et la quantification des mécanismes clés associés à la nutrition phosphatée des cultures dans des conditions au champ. De l'ordre de 30 à 40 kg de P est absorbé par la plante durant sa période de croissance, mais seule une faible portion provient de la solution du sol. La diffusion des ions phosphate à l'interface solide-solution semble être le principal mécanisme de réapprovisionnement de la solution du sol en ions phosphate. Toutefois, les recherches sur ce mécanisme ont rarement pris en compte les processus biologiques. Le phosphore organique du sol (POS) représente 30 à 40% P total du sol. En outre, les sols cultivés abritent une communauté microbienne capable de minéraliser le POS. Ainsi, il existe un consensus pour reconnaître que le POS pourrait jouer un rôle dans la nutrition des plantes en libérant des ions phosphate par minéralisation enzymatique. La vitesse de minéralisation du POS (V_m -POS) dans les conditions du champ reste largement méconnue, ce qui ne permet pas d'estimer l'importance de ce processus dans l'offre du sol en P phytodisponible. Dans cette thèse, nous avons cherché à quantifier la minéralisation à long-terme du POS dans les conditions du champ et d'identifier les facteurs de contrôle (e.g. spéciation du POS, propriétés du sol, conditions climatiques).

Pour répondre à ces questions de recherche, quatre dispositifs expérimentaux de longue durée (LTFE) ont été utilisés. Deux appartiennent au réseau des LTFE de l'INRAE sur la fertilisation minérale et les deux autres à l'observatoire de recherche en environnement sur les produits résiduels organiques (SOERE-PRO). Ces quatre sites ont été sélectionnés pour couvrir une large diversité de situations agropédoclimatiques. Nous avons ainsi testé l'hypothèse que la nature (superphosphate, composts urbains, boues de STEP, fumier de vache) et la dose (entre 0 et $112 \text{ kg P ha}^{-1} \text{ an}^{-1}$) des apports d'engrais, la gestion des résidus de culture, le type de sol, les conditions climatiques, la succession culturale, pourraient affecter V_m -POS. Les quatre LTFE étudiés présentent des bases de données complètes de

séries chronologiques de mesures sur les cultures et les sols, ainsi que des échantillons de terre régulièrement prélevés et stockés. Cela a permis de déterminer les évolutions des teneurs et stocks de POS et P inorganique du sol ($PIS = P \text{ total du sol} - POS$) sur plusieurs décennies, ainsi que le cumul du bilan phosphaté des parcelles [$Bcum = \sum (P \text{ apporté} - P \text{ exporté dans les récoltes})$]. Vm-POS a été calculée en transposant au POS le modèle bi-compartimental de Hénin and Dupuis (1945). Ce dernier décrit l'évolution annuelle du stock de POS en fonction de sa minéralisation et de l'incorporation de P au POS issu de la décomposition des résidus de culture et des PRO. Dans deux des quatre LTFE, la spéciation du POS et du PIS a été déterminée par résonance magnétique nucléaire du P dans des solutions de NaOH-EDTA (RMN-P ; Cade-Menun and Preston 1996). Les trois chapitres portent sur les thèmes suivants : (1) Le calcul de Vm-POS au champ dans un LTFE et sa relation avec la spéciation du P du sol, sous une monoculture de maïs avec trois taux de fertilisation minérale différents ; (2) le calcul de Vm-POS et la comparaison de ces vitesses dans trois LTFE, qui diffèrent selon le type de sol, le climat et les pratiques de gestions ; (3) l'effet de la fertilisation répétée sur le long terme de différents PRO sur le statut et la spéciation du P du sol.

L'objectif du **chapitre 1** était de modéliser la dynamique à long-terme du POS dans un sol cultivé sous grandes cultures, en considérant que des régimes contrastés de fertilisation minérale phosphatée pourraient modifier la spéciation des résidus de culture et du POS, modifiant ainsi leurs capacités à libérer des ions phosphate. Nous nous sommes appuyés sur un essai agronomique de 28 ans, entre 1972 et 2000, situé à Tartas (40) en France (LTFE0). L'essai comprenait trois régimes de fertilisation minérale (4 répétitions disposées en blocs), apportée sous forme de triple superphosphate, avec : i) pas de fertilisation phosphatée (TEM_0) ; ii) 44 kg P ha⁻¹ apportés (TSP_{44}) ; iii) 96 kg P ha⁻¹ apportés (TSP_{96}). Le sol légèrement acide ($pH_{eau} = 5.9$) est un Arénosol luviq de texture sablo-limoneuse et cultivé sous une monoculture de maïs. Les rendements en grains ainsi que leurs teneurs en P ont été mesurés chaque année. Les résidus de culture aériens ainsi que leurs teneurs en P ont été mesurés en 1993, 1995, 1996, 1997 et 1998. La relation entre l'indice de rendement phosphaté (rapport entre la masse de P dans la récolte et la masse de P dans l'ensemble de la biomasse aérienne) et Bcum a permis d'extrapoler la teneur en P des résidus de culture aériens aux autres années de l'essai. La quantité de P retourné au sol dans les résidus de maïs a ainsi pu être calculée à partir du rendement et de la teneur en P des grains. Des échantillons de sol ont été prélevés dans la couche labourée (0–25 cm) dans chaque parcelle en 1976, 1977, 1978, 1980, 1983, 1986, 1988, 1992, 1995, 1998 et 2000. Ces échantillons ont été analysés pour des indicateurs du statut phosphaté du sol : i) le P total du sol (TP_{HF}), extraction par digestion avec les acides fluorhydrique et perchlorique concentrés (NF X 31-147) ; ii) le POS (Saunders and Williams 1955) ; iii) le PIS ; iv) le P du sol, disponible pour les plantes (C_P : concentration des ions orthophosphates dissous après mise en suspension ; rapport V/M de 10) ; v) le P extrait (P-Olsen) par une solution

de bicarbonate de sodium 0.5 M (Olsen et al. 1954). Les échantillons de sol de 2000 ont été analysés par RMN-P. Pour déterminer Vm-POS comme présenté plus haut, les variables d'entrée du modèle Hénin and Dupuis (1945) transposé au POS sont : i) le stock initial de POS ; ii) les apports de P au sol par les résidus de culture, avec les grains perdus à la récolte (3% du rendement), les résidus aériens et les résidus souterrains (calculés avec un rapport biomasse racinaire/aérienne de 0.18). Les paramètres du modèle sont : i) h, le coefficient d'incorporation au POS après 1 an du P pour chaque type de résidus, il est de 0.14 pour les résidus aériens de maïs, de 0.17 pour les résidus racinaires et 0.4 pour les grains perdus à la récolte ; ii) k, le coefficient de minéralisation brute annuelle du POS. Le modèle calcule la valeur de k en minimisant les écarts entre les valeurs observées et les valeurs simulées de POS chaque année. Par la suite, nous avons calculé le flux d'ions phosphate issus de la minéralisation du POS et de la décomposition des résidus de culture avant leur incorporation au POS.

Le rendement annuel en grains (moyenne des 28 récoltes et des 3 traitements) était de 9.9 ± 1.5 t MS ha⁻¹. Le rendement décroît systématiquement dans le traitement TEM₀ à partir de 1992 et accélère avec la durée de l'essai jusqu'à -9.1% du rendement du traitement TSP₄₄ sur la période 1995–2000. La concentration moyenne en P des grains était de 3.0 ± 0.4 mg P kg⁻¹ MS. La quantité moyenne de P exporté était de 29.2 ± 6.0 kg P ha⁻¹ an⁻¹. Sur la période de l'essai, entre 1972 et 2000, le stock de POS est resté constant quel que soit le régime de fertilisation phosphatée. Le stock initial était de 368 kg P ha⁻¹ et tend à augmenter de façon non significative de $+1.6 \pm 0.9$ kg P ha⁻¹ an⁻¹. À l'inverse, le PIS est fortement affecté par le régime de fertilisation phosphatée : le stock décroît de -19.1 ± 3.0 kg P ha⁻¹ an⁻¹ dans TEM₀ ; augmente légèrement de $+9.2 \pm 3.0$ kg P ha⁻¹ an⁻¹ quand la fertilisation correspond aux exportations de P dans la récolte (TSP₄₄) ; et augmente de $+31.8 \pm 3.0$ kg P ha⁻¹ an⁻¹ quand les apports de P sont largement supérieurs aux exportations (TSP₉₆). L'optimisation du coefficient de minéralisation brute annuelle k a donné une valeur moyenne de 0.0047 ± 0.0049 an⁻¹, ce qui correspond à un temps de résidence moyen du P dans le POS de 212 ans. Vm-POS était de 1.7 ± 1.2 kg P ha⁻¹ an⁻¹. La quantité de P retourné au sol dans les résidus de culture représentait 17 kg P ha⁻¹ (moyenne sur les trois régimes de fertilisation et sur l'ensemble des organes végétaux), avec un taux d'incorporation au POS après un an de 17%. En moyenne sur les trois régimes de fertilisation, les résidus de culture ont émis par décomposition (< 1 an) 14.2 kg P ha⁻¹ an⁻¹ d'ions phosphate. En 2000, la solution de NaOH-EDTA a extrait 81% du TP_{HF}. 76% du P_{NE} était sous forme inorganique, dont 98% était des ions orthophosphates. 24% du P_{NE} était organique, dont 77% sous forme d'orthophosphate monoesters, 20% sous forme d'orthophosphate diesters et 3% sous forme de phosphonates. Les inositols hexakisphosphates (IHP) représentaient les principales formes de P organique (50%), en majorité sous forme de *myo*-IHP (23% du P organique extrait).

L'objectif du **chapitre 2** était de déterminer Vm-POS dans différentes situations agropédo-climatiques. L'approche par modélisation, proposée dans le chapitre 1, a été utilisée pour calculer Vm-POS dans trois LTFE. Dans un de ces essais (LTFE1), ont été étudiés, de 1975 à 1992 les effets du superphosphate triple (phosphate monocalcique (45% P_2O_5), engrais minéral de synthèse soluble dans l'eau), apporté à raison de 0, 27, et 79 kg P ha⁻¹ an⁻¹. Le sol est de texture limono-sableuse (Arénosol luvique) et cultivé sous monoculture de maïs irrigué en climat océanique. Dans les deux autres, l'un appelé QualiAgro (LTFE2, 1998-2016) et l'autre PROspective (LTFE3, 2000-2014), les effets de différents PRO (composts urbains, boue déshydratée de station d'épuration urbaine et fumier de vaches) ont été étudiés. Ils ont été apportés à raison de 2 t C ha⁻¹ an⁻¹ en moyenne dans LTFE2, et de 170 kg N ha⁻¹ tous les deux ans dans LTFE3. Ces deux essais comportent aussi un traitement témoin ne recevant pas d'apport de PRO. Compte tenu du mode de raisonnement des apports et de ratio C/P ou N/P variable entre PRO, l'apport de P a varié suivant les PRO entre 24 et 112 kg P ha⁻¹ an⁻¹ dans LTFE2 et entre 17 et 45 kg P ha⁻¹ an⁻¹ dans LTFE3. Le sol de LTFE2 est un limon (Luvisol glossic) du bassin parisien (78) principalement cultivé sous une rotation maïs-blé en climat océanique dégradé. Le sol de LTFE3 est un sol carbonaté (Cambisol calcique) du nord-est de la France (68) cultivé sous une succession blé/maïs/orge/betterave sucrière en climat semi-continentale. Dans les trois essais, le rendement à maturité et sa teneur en P avaient été déterminés chaque année, de même que la quantité de P restituée au sol sous forme de résidus de récolte (parties aériennes, racinaires). Les échantillons de sol ont été analysés pour leur teneur en POS et PIS.

En moyenne, le P des PRO est à 80% sous forme inorganique et 20% sous forme organique (11% pour les composts urbains, 17% pour la boue déshydratée de STEP et 36% pour le fumier de vache). La moyenne générale des rendements à la récolte est de 8.5 t MS ha⁻¹ an⁻¹. La perte moyenne est de -4% et -10%, respectivement dans le traitement témoin de LTFE1 et LTFE2. Pour LTFE3, il n'y a pas de différence significative entre les traitements. La moyenne générale de la quantité de P exporté est de 26 kg P ha⁻¹ an⁻¹ et suit les mêmes tendances que le rendement. La quantité de P restitué au sol sous forme de résidus de récolte (à 68% sous forme inorganique) est de 15.0, 13.5 et 11.5 kg P ha⁻¹ an⁻¹, respectivement pour LTFE1, LTFE2 et LTFE3. Bcum varie significativement entre les années, essais et traitements. Par exemple, les valeurs de Bcum en 2016 dans LTFE2 sont comprises entre -380 kg P ha⁻¹ dans le traitement témoin et +1520 kg P ha⁻¹ en apportant le compost de boue urbaine. Le stock initial de POS diffère significativement entre les essais (de 446 ±13 dans LTFE1 à 1145 ±22 kg ha⁻¹ dans LTFE3). La quantité moyenne de P incorporé au POS par la décomposition des résidus et des PRO est respectivement de 2.5 ±0.1, 11.0 ±1.0, et 7.9 ±0.7 kg P ha⁻¹ an⁻¹, pour LTFE1, LTFE2, et LTFE3, les valeurs du coefficient k de 0.0046, 0.018, et 0.0044 an⁻¹ (soit des temps de résidence de 217, 56 et 227 ans), et Vm-POS de 2.1 ±0.1, 11.2 ±0.5, et 5.4 ±0.3 kg P ha⁻¹ an⁻¹. Finalement,

le stock de POS n'est pas affecté par les valeurs de Bcum. Par contre, le stock de PIS initialement beaucoup plus élevé (de 1048 ± 73 dans LTFE1 à 3104 ± 30 kg ha⁻¹ dans LTFE3) varie significativement à la baisse ou à la hausse en étroite correspondance avec les valeurs de Bcum.

L'épandage en agriculture de matières fertilisantes organiques est à même d'améliorer la fertilité chimique des sols en apportant les nutriments nécessaires à une croissance optimale des plantes. L'objectif du **chapitre 3** était de déterminer comment l'épandage répété de différents composts urbains et d'un fumier modifie les concentrations de P des sols, ainsi que sa spéciation et sa disponibilité, et d'analyser le lien entre la spéciation du P des produits apportés et des sols les recevant. Nous avons exploité les bases de données de QualiAgro (LTFE2, présenté plus haut). Cinq traitements y sont étudiés : i) un compost d'ordures ménagères résiduelles (OMR) ; ii) un compost de déchets verts et/ou broyats de palettes et/ou rafles de maïs et de boues de stations d'épuration urbaines (DVB) ; iii) un compost de déchets verts et de la fraction fermentescible des ordures ménagères (BIOD) ; iv) un fumier de vaches laitières (FUM) ; v) un témoin ne recevant pas d'apport de P (TEM) jusqu'en 2013. Neuf épandages (1998, 2000, 2002, 2004, 2006, 2007, 2009, 2011, 2013) ont été effectués à raison de 4 t C ha⁻¹ et un autre en 2015 de 2 t C ha⁻¹. De 1998 à 2013, toutes les parcelles (témoins inclus) reçoivent chaque année un apport d'azote minéral (solution azotée), calculé selon la méthode du bilan prévisionnel. À partir de 2014, QualiAgro est géré suivant les pratiques de l'agriculture biologique, un engrais organique (mélange de poudre d'os et de farine de viande) est apporté à la place de la solution azotée. Des échantillons de la couche labourée (0-25 cm) ont été prélevés dans chaque parcelle à l'automne 1998 (avant le premier épandage) et début 2016 pour suivre plusieurs indicateurs du statut phosphaté : i) le TP_{HF} ; ii) le POS ; iii) le PIS ; iv) la spéciation des formes inorganiques et organiques de P par RMN-P ; v) C_P ; vi) le P-Olsen.

La teneur en TP_{HF} (moyenne des 10 épandages) de OMR, FUM, BIOD et DVB est respectivement de 3.6, 5.8, 4.7, and 12.8 g P kg⁻¹ MS avec un rapport C/P de 86, 56, 47 et 21. L'apport de P (inclut le P apporté par l'engrais organique à partir de 2014) pendant les 17 années de suivi est en moyenne de 3, 24, 40, 46 et 112 kg P ha⁻¹ an⁻¹, respectivement pour TEM, OMR, FUM, BIOD, et DVB. Le P de ces produits est majoritairement inorganique (moyenne de 87%), composé à 98% d'ions orthophosphate ; les 19% du P restant est sous forme de composés organiques, répartis entre des orthophosphate monoesters (65%), des orthophosphate diesters (24%) et des phosphonates (11%). Le rendement annuel en grains (moyenne des 17 récoltes et des 5 traitements) est de 8.2 ± 1.3 t MS ha⁻¹ avec une teneur moyenne de 3.1 ± 0.6 mg P kg⁻¹ MS. La quantité exportée de P était de 25.6 ± 4.3 kg P ha⁻¹ an⁻¹ pour OMR, FUM, BIOD, et DVB et de 21.9 ± 4.5 kg P ha⁻¹ an⁻¹ pour TEM. Bcum est respectivement de -329 ± 15 , -9 ± 14 , 229 ± 13 , 372 ± 17 et 1544 ± 26 kg P ha⁻¹, pour les traitements TEM, OMR, FUM, BIOD et DVB. Entre

1998 et 2016, le stock de TP_{HF} des échantillons de sol baisse dans TEM, reste quasi-constant dans OMR, augmente dans BIOD, FUM et augmente considérablement dans DVB. $Bcum$ rend précisément compte de l'évolution du stock de TP_{HF} entre traitement ($TP_{HF} = 1.03 \pm 0.08 \times Bcum + 2697 \pm 60$, $R^2 = 0.90$, 20 observations) et aussi des autres indicateurs du statut P des sols (PIS, P_{NE} , P-Olsen et C_P). Le stock de POS augmente significativement de 28% entre 1998 et 2016 dans les 5 traitements sans varier entre les traitements pour une année donnée. L'analyse par RMN-P du P_{NE} des sols, échantillonnés en 1998, indique que 77% du P est sous forme de composés inorganiques (à 96% des ions orthophosphates), et à 23% sous forme de composés organiques, i.e., orthophosphate monoesters (69%), orthophosphate diesters (22%) et phosphonates (8%). En 2016, le stock d'ions orthophosphates varie selon $Bcum$ (Orthophosphate = $0.88 \pm 0.06 \times Bcum + 902 \pm 47$, $R^2 = 0.91$, 20 observations). La concentration de la majorité des formes organiques de P ne change pas significativement entre 1998 et 2016. Seules les teneurs en *myo*-IHP ainsi que des orthophosphates monoesters non identifiés augmente légèrement entre 1998 et 2016 suite à l'apport cumulé massif de P dans les différents PRO. Dans TEM, la spéciation du P reste constante sur 17 ans de culture continue, toutefois, la somme des formes organiques et inorganiques diminuent.

En conclusion, le stock initial de POS était extrêmement variable entre les essais, et compris entre 368 et 1145 kg ha⁻¹. Le P apporté dans les PRO est très majoritairement sous forme d'ions phosphate. Par conséquent, l'effet majeur des épandages successifs est d'augmenter la quantité de P du sol phytodisponible, en proportion de $Bcum$. Par contre, le stock de POS n'est pas (ou peu) affecté par la nature et la dose de P apporté, malgré des valeurs de $Bcum$ considérablement différentes entre traitements. Ainsi, les PRO étudiés ont le potentiel de remplacer les engrais phosphatés solubles dans l'eau. Toutefois, un apport raisonné sur la base d'un apport en C ou en N implique des écarts importants de P apporté entre traitements. $Vm-POS$ était faible (5.1 kg P ha⁻¹ an⁻¹ en moyenne, soit 0.8% du stock de POS avec un temps de résidence moyen de 167 ans) et variable entre essais (comprise entre 1.7 et 11.2 kg P ha⁻¹ an⁻¹ avec un temps de résidence entre 56 et 227 ans). Du fait que les flux d'incorporation et de minéralisation sont équivalents, le stock de POS reste stable au cours des essais. Les résultats de RMN-P indiquent que le POS est majoritairement sous forme d'orthophosphate monoesters, les IHP y étant prédominants. Les faibles valeurs de $Vm-POS$ peuvent être expliquées par cette abondance, avec en particulier le *myo*-IHP, fortement stabilisé par la phase solide du sol. Il nécessite des enzymes spécifiques pour être minéralisé, enzymes dont l'activité pourrait être inhibée par la forte concentration d'ions phosphate en solution. Bien que faible, $Vm-POS$ varie proportionnellement au stock de POS mais les déterminants de ce stock et du coefficient de minéralisation n'ont pu être clairement identifiés, probablement par manque de situations analysées. Le flux de minéralisation du POS est une contribution mineure au P phytodisponible du sol, par rapport au processus de diffusion des ions phosphate à l'interface solide-solution.

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List of Abbreviations

ADEME: *Agence de l'environnement et de la maîtrise de l'énergie;*

AFNOR: *Association française de normalisation;*

AIC: Akaike information criterion;

ANR: *Agence nationale de la recherche (France);*

ATP: Adenosine triphosphate;

Bcum: Plot cumulated P budget (kg P ha⁻¹);

BIOW (Fr: **BIOD**): composted biowastes (Fr: *Biodéchets compostés*);

CEC: Cation exchange capacity;

clr: Centered log-ratio transformation (for compositional analysis);

COMIFER: *Comité français d'étude et de développement de la fertilisation raisonnée;*

CON (Fr: **TEM**): Control (Fr: *Témoin*);

C_p: Phosphate ion concentrations in soil water suspension with a specific volume:mass ratio (e.g. 10);

CycP: Model describing cycling of P in agrosystems (Stroia et al. [2007](#); Messiga et al. [2012](#); Morel et al. [2014](#); Li et al. [2019](#));

DM: Dry matter;

FAO: Food and agriculture organization of the united nations;

FYM (Fr: **FUM**): Dairy farmyard manure (Fr: *Fumier de ferme laitière*);

FYMC (Fr: **FUMC**): Composted dairy farmyard manure (Fr: *Fumier de ferme laitière composté*);

GWS (Fr: **DVB**): Green waste and sewage sludge compost (Fr: *Déchets verts plus boue de station dépuración compostés*);

h_{agr}, **h_{bgr}**, and **h_{grr}**: Incorporation coefficients (dimensionless) to SOP of P in above-ground, belowground residues, and grains returned to the soil during the annual crop cycle, respectively;

HI_p: P harvest index; ratio of P in grain to P in grain and aboveground residues;

ICP-OES: Inductively coupled plasma optical emission spectroscopy;

IHP: Inositol hexakisphosphate; stereoisomers include *myo*-, *scyllo*-, *neo*-, and *D-chiro*-IHP;

INRAE: *Institut National de Recherche pour l'Agriculture, l'Alimentation et l'Environnement*;

k: Coefficient of gross SOP mineralization (yr^{-1}); **1/k** is the residence time (yr);

LAS: *Laboratoire d'analyse des sols (INRAE)*;

LTFE: Long-term field experiment;

MSW (Fr: **OMR**): Composted municipal solid waste (Fr: *Ordures ménagères résiduelles compostées*);

NaOH-EDTA: solution of NaOH and Na₂EDTA, with **EDTA**: Ethylenediaminetetraacetic;

NMR-P_i: Inorganic P compounds (phosphate ions, pyrophosphate, polyphosphosphate), determined by P-NMR in NaOH-EDTA solution;

NMR-P_o: Soil organic P compounds (orthophosphate monoesters, orthophosphate diesters, etc.), determined by P-NMR in NaOH-EDTA solution;

N_{tot}: Soil total nitrogen;

OWP (Fr: **PRO**): Organic waste product (Fr: *Produit résiduaire organique*);

P_{agr}, **P_{bgr}**, and **P_{grr}**: P amount in aboveground and belowground residues, and in grains that returned to soil during the annual crop cycle ($\text{kg ha}^{-1} \text{yr}^{-1}$), respectively;

PCA: Principal component analysis;

PLA: Percentage lack of accuracy;

PLP: Percentage lack of precision;

P_{NE}: P extracted by NaOH-EDTA solution for P-NMR analysis;

P-NMR (Fr: **RMN-P**): ³¹P nuclear magnetic resonance spectroscopy (Fr: *Résonnance magnétique nucléaire du ³¹P*);

P-Olsen: P concentration determined in bicarbonate extraction according to Olsen et al.

(1954);

P_r: Diffusive phosphate ions at the solid-to-solution interface, as a function of C_P and time (according to a kinetic Freundlich equation), and determined using the isotopic dilution approach;

Q_w: Phosphate ions in soil solution, calculated multiplying C_P by the soil-solution ratio of soil suspensions;

RMSE: Root mean square error;

RRMSE: Relative root mean square error;

SIP (Fr: **PIS**): Soil inorganic P, determined as the difference between TP_{HF} and SOP (Fr: *Phosphore inorganique du sol*);

SLU (Fr: **BOUE**): Dehydrated sewage sludge (Fr: *Boue de station d'épuration deshydraté*);

SMA: Standard major axis regression;

SOC: Soil organic carbon;

SOERE-PRO: *Système d'observations et d'expérimentations pour la recherche en environnement sur les produits résiduaux organiques*;

SOM: Soil organic matter;

SOP (Fr: **POS**): Total soil organic P, with SOP determined using the Saunders and Williams (1955) ignition method (Fr: *Phosphore organique du sol*);

TP: Soil total P, with TP_{HF} determined using concentrated hydrofluoric and perchloric acid digestion (NF X 31-147);

TSP: Triple superphosphate;

Vm-POS: *Vitesse de minéralisation du POS*.

À Romane

Les podzols sont durs à bêcher

Anonyme

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Preface

This thesis is organized into three chapters written as scientific papers in English. For each chapter, I established the research objectives and hypotheses, managed the data, performed the statistically analyses, generated all figures, and wrote the first draft. Chapter 1 is a published article inserted in this thesis, of which I am the first author. Chapter 2 and chapter 3 are only chapters.

Chapter 1 – Inserted article – “Mineralization and speciation of organic phosphorus in a sandy soil continuously cropped and phosphorus-fertilized for 28 years” was published in the journal *Soil Biology and Biochemistry* (178, 108938) in March 2023. The co-authors are Barbara Cade-Menun, Alain Mollier, Dalel Abdi, Noura Ziadi, Antoine Karam, and Christian Morel.

Chapter 2 – Chapter – “Organic phosphorus mineralization in cropped soils fertilized by different P sources. Results from three field experiments”. The co-authors are Sabine Houot, Denis Montenach, Alain Mollier, Noura Ziadi, Antoine Karam, and Christian Morel.

Chapter 3 – Chapter – “Phosphorus concentration, availability and speciation in soils after repeated applications of different urban composts and farmyard manure at the same carbon rate”. The co-authors are Barbara Cade-Menun, Sabine Houot, Alain Mollier, Noura Ziadi, Antoine Karam, and Christian Morel.

My work was directed by my thesis supervisors, Christian Morel and Antoine Karam, and co-directed by Alain Mollier and Noura Ziadi. My four supervisors are included in the papers as co-authors. The following co-authors helped with long-term experiment management, experimental design, sampling, and data acquisition: Sabine Houot and Denis Montenach. The following co-authors helped with laboratory work, sampling analysis, and editing of the manuscripts: Barbara Cade-Menun and Dalel Abdi.

GENERAL INTRODUCTION

A General context

Phosphorus (P) plays a critical role in various physicochemical and biochemical processes in living organisms. In the environment, P occurs predominantly as phosphate, a molecule composed of one P atom and four oxygen (O) atoms (PO_4). The biogeochemical cycle of P has no gaseous phase. It is an essential component of cellular metabolism, and it is involved in critical processes such as respiration and photosynthesis. The P also forms the building blocks of important molecules such as DNA and RNA, apatite in bones, or glycerophospholipids in cell membranes (Allen-Durrance 2017). Additionally, P is also vital to the storage and transfer of cellular energy as adenosine triphosphate (ATP), which has high-energy phosphate bonds ($\Delta G_0 = -7.3 \text{ kcal mol}^{-1}$) (Plante 2007).

In soils, P is a necessary and non-substitutable macronutrient for plants and thus for agricultural production (Raghothama 1999). Its availability is variable on a global scale, depending on agropedoclimatic situations (Ringeval et al. 2017). Due to exports in harvest, cropping systems inevitably diminish soil plant-available P reserves, which can lead to depletion, and ultimately to the inability to sustain agricultural production (Elliott et al. 1997; Plénet et al. 2000). It has been shown since the 19th century that the addition of soluble P had a positive effect on crop growth in long-term cropped soils (Boulaïne 2006). The question of the phosphate fertilization reasoning then became of interest to agronomic research. Therefore, long-term agronomic experiments were set up to provide data on the evolution of the phosphate status of cultivated soils and thus to monitor and understand the biogeochemical cycle of phosphorus (Boniface and Trocmé 1988; Johnston 1997; Rasmussen et al. 1998).

Since the middle of the 20th century, agricultural production in industrialized countries has relied on the use of mineral fertilizers from mining sources (Tilman et al. 2002; Cordell et al. 2009). In addition, the global population is projected to reach 10 billion by 2060 (Nations 2019), which will cause significant increase in food demand. Consequently, to meet this demand, there will be an expansion of arable land and thus an increased use of phosphate fertilizers (Figure A.1; Tilman et al. 2001; FAO 2018). The phosphate

rocks exploited for mineral fertilizer synthesis is a finite resource non-renewable at human time-scale (Reijnders 2014), and is unevenly distributed across the globe, with more than 75% of the production located in Morocco, China, and the United States (Cordell et al. 2009; Agreste 2016; U.S.G.S. 2020). Although there is no consensus (Ulrich and Frossard 2014), some author alert on a potential global crisis regarding a possible shortage of rock phosphate and as a result mineral P fertilizers (Cordell and White 2011). European Union has been working since 2011 to direct decision-making and research towards solutions that can alleviate or limit its effects, such as circular, economy, limited and specialized application (e.g. precision agriculture), recycle organic wastes to produce fertilizers, or recycled bio-waste from the food chain (Gislev et al. 2018).

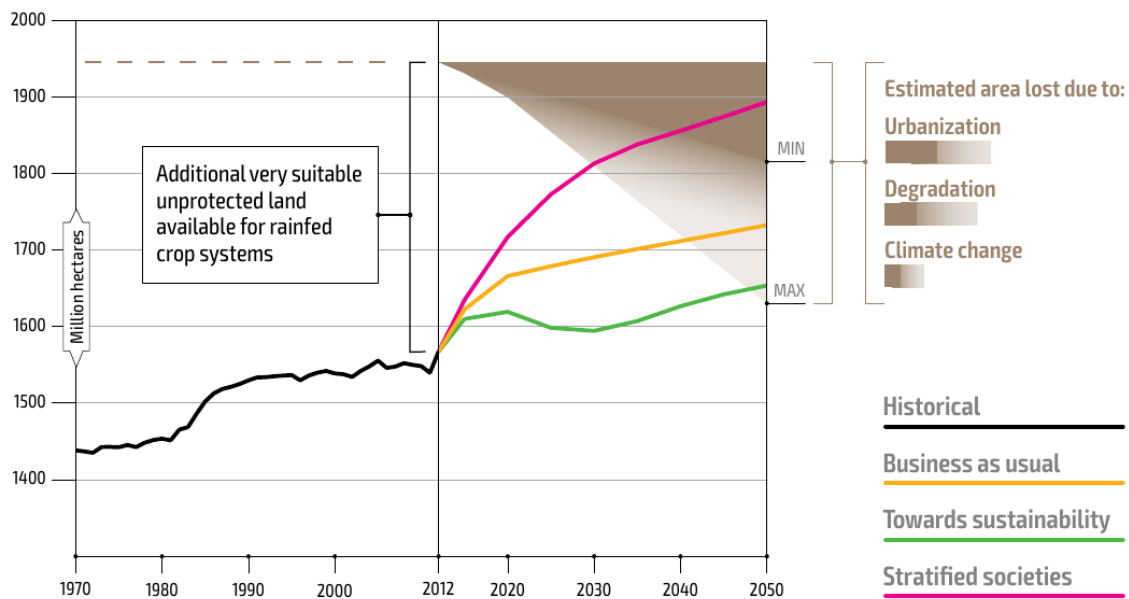


Figure A.1 Global arable land requirements by three different scenarii build in response to future challenges, and estimated losses of agricultural areas to urbanization, degradation and climate change (FAO 2018).

Another concern about soil P, is the risk of eutrophication of downstream aquatic environments. This phenomena of anthropic origin is a "*set of symptoms summarizing the different biological and biogeochemical reactions generated by excessive nutrient inputs*" from human activities (Sharpley et al. 2015; Pinay et al. 2018). Eutrophication causes the proliferation of invasive, sometimes problematic species (i.e. green algae tides), with a strong decrease in biodiversity and the appearance of dead zones (Haygarth and Jarvis 1999; Mee 2006; Diaz and Rosenberg 2008). Due to nutrient cycling alteration, agrosystems can significantly contribute to the transfer of P to aquatic environments (Némery and Garnier 2007). These nutrient fluxes cause significant damages to ecosystems and are expected to increase with the expansion of agricultural land (Tilman 1999).

The management and reasoning of P in agricultural soils is at the crossroads of many issues as: food security, preservation of surface water quality, conservation of the phosphate rock fossil reserves, and recycling of organic products such as farm effluent. The following four subsections review the scientific literature on main issues related to soil P in temperate agrosystems. What is the long-term soil P dynamics in relation to agricultural practices? What are the soil-plant relationships, and common methods to assess plant-available soil P and their limits? Is there new insights to improve the reliability and relevance of plant-available soil P assessment? And finally what are the agronomic questions still to solve to go further in our understanding and characterization for operational purpose of plant nutrition of crop species cultivated in agrosystems?

- i) The first subsection briefly presents the agronomic and environmental issues associated with P in cultivated soils, the current methods for assessing soil P available to plants, their limitations in diagnosing crop behavior and the resulting P fertilizer recommendations. This section also presents the main P input and output flows, as well as the rational management of P fertilization;
- ii) The second subsection gives key knowledge of the biogeochemistry and speciation of P in cropped topsoil;
- iii) The third subsection highlight the need to develop a new approach based on the identification and quantification of main processes, which controls P absorption by plants cultivated in agroecosystems, and major results published;
- iv) The fourth subsection reviewed on the process of soil organic P (SOP) mineralization, first in short-term studies in incubated soils, and then in long-term field experiments. This section gives major published results in order to evidence the lacks of knowledge, leading to needs of researches and to the definition of thesis objectives.

A.1 P fluxes and fertilization managements in agrosystems

A.1.1 Magnitude of P outputs and inputs fluxes in French arable agrosystems

Arable surface (i.e. cultivated land, meadows, orchards, vineyards), in French agriculture represented about 28 million of hectare in 2008 (Agreste [2011](#)). In 2021, about 68 Mt of cereal were product on the French territory, including 37 Mt of wheat, 15.5 Mt of maize, and 11.4 Mt of barley (Agreste [2022](#)). The agricultural production on arable soils in 2021 represented about 13 kg P ha⁻¹ yr⁻¹ exported on average. Among the other possible P outputs of agrosystems, runoff and deep leaching are generally much less important fluxes that depend on the local climate and field plots characteristics, especially slope, and plant

cover among others, and represent in cropped soils about 0.5 (up to 2.5 in cultivated land) kg P ha⁻¹ yr⁻¹ and 0.1 kg P ha⁻¹ yr⁻¹, respectively (Dorioz et al. 1977; Némery and Garnier 2007).

According to the Agreste (2022) report, P application rate of fertilizers in French arable agrosystems represented 17.9 kg P ha⁻¹ in 2021 distributed 10.6 kg were from agricultural effluent and various organic products while 7.3 kg were mineral synthetic fertilizers from mining origin. Mineral P fertilizer imports represented 199 103 t P over the 2020-2021 period. These imports were at their maximum in the 70's and have been decreasing since then (Agreste 2016). As a result, French agrosystems P budget has been decreasing since the 90's and is now stabilized since 2010. In 2021, P budget ranged from -10 to 8 kg P ha⁻¹ on average depending on the region (Agreste 2022).

A.1.2 Rational management of P fertilization in agrosystems

The purpose of P fertilization is to meet crop needs by supplementing soil P supply (Castillon et al. 1995). The rationale for P fertilization is inherent to the assessment of the bioavailable P fraction in soil. The bioavailability of a resource is a function of the ability of an organism to acquire that resource from its environment. When it comes to soil P, we use the term “plant-available soil P” to refer to the fraction of total P in cropped soils that can contribute to plant nutrition (Barber 1984).

The P fertilization reasoning is based on a diagnosis/prescription system that includes empirical relations between chemically extracted P (as an assessment of plant-available soil P) and crop yield. This approach also considers the crop needs and the plot fertilization history. Crop requirements can be defined as the specific nutrient needs of a crop during its growth cycle, including critical, yield-determining parameters such as leaf area, flowering stage, and harvest organ growth. Crop needs can be divided between immediate needs (for a specific growing stage such as flowering), and total need (all need over the growth period). These needs are influenced by the pedoclimatic context and the photosynthetic activity of the plant (COMIFER 2019).

A variety of chemical extraction methods have been developed and are widely used in soil laboratory analysis to estimate the “plant-available” P in soils. The choice of extraction method can vary by country or region; for example, the calcium-acetate-lactate method (Schüller 1969) is commonly used in Austria and Germany, while the Mehlich 3 method (Mehlich 1984) is frequently used in the Czech Republic and much of North America. The Olsen-P method is commonly used for calcareous soils worldwide (Olsen et al. 1954). These methods typically involve adding a specific chemical solution to a soil sample (such as a bicarbonate solution for Olsen-P or a strong acid solution of hydrochloric acid,

ammonium nitrate, and ammonium fluoride for Mehlich 3), which extracts P from the soil and makes it available for measurement using colorimetric or other analytical techniques (e.g. ICP-OES). However, this empirical approach lacks of experimental references and precision. The Figure A.2 illustrates this relation for a low-requirement wheat crop and extraction with bicarbonate solution (Olsen et al. 1954). The extraction method explains only a small portion (< 50%) of the experimental variability on wheat yield response to fertilization, leading to an inaccurate determination of diagnosis thresholds (Morel et al. 1992). Consequently, recommendations for safe fertilization levels are often higher than necessary. There is also a high variability of this relationship among soils, climatic contexts and crops, which limits their generalization. For example, the different extraction method studied in Matar et al. (1992), in Mediterranean dry soils, were highly dependent on local climate and could drastically change with wet or dry year. In addition, the relation variability across soils and crop were also highlighted by Tang et al. (2009).

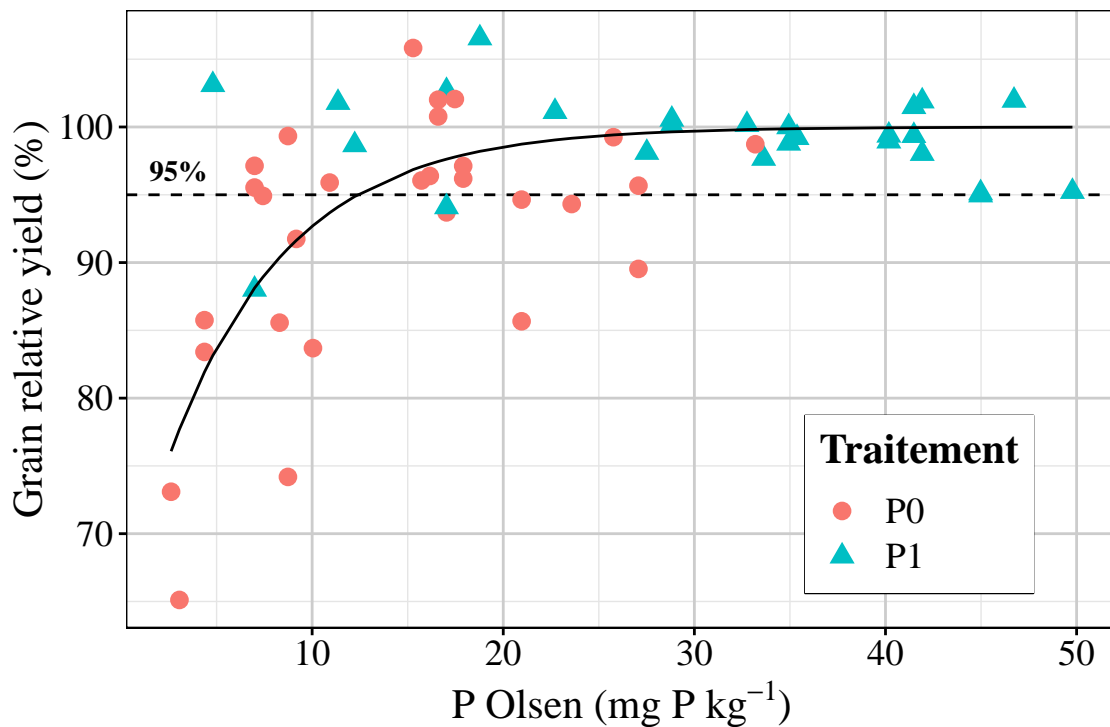


Figure A.2 Relative wheat response to P concentration determined with bicarbonate solution according to the Olsen method. P0: no P fertilization, P1: P fertilization equal to P export in harvest (Source: Morel et al. 1992).

According to Bray (1948), a good extractant to evaluate the “plant-available” soil P should extract all or a proportional fraction of the plant-available P form. Additionally, the amount of extracted P should be correlated with the crop growth and response to P under various conditions (Kamprath and Watson 1980). However, the chemical P extraction methods often used to determine the “plant-available” soil P (e.g. Bray II, Olsen, Mehlich 3) do not

extract only plant-available P (Cade-Menun et al. 2018), and are poorly correlated to crop response to fertilization. In addition, the weaker the extractant (i.e. neutral pH, such as H₂O, CaCl₂), the higher the correlation with plant P uptake, but the lower the P extracted (Zehetner et al. 2018).

Several studies have shown the inadequacy of these methods to correctly determine the plant-available soil P in different agropedoclimatic situations (Fardeau et al. 1988; Zehetner et al. 2018). It is therefore necessary to establish new scientific bases to better justify phosphate fertilization. To do so, it is essential to better understand the biogeochemistry of P in soils, and to rely first on a functional and mechanistic (i.e. agroecological) assessment of the actual plant-available P in soils, and then on its evolution modeling (Sections A.3.3 A.3.4) as a function of cropping practices (e.g. phosphate fertilization, simplified cropping techniques).

A.1.3 Organic waste products as source of P in agrosystems

The organic waste product (OWP) encompasses a wide variety of products, which differ in origin, processing methods, and storage conditions and can generally be categorized, such as animal manure products (and their by-products), sewage sludge, composts, digestates, biochar, ashes, and more exotic options, such as bone powder (Benoît et al. 2014). The ADEME (*Agence De l'Environnement et de la Maîtrise de l'Énergie*) estimates the annual production of OWP in France at 729 million tons of raw materials, of which 300 million are recycled as fertilizers in agriculture (ADEME 2018). Among them, 94% are farm effluents such as manure or slurry. Even with a P concentration the magnitude of a few percent (1 to 37 kg t⁻¹; ADEME 2018), those can constitute a significant source of P.

The major element composition of OWP is highly variable among products and depend on numerous factors, such as animal species, diet, stage of development, treatment applied (e.g. composting, liming), and storage method (Mustin 1987; Houot et al. 2003; Fytili and Zabaniotou 2008; Zdanevitch 2012; Muller and Zdanevitch 2014). The characteristics of the selection of OWP presented in Table A.1 are primarily drawn from the 2014 collective expertise of INRAE (*Institut National de Recherche pour l'Agriculture, l'Alimentation et l'Environnement*) (Houot et al. 2014).

Table A.1 Some characteristics and properties of a selection of OWP. AFI: Agri-food industry; RM: raw material; DM: dry matter; OM: organic matter; FVP: fertilization value in P. Values are compilation of data from Achat et al. (2014); Frossard et al. (1996); Frossard et al. (1992); Guivarch (2001); Kvarnström et al. (2004); El-Motaium and Morel (2007)

OWP	DM	OM	C/N	P	FVP
	(% RM)	(%RM)		(g kg⁻¹ RM)	%
Manure	1.1 – 85	1.2 – 63	2 – 26	0.2 –18	82 – 94
AFI effluent	0.1 – 63	4 – 43	4.5 – 81	0 – 0.3	85 – 91
Composts	28 – 95	15 – 58	6.6 – 65	0.5 – 19	64 – 84
Digestates	1 – 55	-	0.3 –87	0.4 – 55	-
Sewage sludge	1.4 – 30	1.8 – 17	3 – 19	0.2 – 9.6	67 – 98

The ability of OWP to deliver plant-available P depend on various factors, such as the biophysicochemical characteristics of the product (e.g. P speciation), the soil plant-available P, or the edaphic conditions (e.g. pH or soil texture) (Arenberg and Arai 2019). The OWP fertilizing value is generally expressed in relation to a reference mineral fertilizer, such as triple superphosphate (TSP). Field studies conducted over several years have demonstrated an equivalent plant-available P between municipal sewage sludge and TSP, when evaluated at comparable P balances (Morel et al. 2002). Short-term pot studies have also shown that the plant-available P from sewage sludge are equivalent to that of reference mineral fertilizer (Frossard et al. 1992, 1996; Guivarch 2001). However, thermal treatment on sewage sludge slightly decrease its fertilizing value (Morel et al. 2005; Andriamananjara et al. 2016). Farm effluent and raw materials from domestic water filtering also presents a fertilizing value comparable to TSP (Kvarnström et al. 2004; Achat et al. 2014; Dodd and Sharpley 2015). Composting treatments tends to reduce P fertilization value of OWP by increasing the C/N ratio due to microorganism action (Benoît et al. 2014).

The OWP supply is often based on C or N supply to improve soil structure and stability, or nutrient supply for crops (Annabi et al. 2007; Gopinath et al. 2008; Paetsch et al. 2016). However, this approach often results in excessive P inputs beyond crop requirements. Moreover, the variability in OWP forms implies different P speciation and thus different P availabilities (Frossard et al. 1996; Cabeza et al. 2011; He et al. 2011; Giles et al. 2018). The multi-element nature of OWP complicates their management and fertilization considerations. Indeed, P in OWP is 30-40% organic and the C/N/P ratio is highly variable across OWP (Benoît et al. 2014). Furthermore, the massive application of OWP to maintain

sufficient soil C or N status can lead to the introduction of trace element pollutants in quantities exceeding regulatory limits (Besnault and Martin 2011; Benoît et al. 2014).

Long-term field experiments (LFTE) with different soils, crops, and OWP applied are needed to establish a baseline for OWP fertilization reasoning. However, due to the cost of long-term studies and frequent analysis, the number of LFTE is limited. This baseline is generally derived from pot experiments (Morel et al. 2002; Achat et al. 2014), which raises the question of the transposition of these results to field conditions, but also the question of the long-term effect of repeated inputs, and therefore limits its application in the field (Frossard et al. 2002).

A.2 Biogeochemistry of phosphorus in soils

The Figure A.3 shows the main compartments and fluxes of the biogeochemical P cycle in arable agrosystems. Soil total P stock (TP) can be divided into soil inorganic P (SIP) and SOP, characterized by their component molecules. Therefore, P is present in different compounds that interact with the soil phases. Several compartments can be defined: i) P in solution, as phosphate ions, colloids, or dissolved organic molecules; ii) P adsorbed on the soil solid phase, as inorganic forms or organic forms in soil organic matter (SOM); and iii) P in living organisms (inorganic and organic P forms), such as microorganisms.

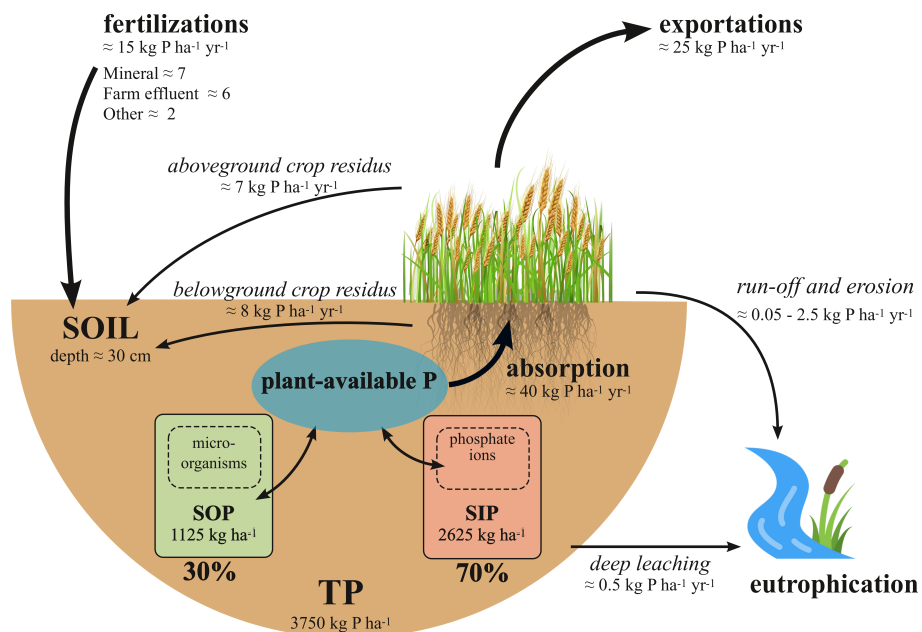


Figure A.3 Average P stocks and fluxes in plough soil layer. Values are a synthesis of AGRESTE, UNIFA and AFAÏA data in 2020. Crop absorption, exportation and return are the average values from the experimentation studied in this thesis.

A.2.1 Phosphorus stock in the plough soil layer

In temperate regions, P stocks in cropped soils varies widely (Johnston et al. 2014). The total P stock in France is about 4000 kg P ha⁻¹, considering 30 cm of plough layer (Smil 2000). A small P fraction is found in the soil solution, with an average concentration of 0.2 mg L⁻¹. The crop takes its nutrients from the soil solution and about 20 kg P ha⁻¹ is exported within its aerial parts. This annual removal represents less than 1% of TP.

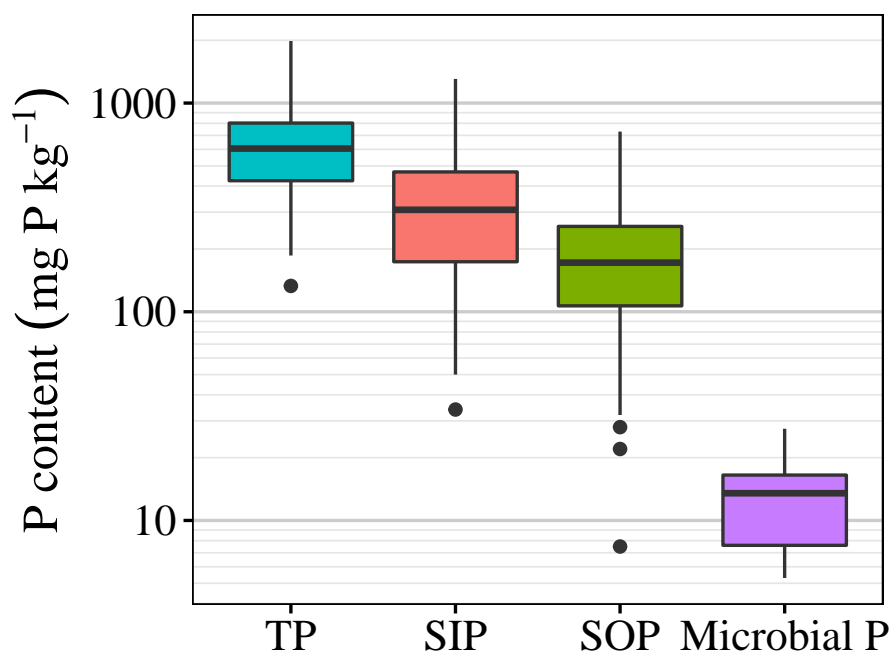


Figure A.4 P concentration (logarithm scale) in the plough soil layer of various agrosystems. Means \pm std. err. (mg P kg⁻¹): TP: 664 \pm 25; SIP: 364 \pm 19; SOP: 202 \pm 9; microbial P: 13 \pm 1; $n = 32$ with 197 combination soil \times treatments. Stocks were evaluated with different methods across studies. Sources: Brookes et al. 1982; Sharpley 1985; López-Hernández and Niño 1993; Rubaek and Sibbesen 1995; Morel et al. 1996; Oehl et al. 2001b,a; Motavalli and Miles 2002; Oehl et al. 2004; Lehmann et al. 2005; Turner 2006; Cade-Menun et al. 2010; Yang et al. 2010; Song et al. 2011; Keller et al. 2012; Ahlgren et al. 2013; Abdi et al. 2014; Liu et al. 2014; Morel et al. 2014; Pizzeghello et al. 2014; Annaheim et al. 2015; Jarosch et al. 2015; Liu et al. 2015; McLaren et al. 2015; Stutter et al. 2015; Cade-Menun et al. 2018; Recena et al. 2018; Glæsner et al. 2019; Liu et al. 2019; Qaswar et al. 2019; van der Bom et al. 2019; Morel et al. 2021.

The TP generally represents less than 0.1% of the total soil mass of the plough soil layer, ranging from 133 to 1983 mg P kg⁻¹. In 3/4 of the situations shown in Figure A.4, P is mainly inorganic (from 34 to 1305 mg P kg⁻¹). The SOP stock represents 32 \pm 1% of TP. However, this fraction considerably varies among the studied situations (Figure A.4). In the plough soil layer of agrosystems, SOP represents 1% to 64% of TP (Figure A.4), making up a stock of 0.04 to 3 t P ha⁻¹ (considering 4 t of TP ha⁻¹). Although microorganisms only

account for a small fraction of TP ($2.1 \pm 0.2\%$), they play a primary role in SOP dynamics. About 80% of the microbial P is in organic form (Oberson and Joner 2005).

A.2.2 Phosphorus speciation in plough soil layer

The temperate cropped soils pH range from about 5.5 (limed soils) to 8.2. Among the three phosphate ionic species in soil solution, dihydrogen phosphate (H_2PO_4^-) and hydrogen phosphate (HPO_4^{2-}) ions are the predominant forms with a pKa of 7.2. The orthophosphate ions (PO_4^{3-}) only occur at high pH.

To measure soil P speciation, the liquid state ^{31}P nuclear magnetic resonance (P-NMR) spectroscopy on NaOH-Ethylenediaminetetraacetic (NaOH-EDTA) extracts is one of the most efficient and commonly used method (Cade-Menun and Liu 2014; Cade-Menun 2017; Menezes-Blackburn et al. 2018). The SOP is characterized by the presence of a bond between P or phosphate and one or more hydrocarbon chains. Orthophosphate monoesters present an ester bond between P and C (P-O-C) (Magid et al. 1996; Condrón et al. 2005), and are the predominant form in SOP ($93 \pm 1\%$ of SOP). They include among others: phosphate sugars, ATP and its derivatives, and inositol phosphates. Among the latter, inositol hexakisphosphates (IHP) are the storage forms of P in seeds (especially the *myo* stereoisomer). They are composed of a C_6 ring, each bonded to a phosphate. Orthophosphate diesters (C-O-P-O-C) are less abundant ($5.3 \pm 0.9\%$ of SOP). They compose part of the phospholipids and nucleotide chains (Cosgrove and Irving 1980; Cade-Menun 2005). Phosphonates are often barely detectable ($2.1 \pm 0.3\%$ of POS) and are characterized by a direct covalent C-P bond (Condrón et al. 2005; Cade-Menun 2017). This bond is difficult to hydrolyze, and very few organisms synthesize or degrade these molecules. They are generally of anthropic origin, being used in particular in glyphosate for their biocidal properties (Hilderbrand 2018). Some P compounds are presented in Figure A.5 to illustrate the different P groups.

On average, SIP is composed of $97 \pm 1\%$ phosphate ions (Table A.2; PO_4^{3-} in NaOH-EDTA extract, as $\text{pH} > 12.4$). The mineral forms detected by P-NMR are phosphate ions adsorbed on the surfaces of soil components, and polyphosphates, which are phosphate polymers bonded by one oxygen. Pyrophosphate is a polymer of only two phosphates. In addition, SIP is composed of more or less crystallized forms not detected by P-NMR analysis, precipitated or of geological origin, such as the phosphate minerals of the apatite family $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH},\text{F},\text{Cl})_2]$ (Nriagu and Moore 1984; Lindsay et al. 1989).

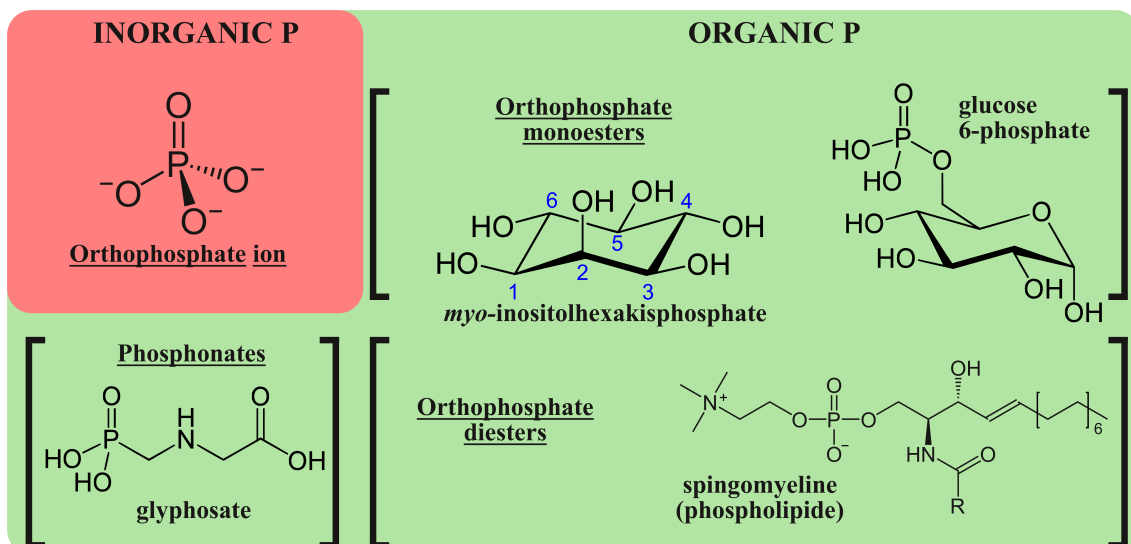


Figure A.5 Example of some P compounds which represents the main P groups determined by P-NMR.

Table A.2 Synthesis of published results on cropped soil P speciation determined by P-NMR spectroscopy; Analyses performed on NaOH + EDTA extraction; $n = 14$ references; 118 soil \times treatments. Sources: Turner 2006; Cade-Menun et al. 2010; Ahlgren et al. 2013; Liu et al. 2014; Annaheim et al. 2015; Jarosch et al. 2015; Liu et al. 2015; McLaren et al. 2015; Stutter et al. 2015; Cade-Menun et al. 2018; Recena et al. 2018; Glæsner et al. 2019; Liu et al. 2019; van der Bom et al. 2019

	Means	Standard error	Median	Maximum	Minimum
	mg P kg ⁻¹				
Total P	689	431	590	3435	133
NaOH-EDTA extraction	461	396	348	2966	65
SIP	325	317	226	2520	34
Orthophosphates	318	316	221	2520	30
Pyrophosphate	5.3	4.1	4.0	20.0	0.2
Polyphosphates	3.0	2.7	2.7	10.0	0.0
SOP	151	94	139	482	7.5
All monoesters	142	89	130	445	1.5
Inositolhexakisphosphates	51	87	14	427	0.0
Choline P	2.4	1.7	2.0	8.0	0.0
Glucose P	6.5	8.7	3.0	31	0.5
Other monoesters	87	68	66	315	0.0
All diesters	7	14	1	90	0.0
DNA	7	12	3	78	0.1
Other diesters	6	12	2	79	0.0
Phosphonates	2.1	2.3	1.5	8.5	0.0

Hundreds phosphates minerals have been identified in soils, containing mostly Ca, Al, and/or Fe. Thermodynamic properties of these minerals have been studied considering pure and crystallized forms (Nriagu and Moore 1984; Lindsay et al. 1989). In soil, these crystals occur in more or less amorphous forms.

A.2.3 Phosphate ions and SOP interactions with soil solid phase

In soils, P (as phosphate ions or within organic molecules) can be more or less strongly adsorbed on positively charged soil surfaces, depending on various factors, such as the concentration of phosphate ions in solution, soil surface characteristics, pH, or temperature (Barrow 1987). The higher the binding energy of the interaction, the less labile the phosphorus is. In the immediate vicinity of positive surfaces, anions form high-energy covalent or electrostatic bonds. Weaker bonds can also be formed as hydrogen bridges between the soil solid surface and the water molecules surrounding the anion (Hiemstra and Van Riemsdijk 2006). Thus, a compound containing P can form all the more energetic bonds due to the oxygen atoms in phosphate that can have two or three non-bonding electron doublets (Mackey et al. 2019), and will be poorly mobilized from the solid phase to the soil solution.

Metal oxide hydroxides (e.g. Fe, Al and Mn) and clay minerals form charged surfaces in soils. Oxides and clays edges present surfaces with variable charges depending on the pH. Their overall electric charge is null for a pH usually comprised between 3 and 7 for clays, and between 7 and 9 for metal oxides (Hsu 1989; Schwertmann and Taylor 1989; Hiemstra et al. 1996).

The specific surface area of calcium carbonates can be large with on average $3 \text{ m}^2 \text{ g}^{-1}$ for a sorbing capacity of $0.13 \text{ } \mu\text{mol P m}^{-2}$ (Cole et al. 1953; Carreira et al. 2006). The reaction between phosphate ions and calcium carbonates can form a calcium phosphate precipitate (Johnston et al. 2014). The stability of this precipitate is highly dependent on the pH of the soil solution and is favored by neutral to high pH (>7.2) (Lindsay et al. 1989). The precipitation/dissolution of calcium phosphates also depends on the concentration of the reaction products: the higher the phosphate ions concentration in soil solution and calcium carbonates concentration, the more precipitation (Cole et al. 1953).

The different soil constituents (e.g. oxides, clays, carbonates, organic matter) interact with each others and can form complexes, such as SOM with clays or metal oxides, modifying surface charges and potential interactions with phosphates ions (Violante et al. 2002; Pierzynski et al. 2005).

A.3 Uptake of plant-available phosphorus

The P is found in cell membranes and cytoplasm, and contributes to maintain their pH neutral. It makes up about 0.1 to 1.1% of plant dry matter under non-limiting fertilization. At plant maturity, it is mostly localized in the seed as IHP, which allows for P storage. It is a nutrient reserve to be released during germination (Broadley et al. 2004; White and Hammond 2008).

A.3.1 Mechanisms of P mobilization by the root

Plant roots take up P in the soil solution as phosphate ions through roots and mycorrhizae, which may be associated. The volume of soil affected by the action of plant roots is called the rhizosphere. In the case of P, this volume is of the order of few millimeters from the root (Barber 1984; Hinsinger 1998). Root uptake involves cell membrane transporters and root hairs, where phosphate ions are transferred into the cell by active transport (i.e., energy consuming transport), along with protons (Raghothama and Karthikeyan 2005). Root P uptake decreases the phosphate ions concentration in the rhizosphere solution. The required contact between roots and phosphate ions for root P uptake is conditioned by two processes (Richardson et al. 2009): i) root and mycorrhizal growth, which increases the explored volume of soil and allows access to new resources; and ii) movement of phosphate ions from the solid phase to the soil solution and then to the root surface.

Under certain experimental physicochemical conditions (e.g. significant P deficit), some particular plants can develop morphological and physiological adaptation strategies at the root level to improve the P plant-availability. Morphological strategies are an increase of the roots surface-to-volume ratio, e.g. by increasing the size and number of root hairs (Mollier and Pellerin 1999). Physiological strategies are, for example, the release of protons into the rhizosphere, which alters the soil physicochemical equilibrium and facilitates the dissolution of usually insoluble phosphate minerals such as apatite (Keerthisinghe et al. 1998). Under extremely low level of plant-available soil P, some species such as the white lupin (*Lupinus albus* L.) have the ability to develop proteoid roots capable of excreting citric acid (Keerthisinghe et al. 1998). Under common conditions in agricultural soils, in which plant-available soil P levels are generally sufficient, root network development is favored (Vance et al. 2003).

The ability of plants to take up phosphate ions depends on phosphate ions in solution at the root contact. After the depletion of phosphate ions at the contact sites, it is necessary to replenish the soil solution through various mechanisms (Figure A.6). The phosphate ions absorption through mass flow (i.e. along the water uptake driven by evapotranspiration) is lower than the absorption capacity by roots. Therefore, other mechanisms at the solid-to-

solution interface come into play to enable plant nutrition (Barber 1984).

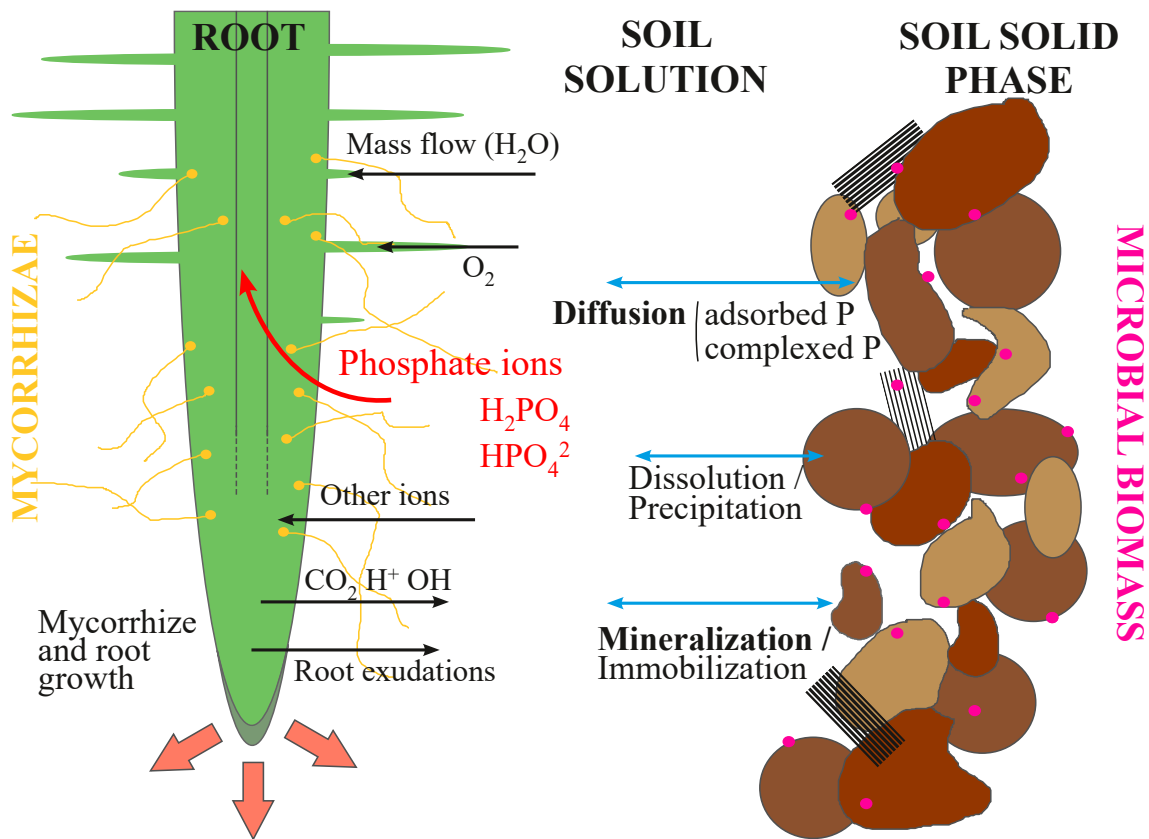


Figure A.6 Schematic representation of the biophysicochemical mechanisms involved in the phosphate ions transfer in the soil-solution-root system (blue arrows). Red arrow is the plant phosphate ions absorption. Black arrows are other possible mechanisms between root and soil within rhizosphere.

A.3.2 Mechanisms of P mobilization at the soil solid-to-solution interface

When comparing the amount of phosphate ions absorbed by the crop aboveground (about $20 \text{ kg ha}^{-1} \text{ yr}^{-1}$) with the stock of phosphate ions in solution (about 250 g ha^{-1} at 30% moisture and a bulk density of 1.34), it appears that about 1% of the removed phosphate ions originate from the soil solution. This means that 99% of the absorbed phosphate ions originate from the solid phase, and must have been transferred to the solution beforehand. Considering the diverse P forms present in the solid phase, many biophysicochemical mechanisms may be able to mobilize solid-phase-associated phosphate ions into the soil solution and thus contribute to plant P nutrition (Figure A.6) These mechanisms can be divided into two processes: i) diffusion (i.e. rapid and slow molecule movement under a gradient of concentration; Barrow 2015) of phosphate ions at the solid-to-solution interface; and ii) mineralization of soil SOP (Section A.4). Phosphate ions from desorption, dissolution and decomplexation diffuse into the soil solution. Dissolution of phosphate minerals (e.g. francolites) and decomplexation are minor processes that release little

phosphate ions under typical agricultural soil conditions (pH 5.5 to 8.2; Lindsay et al. 1989; Fardeau et al. 1991; Frossard et al. 1995; Wang et al. 2016).

Molecular diffusion is the movement of chemical compounds by Brownian motion within or between medium phases along a concentration gradient, from the most to the least concentrated areas. The greater the difference in concentration, the greater the rate of diffusion (Darrah 1993). In the case of P, it is the decrease in phosphate ions concentration at the root surface that causes a concentration gradient to appear, thus a diffusion flux from the solid phase to the solution and then to the roots. Diffusion kinetics tends to homogenize the phosphate ions concentration in soil solution (C_P ; determined in soil water suspension with volume:mass ratio of 10) with a very fast initial rate which keeps decreasing. This transfer kinetics at the solid-to-solution interface continues for several months, probably even years, and seems to never reach equilibrium (Arai and Sparks 2007).

A.3.3 Isotopic outlook of plant-available soil P

Isotopic dilution method is a very accurate method for quantifying and determining the origin of plant P uptake. It is considered one of the most reliable methods currently available (Fardeau 1995). This method uses ^{31}P , ^{32}P and ^{33}P , the latter two being radioactive isotopes with half-lives of 14.3 d and 25.3 d, respectively, and considers that these isotopes are not discriminated by biophysicochemical processes. Its principle is inspired by abundance estimation methods used in ecology. It consists of adding a known amount of radioactively labelled phosphate ions (R) to the compartment studied, and then homogenized. Subsequently, both labelled and unlabelled phosphate ions are measured simultaneously. Following the isotopic composition kinetics (i.e. labelled/unlabelled phosphate ions) of the compartment studied allows to study the process "diluting" the amount of labelled phosphate ions.

The isotopic dilution principle assumes an identical isotopic composition between the whole compartment and its aliquot, and allows the calculation of:

- soil plant-available P, named the L value (Larsen 1952, 1969), generally determined in pots experiments, is calculated according to following equations:

$$\frac{R}{L} = \frac{r_{plante}}{p_{plante}} \quad \text{(Eq. A.1)}$$

$$\implies L = p_{plante} \times \frac{R}{r_{plante}}$$

- E value: amount of phosphate ions in soil participating to ^{32}P -dilution ($E = Q_w + P_r$), measured in soil suspensions at steady-state; P_r value: amount of phosphate

ions bound onto the soil solid that participated to ^{32}P -dilution by diffusion at the solid-to-solution interface of soil (McAuliffe et al. 1947; Russell et al. 1954) are determined in soil suspensions using the following equations:

$$\begin{aligned}\frac{R}{E} &= \frac{r_{\text{solution}}}{Q_w} = \frac{R - r_{\text{solution}}}{Pr} \\ \implies P_r &= Q_w \times \frac{R - r_{\text{solution}}}{r_{\text{solution}}} \\ \implies E &= Q_w \times \frac{R}{r_{\text{solution}}}\end{aligned}\tag{Eq. A.2}$$

Where R is the carrier-free amount of phosphate ions labelled with ^{32}P introduced into the soil-plant or soil-solution system; r_{solution} and Q_w the respective amounts of ^{32}P and ^{31}P ions in the soil solution; r_{plant} and p_{plant} the respective ^{32}P and ^{31}P ions taken up by plant. Q_w is calculated multiplying C_p by the soil-solution ratio of soil suspensions. In suspensions at steady state, the transfers of phosphate ions, either from solution to soil (sorption) or from soil to solution (desorption) are equal, i.e. the net transfer is nil and C_p did not vary significantly with time.

Isotopic dilution technique has been used to study the capacity of different cultivated species, mycorrhized or not, to take up phosphate ions from the soil (Morel and Plenchette 1994). The principle of this approach is to compare L values among treatments, soil types, etc. Results show no significant difference in L values between mycorrhized and non-mycorrhized crops, although the former absorb much more phosphate ions (Bolan 1991; Morel and Plenchette 1994). Thus, different crops take up phosphate ions from the same plant-available P sources, with mycorrhizal symbioses essentially allowing exploration of a larger soil volume.

The isotopic dilution technique also reveals the close and highly significant relationship between L values, determined in pots experiments with plants, and E values, determined in soil suspensions without biological activity, when the E value is determined for the same time steps as the cropping period in which the L value is measured. This relationship was shown for different soil types, P statuses, crop species, cropping periods, and P inputs (Figure A.7). The L value slightly increases with the duration of cultivation, just as the E value increases with increasingly long times of isotopic dilution (Fardeau 1981). The E value calculated for a transfer time equal to the cultivation time is very close to the L value, and they often do not differ significantly (Figure A.7).

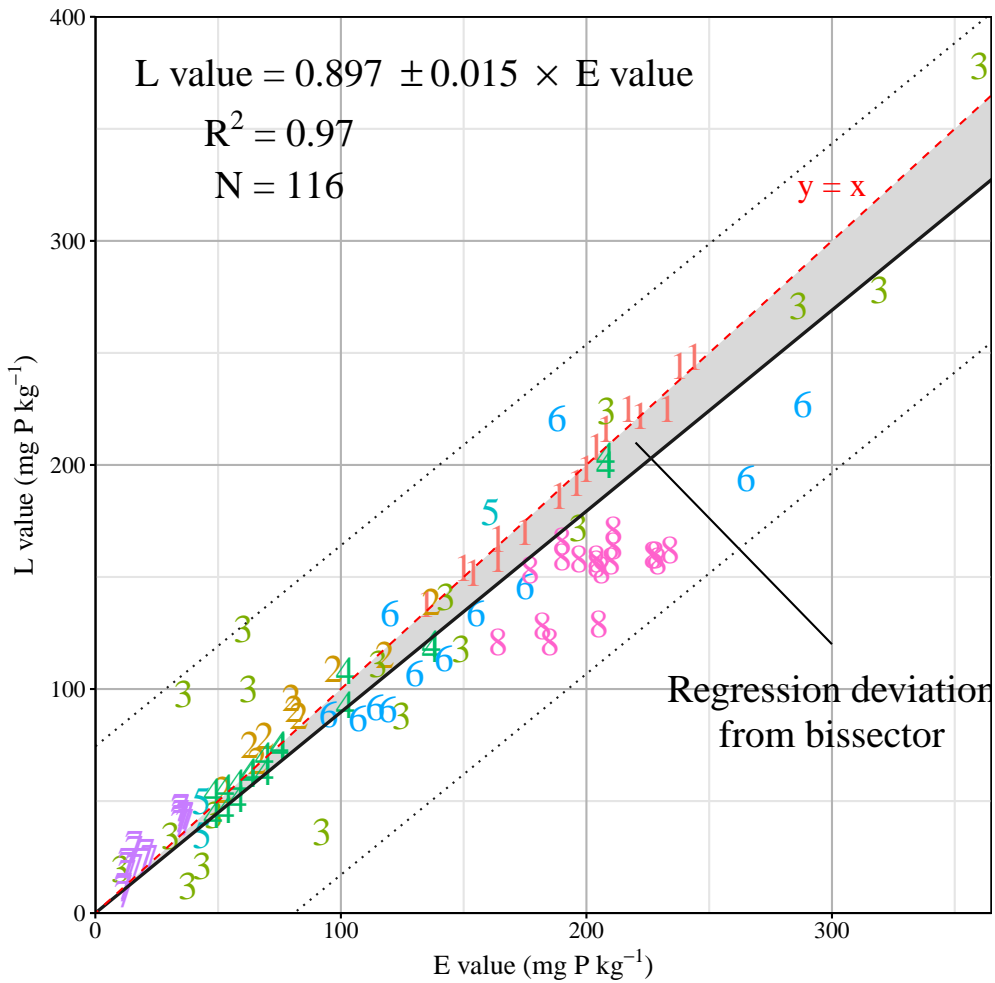


Figure A.7 Linear relation between L and E values published in literature. Sources: **1:** Fardeau 1981 (and Fardeau and Jappe 1976); **2:** Morel 1988; **3:** Frossard et al. 1994; **4:** Morel and Plenchette 1994; **5:** Morel (personal communication); **6:** Bühler et al. 2003; **7:** Pypers et al. 2006; **8:** Achat et al. 2014

The E values for durations equivalent to those of plant P uptake in pot studies (several weeks to several months) was determined with a laboratory experimental approach accounting for rapid and slow reaction kinetics. This approach allows to determine the parameters of the following simplified equation describing E vs elapsed time of isotopic dilution (Fardeau 1981):

$$E = E_{1min} \times t^n; \quad E \text{ value lower than soil inorganic P (SIP)} \quad (\text{Eq. A.3})$$

With E_{1min} and n are fitted parameters which are C_P specific for a given soil sample. They are obtained from an experimental approach, which consists of determining in soil-solution suspensions, a dataset over short time steps to parameterize an equation that allows extrapolation of the E value over longer time steps (one day, three months, and one year) by the power function of time (Eq. A.3) (Fardeau et al. 1985, 1991; Fardeau 1993). Because, the limit of E value can not be determined experimentally due to the persistence

of slow reactions over several months, it is bounded by the theoretical maximum value which is at most the SIP concentration.

The relationship between L value and E value shown in the Figure A.7 is close to 1:1, i.e. for the same time, the amount of soil plant-available P does not differ significantly from the sum of diffusible phosphate ions at the solid-to-solution interface and phosphate ions in the soil solution ($E = P_r + Q_w$). Therefore, in general, diffusion is the main mechanism of phosphate ions mobilization at the solid-to-solution interface during plant phosphate ions uptake. However, the linear regression coefficient is slightly less than 1: about 10% of the L value is not explained by the E value. Thus, at long period of diffusion (and high amounts of diffused phosphate ions), the L value underestimates the stock of plant-available P. One explanation for this result is that the diffusion of phosphate ions at the solid-to-solution interface is not the only mechanism contributing to plant-available P. Furthermore, these results are from incubation experiments, where the E value is calculated for stable physicochemical conditions and does not account for processes, such as microbial activity.

A.3.4 Functional and mechanistic assessment of plant-available P

To assess plant-available soil P considering the diffusion process occurring during absorption of phosphate ions in solution by plant roots and mycorrhizae, (Morel 2002) proposed a general mathematical equation, called kinetic Freundlich equation (Chardon and Blaauw 1998), accounting accurately for both time and C_P effects to describe $[P_r \text{ vs } (C_P, t)]$ relationships in agricultural soils:

$$P_r = v \times C_P^w \times t^p; \quad P_r < SIP \quad (\text{Eq. A.4})$$

With P_r is in mg P kg^{-1} , C_P , in mg P L^{-1} , t is in minutes, and v , w and p are fitted parameters: v is the P_r value when C_P is 1 mg P L^{-1} and t is 1 minute; the w parameter (<1) accounted for C_P effect; the p parameter (<0.5) accounted for time effect. With this method one can determine and describe mathematically the rapid and slow transfer of phosphate ions between the solid phase and the liquid phase. This equation has been used successfully to describe $[P_r \text{ vs } (C_P, t)]$ relationships for agricultural soils (Morel et al. 2000; Ehlert et al. 2003; Stroia et al. 2007), and for fluvial sediments (Némery et al. 2005).

A typical example of $[P_r \text{ vs } (C_P, t)]$ relationships is presented in Figure A.8. It illustrates that P_r values (symbols) increased less than proportional with C_P and also less than proportional with time. It illustrates also that the kinetic Freundlich equation (lines) strongly fitted to experimental data. From the $[P_r \text{ vs } (C_P, t)]$ relationships, many indicators of phosphate ions behavior at the solid-to-solution interface can be calculated such as

phosphate ions buffering capacity and sorption at any values of C_P and time, amounts of P sorbed or desorbed for a given gradient of concentration and a given time, etc.

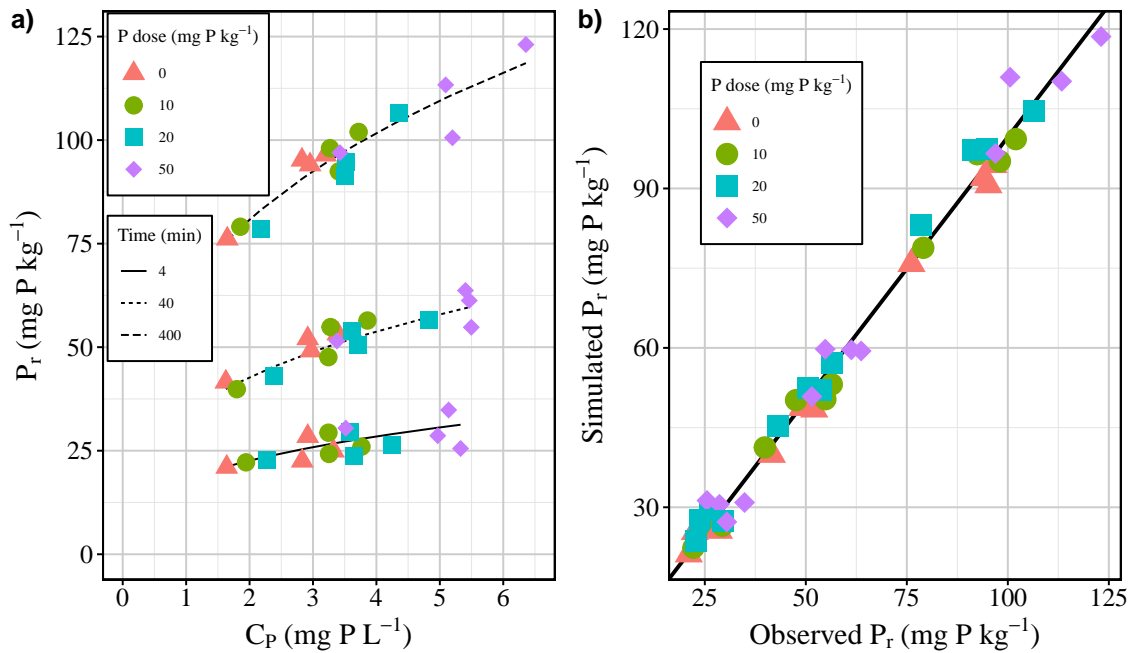


Figure A.8 Typical P_r vs (C_P , t) relationships.

(a) Experimental values (symbols) and fitted values (lines) of the amount (P_r) of phosphate ions transferred by diffusion (P_r) as a function of both phosphate ions concentration in soil solution (C_P) and time (4, 40, and 400 minutes). Lines are the following kinetic Freundlich equation: $P_r = 12.2 \times C_P^{0.33} \times t^{0.28}$ ($n = 48$). Results were obtained for four topsoils, sampled from the four replicates of the N0P50 treatment of the Gramond field experiment studied in Stroia et al. (2007). The C_P range in soil suspensions was obtained by adding 0, 10, 20, and 50 mg P kg^{-1} and equilibrating for 40 h to reach a steady-state during isotopic dilution kinetics.

(b) Correlation between experimental and calculated P_r values.

P_r and C_P values were obtained combining sorption-desorption reactions for 40 h, and isotopic dilution kinetics. Details on experimental procedure are in Stroia et al. (2007).

The rate and extent of soil-solution transfer of phosphate ions depend both on soil solution phosphate concentration and on time as shown in many studies using methods either based on sorption (Chardon and Blaaup 1998; Barrow 2023), desorption (Sharpley 1983; Delgado and Torrent 1997), electroultrafiltration (Steffens 1994), and isotopic dilution (Fardeau et al. 1991; Frossard et al. 1994; Morel et al. 2000). Schneider and Morel (2000) shown in a clay textured Haplic Luvisol that the same amounts of phosphate ions that participated in the soil-solution dynamics, have been assessed either using [P_r vs (C_P , t)] relationships, obtained by isotopic dilution kinetics, or by desorption with resin-strips.

Agronomic applications of this functional and mechanistic assessment of plant-available soil P have been developed: one to describe its dynamics under different agricultural

practices; the other to test its ability to better predict yields response to P fertilization rates for a given crop, cultivated in many soils (Morel et al. 2021).

The model describing cycling of P in agrosystems (CycP) was built using a mass balance equation to associate plant-available soil P dynamics to annual budget of P inputs and outputs at the field plot scale. Plant-available soil P was assessed by the $[P_r \text{ vs } (C_P, t)]$ relationships, which describes the transfer of phosphate ions between liquid and solid phases of soil. So, CycP assumes that diffusion of phosphate ions at the solid-to-solution interface is the dominant process replenishing the soil solution in phosphate ions during plant nutrition. The CycP model (Figure A.9) was used to simulate C_P dynamics with years under different P applications rates in grassland experiments (Stroia et al. 2007; Messiga et al. 2012) and cropland experiments (Morel et al. 2014; Messiga et al. 2015; Li et al. 2019).

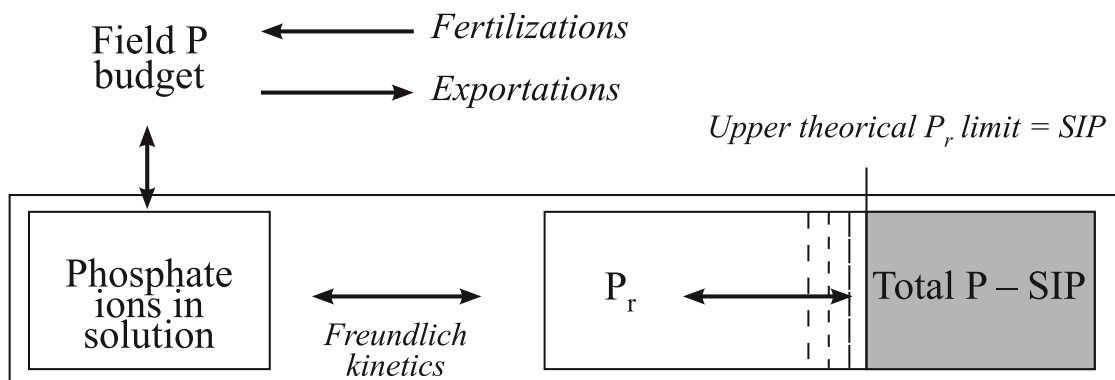


Figure A.9 Conceptual diagram of the CycP mass balance model. CycP equilibrates plant-available P in the upper soil layer to the annual P budget between P inputs and outputs. Plant-available soil P is assessed by the soil solution phosphate ions concentration in solution of soil suspensions and phosphate ions that can diffuse at the solid-to-solution interface, i.e. $[P_r \text{ vs } (C_P, t)]$ relationships (adapted from Messiga et al. 2012)

Overall of the published studies, CycP simulated correctly C_P dynamics considering different scenarios of P fertilization rates, i.e., no P applied; P application rate equivalent to P exported; P applied greater than P exported (Morel et al. 2014). The ability of CycP to predict C_P for 10 years of cropping was good in a timothy pastures (Messiga et al. 2012). However, in cropped soil under maize monoculture for 17 years, CycP tend to overestimate C_P when no P was applied (Messiga et al. 2015). Using CycP to simulate different scenarios, the main explanations proposed were a replenishment time of phosphate ions by the solid phase of the soil much longer than one year, and a significant contribution to P nutrition of the soil layer below the ploughed layer.

A.4 Mineralization of organic P in the plough soil layer

In a process-based approach to assess plant-available soil P, it is likely that the SOP could also contribute to replenish the soil solution in phosphate ions through its mineralization. This process is the transformation of various organic P molecules into phosphate ions (Figure fig:cA-10). Although microorganisms account for only about 2% of the TP in the plough soil layer (Section A.2.1), they are the main actors in the decomposition of SOP (Richardson 2001).

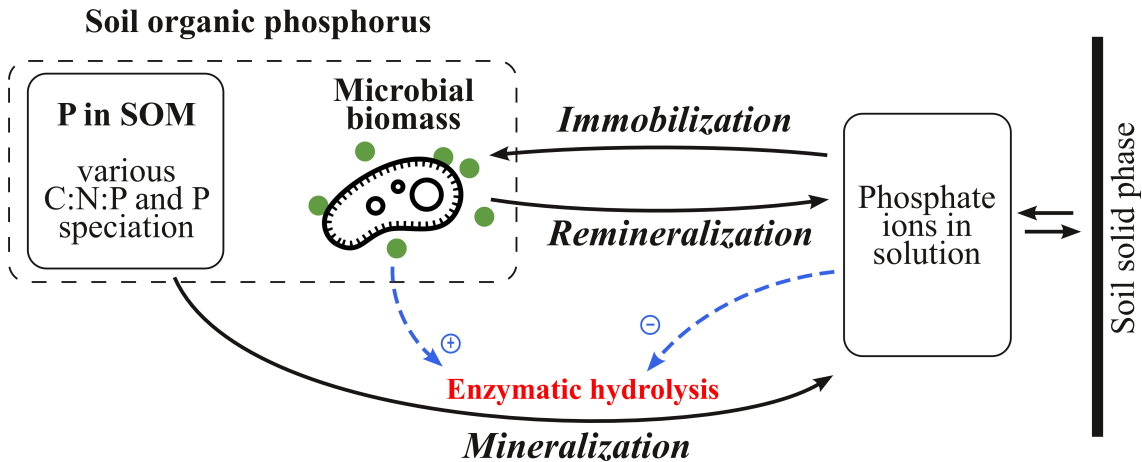


Figure A.10 Schematic representation of P fluxes and interactions between SOP and soil solution.

A.4.1 Microorganisms phosphorus and enzymatic activity

The microorganisms C:N:P ratio is variable depending on their environment, with 60% of P as nucleic acids and lipids, 10% as inorganic and 10% as organic in the cytoplasm, and 20% as polyphosphates (Bünemann et al. 2011). Thus, about 70% of microbial P is organic. Microorganisms degrade SOP by enzymatic hydrolysis with phosphatase enzymes. This family includes a wide variety of molecules, each hydrolyzing a specific chemical bond. For example, phytases degrade inositol phosphates (Nannipieri et al. 2011). In general, two main groups of enzymes can be distinguished (Vincent et al. 1992): i) acid phosphatases with an optimal activity in slightly acidic to neutral conditions; and ii) alkaline phosphatases (of microbial origin) with an optimum at slightly basic pH (Richardson 2001; Richardson and Simpson 2011). Phosphatase activity is expressed as $\mu\text{mol product g}^{-1} \text{h}^{-1}$, and can take place either in solution as free compounds, either on the microorganisms' surface.

Phosphatase activity is usually assessed using an artificial substrate and monitoring the concentration of the hydrolysis product (Nannipieri et al. 2011). Phosphatase activity is higher in the rhizosphere, dominated by alkaline phosphatases, than in the rest of the soil

(Joner et al. 2000; Spohn and Kuzyakov 2013). Tarafdar and Jungk (1987) highlighted the correlation between enzyme activity location and decrease of SOP stock. However, phosphatase activity and SOP mineralization can be influenced by numerous factors, such as the molecular speciation of the substrate. For example, a high phosphate ions concentration in soil solution value can negatively affect the enzymatic activity (Olander and Vitousek 2000). Jarosch et al. (2019) found the activity of phosphomonoesterases is limited by substrate availability, whereas that of phytases and phosphodiesterases is limited by enzyme availability. This implies a higher degradation capacity of monoester phosphates (non-IHP).

The ability to synthesize phosphatases is widespread within soil microbial communities (Jones and Oburger 2011), in order to acquire energy through covalent bond break, or biomass (P and/or C) (McGill and Cole 1981). Several P fluxes are generally distinguished according to the substrate nature: i) SOP gross mineralization; ii) P immobilization in microorganisms biomass; and iii) remineralization (Dalal 1977; Oehl et al. 2001b; Bünemann 2015; Arenberg and Arai 2019). Microorganisms P absorption in soil solution compete with root P uptake (Johnson et al. 1996). When mineralization is the dominant process, SOP stocks would be able to replenish the solution in phosphate ions and thus to contribute to plant nutrition.

A.4.2 SOP mineralization driving factors

Considering SOP represents on average 30% of TP in cropped soils (Section A.2.1), it can be expected to contribute to the plant-available P. The presence of microorganisms and enzymatic activity also suggests that SOP should significantly contribute to plant-available P in the plough soil layer (Diacono and Montemurro 2011).

Mineralization and the resulting phosphate ions flux depend on many biophysicochemical factors (Dalal 1977; Condon et al. 2005). It requires: i) a mineralizable substrate; ii) access of microorganisms to the substrate; iii) physicochemical conditions necessary for substrate degradation (Krull et al. 2003; Basile-Doelsch et al. 2020).

Substrate appetite for microorganisms is influenced by its chemical recalcitrance, stoichiometry, and speciation (Nannipieri et al. 2011; Barré et al. 2016; Bertrand et al. 2019; Jarosch et al. 2019). Microbial access to the substrate is limited by aggregates occlusion and adsorption strength. The ability of soils to protect SOM can be approximated by assessing soil texture, metal oxide concentration, and aggregation (Hassink et al. 1993; Balesdent et al. 2000; Rasmussen et al. 2018). Microbial biomass and phosphatase enzyme activity are influenced by pH, temperature, soil water concentration and phosphate ions in solution (Amundson 2001; Quiquampoix and Mousain 2005; Jones and Oburger 2011).

As a comparison, the mineralization coefficient of soil organic C in AMG model (Andriulo et al. 1999) is function of several factors such as the mean annual air temperature, the difference between annual water inputs and potential evapotranspiration, the CaCO₃ and clay soil concentration, soil water pH, and SOM C/N (Clivot et al. 2019).

A.4.3 Published results on SOP mineralization: short-term studies

Short-term incubated soil studies and LTFE have been implemented to quantify the phosphate ions flux from SOP mineralization.

These studies are based on the isotopic dilution technique, which allows the measurement of a raw flux of phosphate ions. The general principle of this approach is to measure and compare isotopic dilution between a sterile sample (physicochemical processes) and a non-sterile sample (physicochemical processes + biological activity). The difference gives the contribution of isotopic dilution due to biological activity. Subsequently, several methods have been developed, based on the following hypotheses:

1. Physicochemical processes and microbial biomass do not contribute to isotopic dilution (Figure A.11). All observed variations in isotopic composition are attributed to biological activity, i.e. mineralization (López-Hernández and Niño 1993; Lopez-Hernandez et al. 1998; Randhawa et al. 2005).

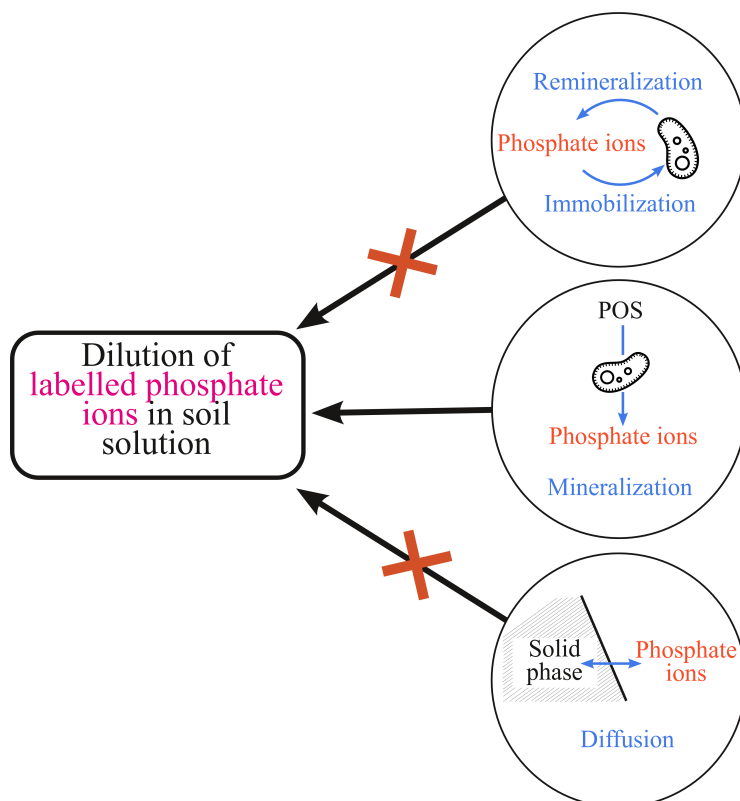


Figure A.11 Schematic representation of isotopic dilution hypothesis in López-Hernández and Niño (1993), Lopez-Hernandez et al. (1998), and Randhawa et al. (2005).

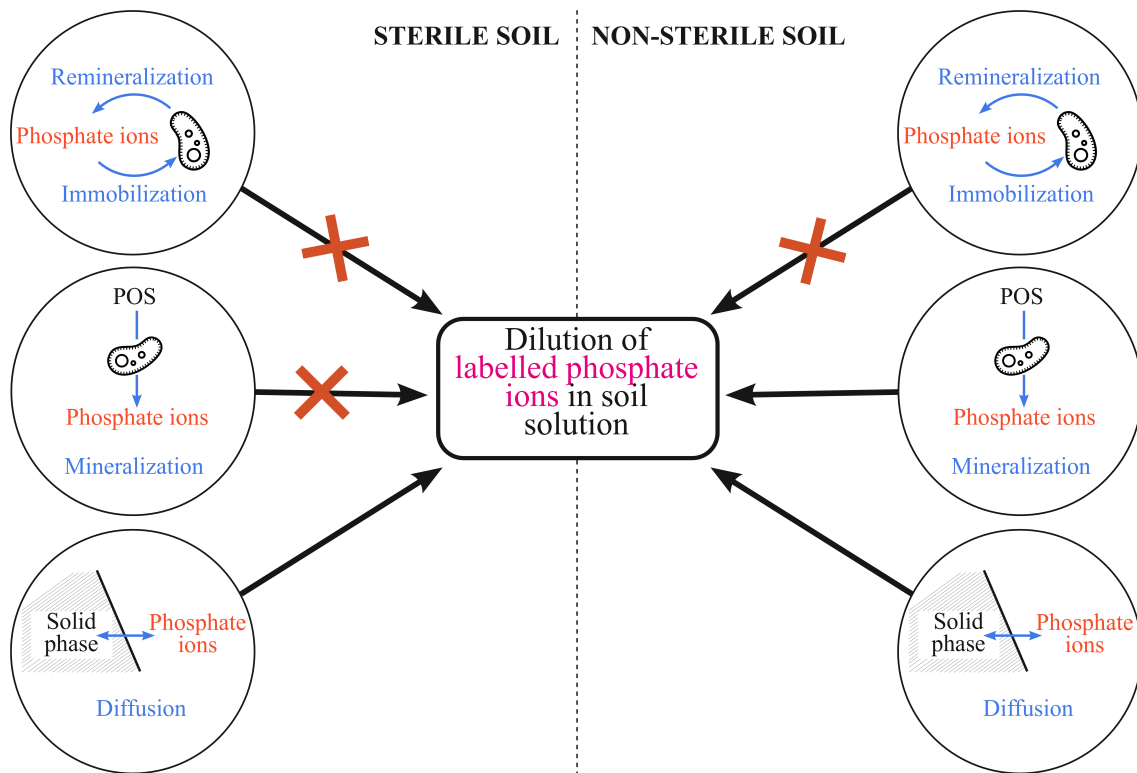


Figure A.12 Schematic representation of isotopic dilution hypothesis in Oehl et al. (2001a, 2004) and Bunemann et al. (2007).

2. Microbial biomass in sterile soil does not interfere with isotope dilution for short time steps. These studies, conducted under basal conditions (i.e. constant soil respiration and steady state), assume that remineralization and immobilization fluxes are negligible in non-sterile soil, and that only mineralization releases phosphate ions other than physicochemical processes (Figure A.12) (Oehl et al. 2001a, 2004; Bunemann et al. 2007).

Achat's work between 2009 and 2010 (Achat et al. 2009, 2010b,a) was carried out under optimal conditions for mineralization: high microbial activity, high SOP stocks and no physicochemical processes contribution to isotopic dilution after a few days (i.e. isotopic equilibrium with the solid phase is quickly reached). This allowed the study of SOP mineralization and remineralization (Figure A.13).

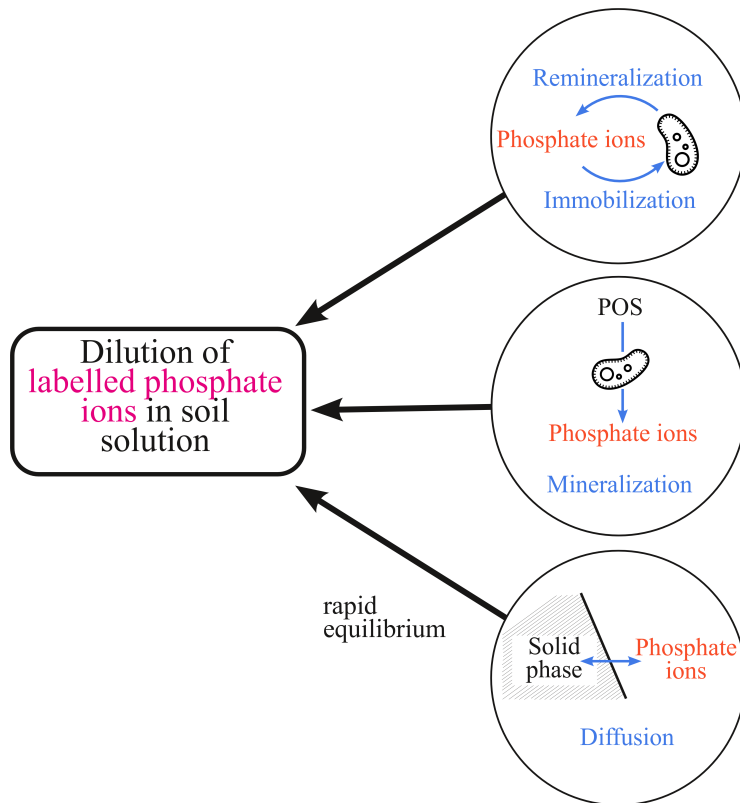


Figure A.13 Schematic representation of isotopic dilution hypothesis in Achat et al. (2009, 2010b,a).

The results in the Table A.3 show a very large variability in mineralization rates between studies, and a large uncertainty within each study, with standard deviations sometimes including null mineralization rates. In Achat's work, microorganisms have assimilated about 34% of introduced radioactivity after 1 day, and have released it slowly over time, suggesting that extrapolation of the amount of ions exchanged by diffusion over long time steps should be reconsidered. In these studies, remineralization is the major flux of isotopic dilution (up to 97%). While microbial activity and SOP contribution to plant-available P is generally negligible, biological processes may be important under certain conditions. Finally, incubation studies do not take into account the presence of plants, even though they drive the main phosphate ions fluxes in agrosystems soils.

Table A.3 Mineralization rates determined in short-term incubation studies by isotopic dilution.

Reference	Soil classification	Treatments	Duration (days)	Mineralization (mg P kg ⁻¹ d ⁻¹)
Lopez-Hernandez et al. 1998	Paleustolls		51	0.22
	Typic Haploborolls		51	0.47
	Pachic Haplustoll		51	0.67
	Typic Haploborolls		51	0.82
Randhawa et al. 2005	Udic ustochrept	No fertilization		0.06
		Lupin green manure (45 t ha ⁻¹)	21	0.27
Oehl et al., 2001	Haplic Luvisol	Manure and slurry (29 kg P ha ⁻¹ yr ⁻¹)	3	1.1 ±1.3
			7	1.7 ±0.2
			10	0.2 ±0.1
Oehl et al. 2004	Haplic Luvisol	Mineral (28 kg P ha ⁻¹ yr ⁻¹)	7	1.5
			10	1.4
		Manure and slurry (29 kg P ha ⁻¹ yr ⁻¹)	7	1.7
			10	1.6
		Manure and slurry (25 kg P ha ⁻¹ yr ⁻¹)	7	2.5
			10	1.9
Bünemann et al. 2007	Red chromosol		7	0.9 ±0.7
			14	0.5 ±0.3
Achat et al. 2009	Podzol	Forest	154	Remineralization: 0.09

A.4.4 Published results on SOP mineralization: long-term studies

There are two approaches in LTFE: the diachronic approach measures the studied variable over several years under different treatments using time series data, while the synchronic approach measures the system only at its final state (Dimassi et al. 2014).

On SOP, synchronic studies compare different treatments to the control, but the single measurement does not consider variations on the baseline (control). In fact, the mineralization induced by treatments may be lower than in the control (Rubaek and Sibbesen 1995; Motavalli and Miles 2002; Koch et al. 2018; van der Bom et al. 2019). Under these conditions, only diachronic studies are of interest to assess the SOP mineralization.

Few studies have examined the SOP from a diachronic approach, some studies are detailed in the following Table A.4.

Table A.4 Published results on SOP mineralization rates in long-term field experiments.

Reference	Zhang & MacKenzie 1997	Chatter et al. 1980	Song et al. 2011
Country	Canada	UK	China
Duration (yr)	5	10	14
Treatments	Mineral fertilization	Organo-mineral fertilization	Organo-mineral fertilization
SOP analysis	Hedley et al. (1982) fractionation (sum of organic P)	Saunders & Williams (1955) (Calcination & H ₂ SO ₄)	Legg & Black (1955) (Calcination & HCl)
SOP mineralization (kg P ha ⁻¹ yr ⁻¹)	25	4.05	9.6
Extreme values	29 – 22(ns)	8,5 – 0,5	11 – 8
Sampling date	1988 – 1989 1991 – 1993	1968 – 1973/74 1977/78	1993 – 2007

In these studies, SOP stock change slowly over time, although the experimental duration is typically less than a decade (Chater and Mattingly 1980; Zhang and MacKenzie 1997; Song et al. 2011). When studied, organo-mineral fertilization appears to enhance SOP mineralization. However, studies with mineral fertilization sometimes show higher mineralization rates. Therefore, the results show a high variability between studies, with sometimes important uncertainties and contradictory results. These differences cannot be explained by soil and/or crop effect alone, but other factors such as SOP speciation may explain part of this variability. Finally, these studies have focus on the variation of SOP stock and have only taken samples at a few specific dates (usually at the beginning and end of the experiment). This approach has enabled the estimation of net SOP mineralization, but it hasn't yielded any data on gross SOP mineralization. Currently, there are no results on gross SOP mineralization available at a field scale.

Therefore, diachronic studies with repeated measure over time in LTFE are needed to calculate mineralization rates in the SOP, focusing on the factors controlling the variation in mineralization rates. Modelling approaches are also needed in order to calculate SOP gross mineralization.

A.5 Conclusion

The routine chemical extraction methods used to evaluate the plant-available P have been found to be unsatisfactory. Hence, it is imperative to shift the existing paradigm and adopt a more efficient approach that involves analyzing, comprehending, and quantifying the key mechanisms associated with crop P nutrition under field or representative conditions.

Plant roots absorb 30-40 kg P during the growing period, of which only a small fraction comes from the soil solution. Diffusion of phosphate ions at the solid-to-solution interface appears to be the main mechanism that replenish the soil solution with phosphate ions. However, research on this process have seldom considered biological processes and has not been frequently conducted in field experiments. The contribution of SOP mineralization to this replenishment process has not been quantified yet.

On average, 30% of TP is organic in the plough soil layer. In addition, cropped soils harbor a microbial community which can mineralize SOP. Therefore, SOP mineralization is expected to significantly contribute to phosphate ions release into the soil solution. However, this mechanism has been poorly studied, especially under different agropedoclimatic conditions. Monitoring the SOP stock kinetics based on LTFE is promising to calculate the SOP mineralization for different soil types and P fertilizations. The results will contribute to provide new insights on SOP dynamics. It will also allow to test the influence of different agropedoclimatic parameters on this P resource.

B Objective and hypothesis

In order to understand the replenishing of the plant-available P pool in soils, the explanation most commonly advanced in literature is the diffusion of phosphate ions at the solid-to-solution interface. However, in cropped soils, the soil organic P (SOP) stock in the plough layer represents a significant proportion of the total P concentration, and is often highlighted as a potential source of phosphate ions to replenish the soil solution. Yet, the actual quantification of SOP mineralization to the plant-available P pool in cropped soils and its potential drivers remains a largely uninvestigated question.

The main objectives of this thesis were:

- (i) to quantify the annual rates of SOP mineralization in the plough layer of different temperate agrosystems cropped on the long term, in order to determine the extent of this mechanism to replenish the soil solution in phosphate ions, and therefore, its contribution to the plant-available P;
- (ii) to determine the drivers of SOP mineralization in the plough layer, especially the effect of P molecular speciation in the SOP stock, and the effect of these controlling factors on mineralization rates.

The evaluation of SOP mineralization was conducted by monitoring the evolution of the SOP stock over several decades, working under the hypothesis that (H1) the P budget determines the mineralization rate, because repeated applications of mineral or organic P fertilizers would modify crop residue P, affecting the soil P speciation and thus the rate SOP mineralization. The SOP dynamics was analyzed through a modelling approach that accounts for P input into the SOP stock by the decomposition of crop residues and organic fertilizers, and for the gross mineralization of the initial soil SOP stock. The model was run under the assumptions that (H2) the differences in P speciation and quantity among fertilizers are reflected by different mineralization rates, and similarly (H3) differences between agrosystems (i.e. soil characteristics, fertilization type and amount, crop succession and management, irrigation, climate) imply different mineralization rates.

These two objectives were developed into three chapters, in which the study of SOP mineralization and its driving factors is divided as follows: (1) the calculation of SOP mineralization rate in a long-term field experiment (LTFE), and its relation to soil P speciation, under maize monoculture with three different rates of mineral P fertilization; (2) the calculation and comparison of the respective SOP mineralization rates in contrasting agrosystems, with different soil type, different climates, and different management practices; and (3) the respective effect of the long-term application of different organic waste products (OWP) as fertilizers on the soil P status and molecular speciation.

C Materials and methods

C.1 Presentation of the four long-term field experiments

To answer our research questions, we used data from four different long-term field experiments (LTFE) in France. The description of the LTFE and the analytical methods used are presented in this introductory section. Further details are provided in each chapter according to the LTFE studied.

C.1.1 LTFE selection

The four LTFE were selected according to different criteria based on our research questions and operational needs. The LTFE must have:

- i) a duration of more than a decade (the longer the better);
- ii) a complete database of times series on plant (yield, its P concentration; aboveground biomass of crop residues and its P concentration) and soil measurements;
- iii) frequent soil sampling in order to have time-series data set over long periods (>10 years to almost three decades);
- iv) different agropedoclimatic situation among the four sites, with different soil classifications, different climates, and different fertilization (form and rates) being studied.

To make the study possible, LTFE also needs to have the soil samples stored for possible reanalysis, and a directly available database on agronomic management, soil parameters, and climate. The four LTFE locations on the French territory are shown in Figure C.1.

The first two LTFE are part of the French network on P fertilization (Boniface and Trocmé 1988), and the two remaining are part of the [SOERE-PRO](#) (*Système d'Observations et d'Expérimentations pour la Recherche en Environnement sur les Produits Résiduaire Organiques*) network. All the experimental designs were set up as randomized complete block design with four replications for each treatment and control.

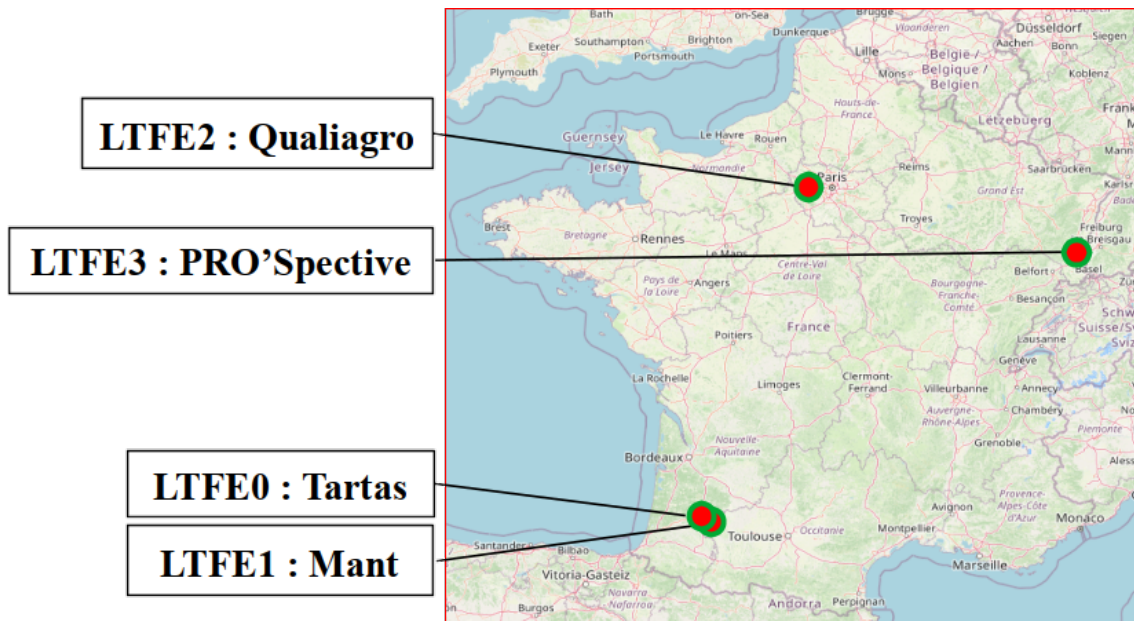


Figure C.1 Localisation of the four LTFE across the French territory.

C.1.2 Description of the four LTFE studied

LTFE0

This experiment was started in Tartas on a maize monoculture (43°52' N, 0°44' W; altitude: 55 m; Landes, Nouvelle Aquitaine), from 1972 to 2000. The local climate is temperate subhumid (Cfb in the Köppen classification). Average monthly rainfall+irrigation and temperatures over the experimentation periode are in Figure C.2. The experimental site was established on a farm with maize cultivation since the 1950s, with poultry litter applications until the end of the 1960s. The soil is a Luvic Arenosol according to the FAO (2014) classification.

Phosphorus fertilization was applied as commercial triple superphosphate at three different rates: 44 (TSP₄₄), and 96 (TSP₉₆) kg P ha⁻¹ yr⁻¹, and a control treatment (CON₀) receiving no P. In addition, all plots were fertilized with N and K according to soil analysis and local recommendations for non-limiting conditions. Soils were limed with dolomite every 4 – 5 years to maintain a soil pH of approximately 6.0. Aboveground maize residues were returned to the soil surface at harvest and then buried a few weeks later. The experiment design is presented in Figure C.3.

In 1976, 1977, 1978, 1980, 1983, 1986, 1988, 1992, 1995, 1998 and 2000, in March-April before P fertilization, ploughing, and seedling, the soils of all experimental plots were sampled in the plough layer. In 1998, soils were sampled in June. Grain yield was measured at maize maturity on plant sample in the two central rows on an 8-m length of each experimental plot.

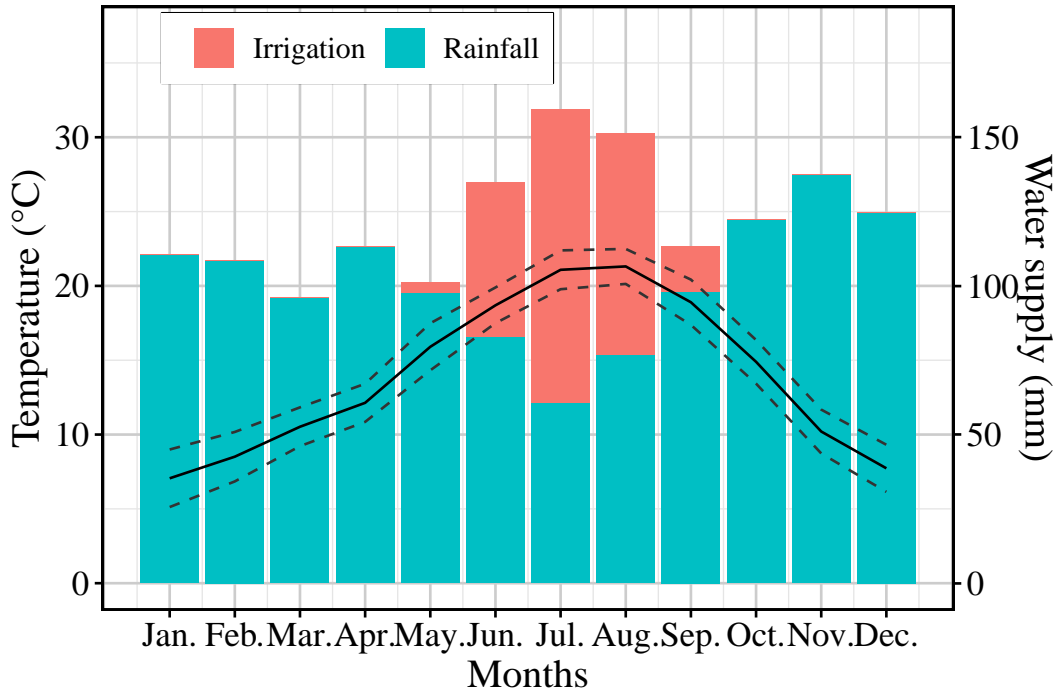


Figure C.2 Average monthly rainfall (mm) and temperatures (°C) at Mont-de-Marsan, the nearest MétéoFrance station from LTFE0 and LTFE1. Irrigation is the water supply in LTFE0.

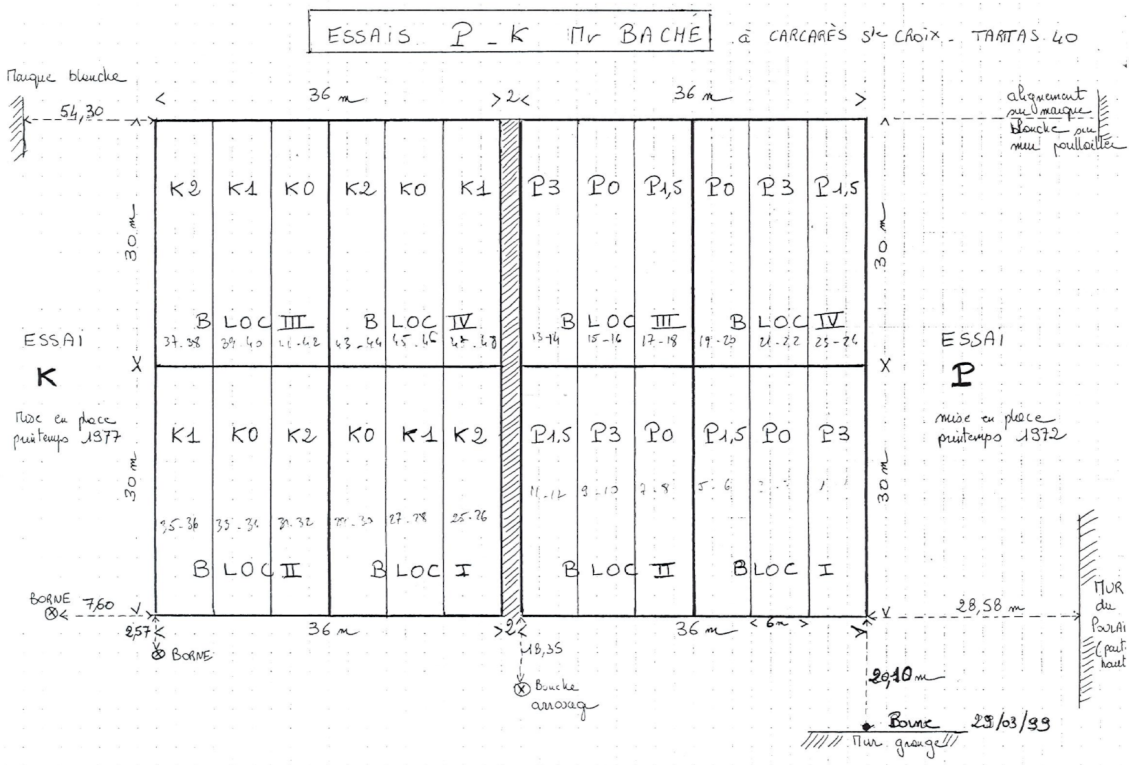


Figure C.3 On the right side of the plan, presentation of the LTFE0 experimental set-up including four blocks of three doses of triple superphosphate : on average 0, 44, and 96 kg P ha⁻¹ yr⁻¹, denoted P0, P1.5 and P3 in the plan, applied for 28 years.

LTFE1

This experiment was started in 1975 at a location close to LTFE0, in Mant (43°35' N, 0°30' W; altitude: 188 m; Landes, Nouvelle Aquitaine), and ended in 1991. Like LTFE0, the local climate is oceanic sub-humid (Cfb). Average monthly rainfall and temperatures over the experimentation period are in Figure C.2. The experiment was conducted on a silt loam luvisol according to the FAO (2014) classification under maize (*Zea mays* L.) monoculture.

Mineral P fertilization was applied annually as triple superphosphate (TSP) at 0 (CON₀), 27 (TSP₂₇), and 79 (TSP₇₉) kg P ha⁻¹ yr⁻¹. As for LTFE0, plots were fertilized with N and K for non-limiting conditions, and limed to maintain pH neutral. In addition, aboveground maize residues were also returned to the soil at harvest and then buried. The scheme of the experimental design is presented in Figure C.4.

Soils in the plough layer of the 12 plots were sampled at the beginning of the experiment and after 7, 12, and 17 years of cropping. Crops were annually sampled for yield and P concentration before harvest from the two central rows of maize on 8–10 m of length (area of 12–15 m²).

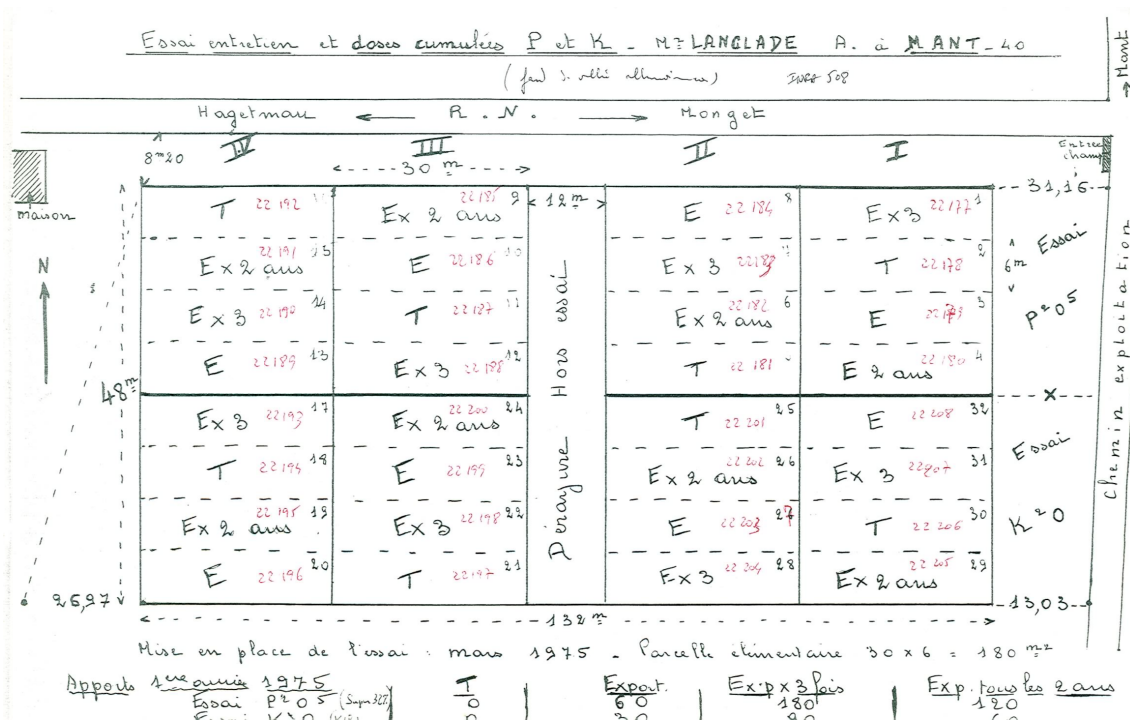


Figure C.4 Plan of experimental set-up of LTFE1 on P fertilization (see *essai P₂O₅* in the upper part) near the village of Mant (LTFE1) with four blocks of 4 applications rates of triple superphosphate. In this thesis, we only consider three rates: no P applied; P applied is equal to P exported in grain the previous year; P applied at 3 times the P exported in grain the previous year, denoted (T, E, and E×3 in the plan).

LTFE2

This LTFE was established at Feucherolles (48°53'N, 1°58'E; altitude: 177 m; Yvelines, Île-de-France) as part of the [QualiAgro](#) long-term study (Houot et al. 2002). The local climate is oceanic sub-humid degraded, also classified as Cfb. Average monthly rainfall and temperatures over the experimentation period are in Figure C.5. This experiment was conducted for 17 years on a glossic luvisol (FAO 2014), under annual rotation of maize/wheat (*Triticum spp.*). Barley were cropped in 2007 and 2015. About 1/3 of wheat and barley straw were exported at harvest. The remaining aboveground residues were returned to the soil, as for all the maize residues.

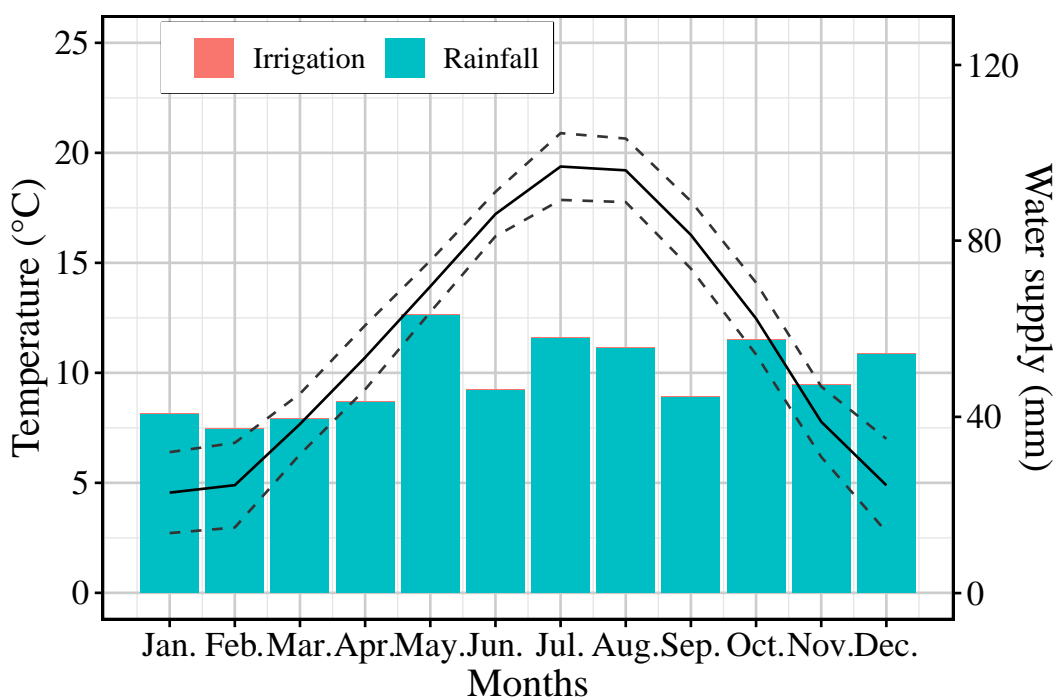


Figure C.5 Average monthly rainfall (mm) and temperatures (°C) at LTFE2. Data are from the INRAE [CLIMATIK](#) platform, managed by the AgroClim laboratory of Avignon, France.

Four OWP were applied at $4 \text{ t C ha}^{-1} \text{ yr}^{-1}$ every tow year from 1998 to 2013 and at $2 \text{ t C ha}^{-1} \text{ yr}^{-1}$ in 2015. With the control, no P applied (CON), five fertilization treatments were studied, three urban composts: a municipal solid waste compost, supplying 24 kg P ha^{-1} (MSW); a biowaste compost, supplying 46 kg P ha^{-1} (BIOW); a green waste and a dehydrated urban sewage sludge compost, supplying 112 kg P ha^{-1} (GWS), and a cattle dairy farmyard manure, supplying 40 kg P ha^{-1} (FYM) (Annabi et al. 2011). In addition, until 2013, plots were annually fertilized with mineral N for optimal N supply. In 2014, this was changed to a mixture of meat and bone powder and blood flour (AXE-NP-BIO®; AFNOR standard NF U42-001). This product contained 2.2% of P. Therefore, CON received 47 kg P ha^{-1} in 2014, while other plots received an additional 16 kg P ha^{-1} in

2015. Plots were not fertilized for synthetic P or K supply. As for LTFE0 (an all other LTFE studied), the experimental designs were set up as a randomized complete block design with four replications for each treatment and control (Figure C.6).

Soil was sampled in the plough layer within each experimental plot prior to each OWP application. Crops were sampled each year in height subplots (1 m² or 0.5 m² for maize, and wheat and barley, respectively) within each experimental plot.

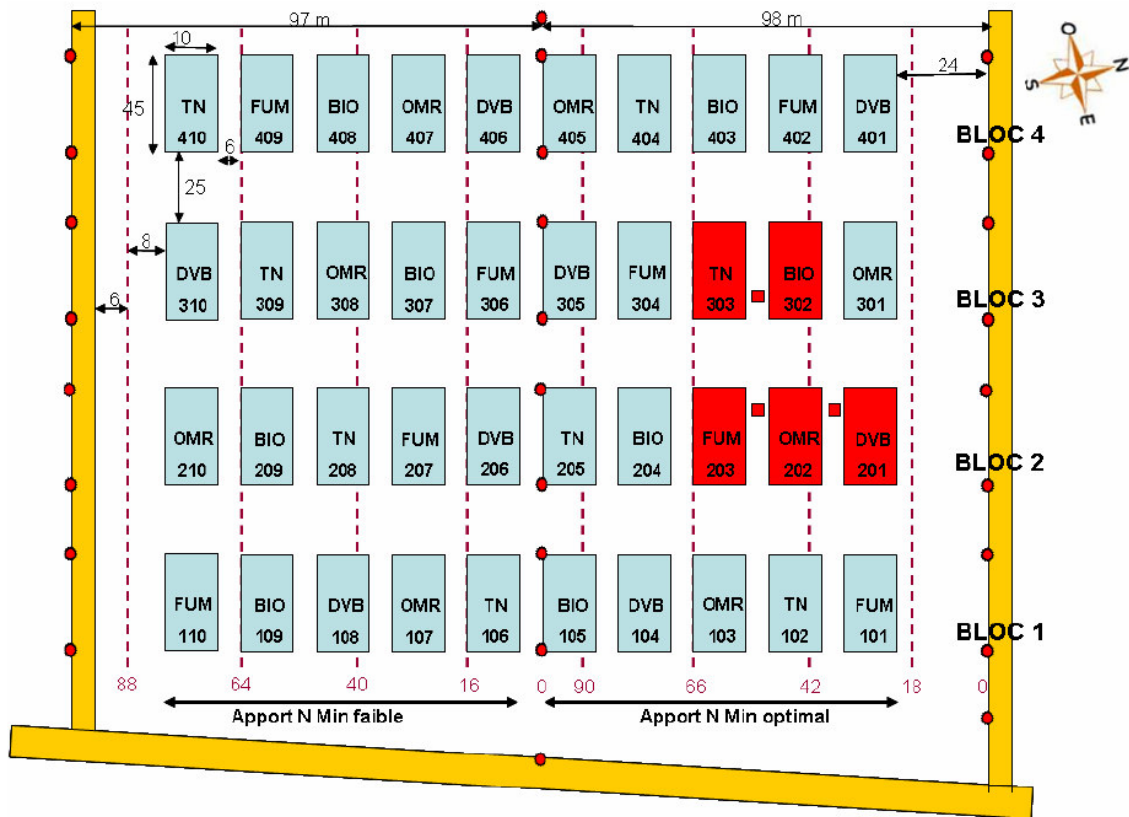


Figure C.6 Design of LTFE2 with four blocks of 10 plots. Within blocks, the 5 plots on the right were N-fertilized and studied in this thesis. The 5 red plots were equipped with devices to collect soil solutions. Source: Bodineau et al. 2007.

LTFE3

The LTFE3 took place between 2000 and 2014 at the INRAE research center in Colmar (48°04'N, 7°21'E; altitude: 205 m; Haut-Rhin, Alsace). The experiment was established on a calcareous cambisol, and the local climate is semi-continental (Cfb). Average monthly rainfall and temperatures over the experimentation period are in Figure C.8.

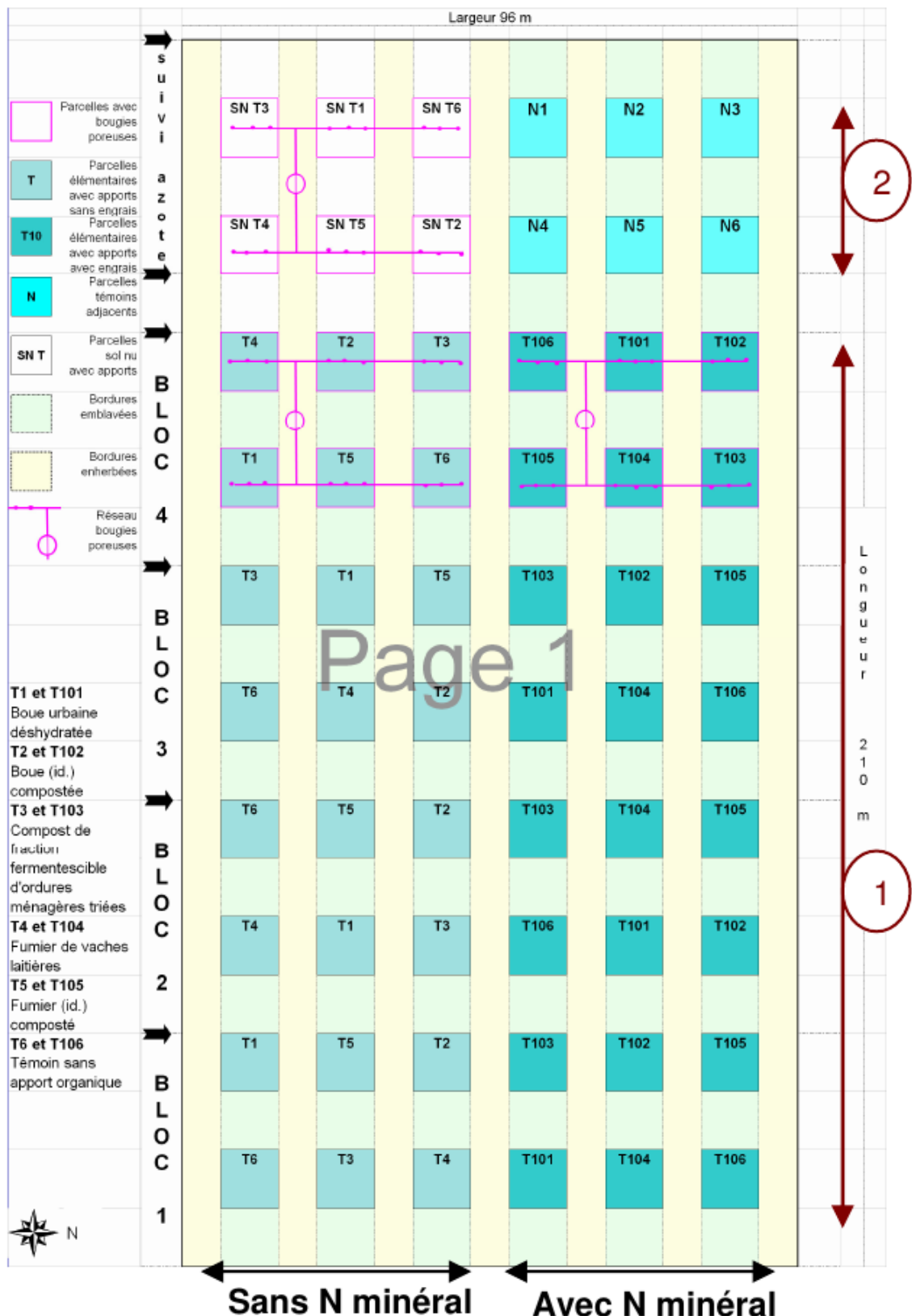


Figure C.7 Layout of LTFE3 with four blocks of 12 plots (1 section). The 6 blocks on the right were fertilized with mineral N and studied in this thesis. The pink lines are the network of the device for measuring the soil moisture meter. Section 2 (not studied) was dedicated to the study of OWP on bare fallow (left), and only mineral N fertilization (right). Source: Montenach et al. 2007.

Five OWP were applied at the rate of 170 kg organic N ha⁻¹ 2yr⁻¹. The six fertilization treatments and their respective P supply include a control with no P applied (CON₈), a biowaste compost, at 17 kg P ha⁻¹ yr⁻¹ (BIOW₁₇), a dairy farmyard manure, at 21 kg P ha⁻¹ yr⁻¹ (FYM₂₁); iv) the same dairy farmyard manure, composted, at 21 kg P ha⁻¹ yr⁻¹ (FYMC₂₁), a dehydrated urban sewage sludge, at 36 kg P ha⁻¹ yr⁻¹ (SLU₃₆), a green waste and sewage sludge compost, at 45 kg P ha⁻¹ yr⁻¹ (GWS₄₅). The OWP applied to the soil were buried the day after fertilization. All plots were fertilized with mineral N in early spring in order to adjust N supply. When sugar beet was cropped, plots were fertilized with TSP at 46 kg P ha⁻¹ (2007), and at 11, 31 and 72 kg P ha⁻¹ (2011) for FYMC₂₁, BIOW₁₇ and CON₈ respectively. The experimental design is shown in Figure C.7.

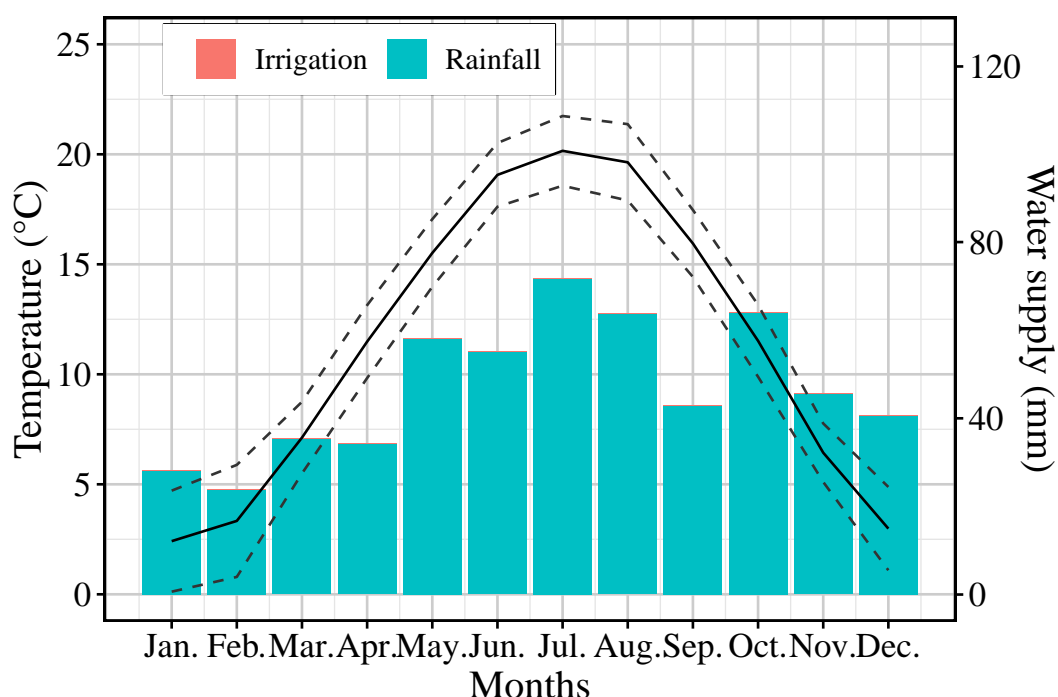


Figure C.8 Average monthly rainfall (mm) and temperatures (°C) at LTFE3. Data are from the INRAE CLIMATIK platform, managed by the AgroClim laboratory of Avignon, France.

Soils were sampled in the plough layer in each experimental plot before the start of the experiment and then every two years. Crops were sampled each year immediately before mechanical harvest.

C.1.3 LTFE database available

Some LTFE characteristics and soil properties are shown in Table 4. Further details are provided in the three chapters of this thesis.

Agronomical management and data

Cropping practices include the type and rate of fertilization, the crop residues annually returned to soil, the annual crop yield (determined on plant sampled in sub-plot and dried at 40°C), as well as the crop P concentration (in aboveground residues and in harvest; method differ among LTFE). The exported P was calculated as the harvest P concentration times the crop yield. In addition, the plot cumulative P budget (Bcum) was calculated by adding up over years the annual budgets.

OWP characteristics in LTFE2 and LTFE3

The main characteristics of the OWP applied in LTFE2 and LTFE3 are presented in Table 2.1. Sampling was performed prior to application, and samples were air-dried and ground (<250 µm) for analysis at the *Laboratoire d'Analyses des Sols INRAE* (LAS, Arras, France) according to standardized procedure (AFNOR 1999). The OWP were analyzed for dry matter (DM), after heating >105°C, pH_{water}, total N, organic C, and CaCO₃ concentration. Total P concentration (TP_{HF}) were determined by ICP-OES after wet digestion with concentrated hydrofluoric (HF) and perchloric (HClO₄) acids. Organic P concentration in OWP were determined by the Saunders and Williams (1955) ignition method. Inorganic P concentration were calculated as the difference between TP_{HF} and organic P in OWP.

Soils characteristics

The main soil properties are presented in Table C.1 and were evaluated according to French AFNOR and ISO standards (AFNOR 1999). Soils textures were determined by sedimentation analysis (NF X 31-107 and ISO 11277). The pH_{water} was measured in a soil suspension (volume:mass ratio = 1:2.5; ISO 10390). Cation exchange capacity and exchangeable cations were determined by the cobaltihexamine method (NF ISO 23470). In LTFE1 and 2, the oxalate-extractable Fe and Al (McKeague and Day 1966) were used as a proxy for the amorphous crystal of Fe and Al. Soil total carbonate concentration was determined according to NF ISO 10693. SOC was determined differently depending on the experiment: in LTFE0, 1, and 3, it was determined by sulfochromic oxidation using excess potassium dichromate solution and sulfuric acid (ISO 14235), while in LTFE2 it was determined by combustion (ISO 10694). Total N was determined by a modified Kjeldahl method (ISO 11261) in LTFE1 and 2, and by total elemental analysis CN (ISO 13878) in LTFE 2 and 3. Soils characteristics were determined as concentrations. When needed, stocks were calculated by multiplying concentration by soil mass (depends on sampling depth and soil bulk density).

Soil P status

Soil TP_{HF} was determined using the standard NF X 31-147 procedure as described for OWP. The SOP was determined using the Saunders and Williams (1955) procedure. The SOP value was calculated as the difference between the P concentration in the ignited soils and the P concentration in the non-ignited samples. Soil inorganic P stock (SIP) was calculated as the difference between TP_{HF} and SOP. The phosphate ions in solution of soil suspensions, C_P, was determined at a volume-to-mass ratio of 10. The Olsen-P was determined in bicarbonate extraction according to Olsen et al. (1954); NF ISO 11263. Phosphate ions concentration in extraction solution was determined by the green malachite colorimetric method (Van Veldhoven and Mannaerts 1987), with a spectrophotometer at 610 nm.

Table C.1 LTFE characteristics and main soil physicochemical properties of the plough layer at the four studied LTFE. Values are means \pm std. dev. For LTFE0, values are means ($n = 4$) for soils sampled in TSP₄₄ treatment in march 1995. For LTFE1, values are means ($n = 4$) for soils sampled in TSP₂₇ treatment in March 1992. For LTFE2 and LTFE3, values are means for all experimental plots and years of soil sampling ($n = 140$ and $n = 144$, for LTFE2 and LTFE3, respectively).

Characteristic	LTFE0	LTFE1	LTFE2	LTFE3
LTFE characteristics and cropping practices				
Duration (yr)	28	17	17	14
Annual rainfall (mm)	950	917	695	556
Annual irrigation (mm)	242	298	0	0
Annual temperature (°C)	13.2	13.2	11.0	10.9
Crops succession	Continuous maize	Continuous maize	Maize / Wheat	Maize / Wheat / Barley / Sugar beet
Sampling depth (cm)	25	25	25	28
Bulk density (g cm ⁻³)	1.56	1.40	1.32	1.34
Main soil properties at four LTFE				
Clay [$< 2 \mu\text{m}$] (%)	6 \pm 1	12 \pm 1	15 \pm 7	21 \pm 1
Silt [5 – 50 μm] (%)	13 \pm 3	52 \pm 1	78 \pm 5	70 \pm 1
Sand [50 – 200 μm] (%)	81 \pm 7	36 \pm 1	7 \pm 4	9 \pm 1
pH	5.9 \pm 0.2	7.3 \pm 0.4	7.2 \pm 0.3	8.3 \pm 0.1
CaCO ₃ (g kg ⁻¹)	<1	<1	<1	114 \pm 13
SOC (g kg ⁻¹)	10.3 \pm 3.1	9.3 \pm 0.9	12.5 \pm 2.0	14.6 \pm 1.0
Total N (g kg ⁻¹)	0.8 \pm 0.2	1.0 \pm 0.1	1.2 \pm 0.2	1.4 \pm 0.1
CEC (cmolc kg ⁻¹)	3.6 \pm 0.7	5.9 \pm 0.8	9.8 \pm 0.9	16.9 \pm 0.5
Fe _{ox} (mmol kg ⁻¹)	20.1 \pm 4.7	21.1 \pm 0.2	nd ^z	nd
Al _{ox} (mmol kg ⁻¹)	21.5 \pm 4.4	44.1 \pm 0.4	nd	nd
Initial TP _{HF} (mg kg ⁻¹)	375 \pm 30	431 \pm 10	660 \pm 9	1144 \pm 8
Initial SOP (mg kg ⁻¹)	94 \pm 5	127 \pm 4	161 \pm 8	305 \pm 6
Initial SIP (mg kg ⁻¹)	281 \pm 258	303 \pm 8	499 \pm 13	839 \pm 11
Initial C _P (mg L ⁻¹)	1.11 \pm 0.13	0.94 \pm 0.07	1.04 \pm 0.05	0.66 \pm 0.02

^z nd: not determined

C.2 SOP mineralization

The dynamics of SOP in the plough layer has been addressed by two different approaches. i) The first one focuses on the inter-annual variation of SOP by monitoring the stock over time using long time-series data. This variation can be negative, neutral or positive and corresponds to a net change in SOP stock due to the different inputs and outputs P fluxes associated with this compartment. ii) The second focuses on a more detailed approach of the SOP dynamics by estimating an incorporation P flux (input) and a gross mineralization P flux (output).

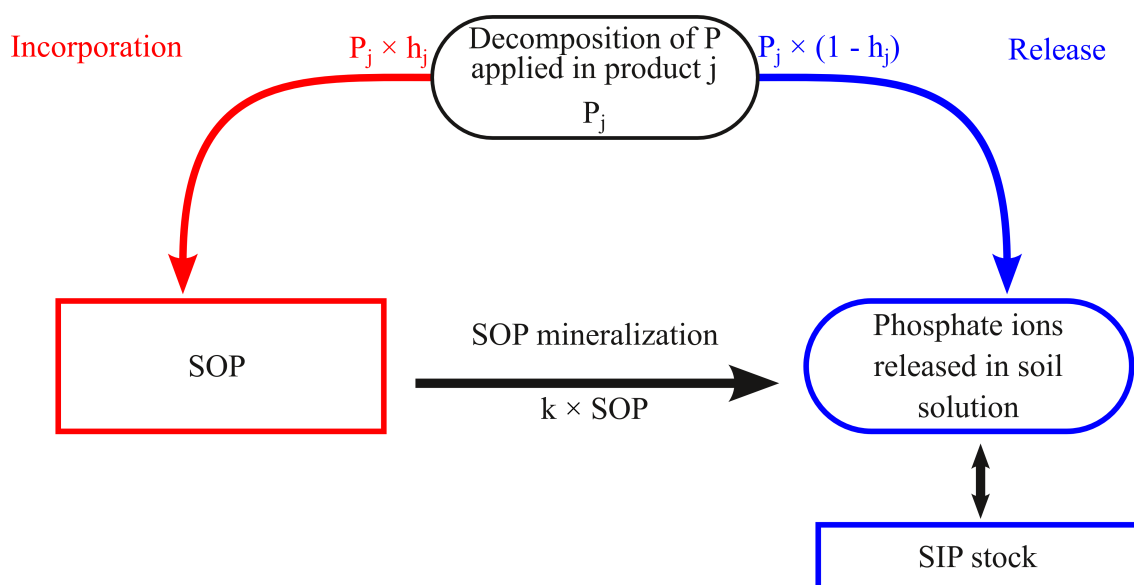


Figure C.9 Diagram of the model describing the dynamics of SOP stock, P fluxes and processes that drives its dynamics. The P applied in product j (P_j) is either released [$P_j \times (1-h)$] in solution as phosphate ions or incorporated ($P_j \times h$) into SOP. The SOP stock mineralizes according to the k mineralization constant.

Within the latter approach, the SOP dynamics in the plough layer of arable soil were determined using the simple model shown in Figure C.9. This model was adapted from the model developed to monitor SOC in agricultural soils (Hénin and Dupuis 1945). We assumed that this theoretical framework used to describe, simulate and predict SOC dynamics was also valid for SOP, since it describes the dynamics by the balance between inputs and outputs of stocks, at the annual time step.

The model in Figure C.9 considers as input variables the initial SOP stock and the different P input in the different crop residues (i.e. aboveground residues, belowground residues, and grain losses at harvest) or OWP. Crop residues and OWP decomposition during the year after application supply the SOP stock according to the incorporation coefficient (h), and the remaining $(1-h)$ P fraction is released into the solution as phosphate, polyphosphates, and easily degradable organic P compounds. The SOP is mineralized annually according to

first-order kinetics considering k , the constant rate of mineralization, and $1/k$ the residence time. We neglected the contribution of microbial biomass to SOP dynamics through immobilization/(re)mineralization processes. The SOP leaching rate was also considered to be negligible.

The output variables were: i) the calculated SOP stocks; ii) the phosphate ions fluxes supplying the soil solution through either SOP mineralization ($= k \times SOP_t$, for the year t) or through crop residue and OWP decomposition on a time step inferior to the model [$= (\text{residues-derived P at year } t) \times (1-h)$]; iii) the P fluxes from crop residues and OWP decomposition that supplying the SOP stock annually [$= (\text{residues-derived P at year } t) \times (h)$]. The SOP stock calculations were performed according to the following set of equations:

$$\Delta SOP = P_j \times h_j - SOP \times k \quad (\text{Eq. C.1})$$

$$(\text{Eq. C.2})$$

$$SOP_{t+1} = \frac{\sum(P_j \times h_j)}{k} \times (1 - e^{-k}) + SOP_t \times e^{-k} \quad (\text{Eq. C.3})$$

Where:

SOP_t: the SOP stock (kg ha^{-1}) at year t with **SOP₀** being at the onset of the experiment;

k: the mineralization coefficient of SOP (yr^{-1});

j: the product applied to the soil, either crop residues or specific OWP;

P_j: the amount of organic P input through the product j ($\text{kg P ha}^{-1} \text{ yr}^{-1}$);

h_j: is the incorporation coefficient (dimensionless) of the product j ;

t: the model time step (yr).

C.3 SOP speciation determined by P-NMR spectroscopy

Soils sampled in 2000 at LTFE0, soils sampled in 1998 and 2016 at LTFE3, and OWP sampled in 1998, 2007 and 2011 at LTFE3 were analyzed by solution P-NMR to identify and quantify P compounds using the modified Cade-Menun and Preston (1996). Briefly, samples were extracted with 25 mL of 0.25 mol L^{-1} NaOH and 0.05 mol L^{-1} Na₂EDTA solution. The P, Al, Fe, Ca, and Mn were determined by ICP-OES for each sample, and used to determine NMR delay times based on the ratio of P/(Fe+Mn) in the extracts (McDowell et al. 2006; Cade-Menun and Liu 2014). The NMR instrument parameters for spectrum acquisition were slightly different for each LTFE. Details are given in Chapter 1 and 2 according to the LTFE studied. Since some orthophosphate diesters (phospholipids, RNA) are degraded during the procedure to peaks appearing in the orthophosphate monoester region (Liu et al. 2015; Schneider et al. 2016; Recena et al. 2018), orthophosphate monoester

and diester concentrations were corrected by subtracting degradation compounds (α - and β -glycerophosphate and the mononucleotides) from the total orthophosphate monoester area and adding them to the total diester area (Schneider et al. 2016). Chemical shifts of spectra were assigned to P compounds based on (Cade-Menun 2015) and by spiking with reference compounds. Spectra were processed with 7 and 2 Hz line broadening, using NUTS software (2000 edition; Acorn NMR, Livermore, CA), peak areas were calculated by integration and manual calculation. Tables of chemical shifts of identified compounds and example spectra are included in the respective chapters.

C.4 Statistical analysis

This section aims to describe the general statistical approach used in this thesis. Further details and specificities are provided within each chapter. The free software R version 4.1.2 (R Core Team 2021) was used for statistics and modelling analysis.

Across all our data, the normality of residues was tested by Shapiro tests and variance homogeneity was tested by Bartlett tests.

The variations of studied parameters (e.g. SOP stock, SOP mineralization, yield) among LTFE were investigated by linear models using the *lm* function. Within each LTFE, the effects of explanatory variables (e.g. fertilization treatments, years, plot P budget) on response variables were examined by linear mixed effect models, fitted by a restrictive maximum likelihood method, with the *lme* function from the *nlme* (Pinheiro et al. 2022). The explanatory variables tested were set as the fixed effect in the models. To account for spatial pseudoreplication (4 repetitions), blocks were set as the random effect variable. To consider non-independent measurements within plots across time, we used years as the continuous variable we used to fit a first-order auto-regressive variance structure.

The P-NMR results on soils and OWP samples were analyzed following the standard procedure for compositional data (Abdi et al. 2015): data were transformed using centered log-ratio (clr) before further analysis for each P compound and group.

Following clr transformation and linear models, for a given LTFE, the effects of discrete explanatory variables were investigated with one-way or two-way ANOVA. When results showed a significant effect ($\alpha = 0.05$), differences between treatments and/or years were investigated with a post-hoc Tukey test.

The mineralization coefficient k , was determined iteratively for each experimental plot using the *optim* function with the "L-BFGS-B" method, by minimizing the residual sum of squares of simulated versus observed SOP time series data. The "L-BFGS-B" method allows upper and lower boundaries for k optimization, set between 0.001 and 1.

The standardized major axis regression was used to evaluate adequacy between observed and predicted SOP values (Correndo et al. 2021a). This approach allows to fit a symmetric line describing the predicted-observed scatter. Adequacy between observations and simulations was studied with several statistical criteria: the coefficient of determination (R^2), the root mean squared error (RMSE), and the relative root mean squared error (RRMSE). In addition, the model error was decomposed into percentage lack of precision (PLP) and percentage lack of accuracy (PLA). Here are the equations for the statistical criteria:

$$R^2 = \left[\frac{\sum_{i=1}^n (S_i - \bar{S})(O_i - \bar{O})}{\sigma_S \sigma_O} \right]^2 \quad (\text{Eq. C.4})$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (S_i - \bar{S})^2}{n}} \quad (\text{Eq. C.5})$$

$$RRMSE = 100 \times \frac{RMSE}{\bar{O}} \quad (\text{Eq. C.6})$$

$$PLA = 100 \times \frac{\frac{1}{n} \times \sum_{i=1}^n (S_i - \hat{O}_i)^2}{\frac{1}{n} \times \sum_{i=1}^n (O_i - S_i)^2} \quad (\text{Eq. C.7})$$

$$PLP = 100 \times \frac{\frac{1}{n} \times \sum_{i=1}^n (|S_i - \hat{S}_i|)(|O_i - \hat{O}_i|)}{\frac{1}{n} \times \sum_{i=1}^n (O_i - S_i)^2} \quad (\text{Eq. C.8})$$

With: S_i and O_i : the simulated and observed values; \bar{S} and \bar{O} : the respective means of simulated and observed values; $\sum_{i=1}^n (S_i - \hat{O}_i)^2$: the sum of systematic differences; $\sum_{i=1}^n (|S_i - \hat{S}_i|)(|O_i - \hat{O}_i|)$: the sum of unsystematic differences; \hat{S}_i and \hat{O}_i : the parameters derived from the symmetric linear regression; n : the number of simulated-observed pairs, $\sigma_S = \frac{1}{n} \times \sum_{i=1}^n (S_i - \bar{S})^2$ and $\sigma_O = \frac{1}{n} \times \sum_{i=1}^n (O_i - \bar{O})^2$ standard respective deviations of the simulated and observed values. These error metrics were computed using R-code tutorial proposed by Correndo et al. (2021b).

CHAPTER 1

Mineralization and speciation of organic phosphorus in a sandy soil continuously cropped and phosphorus-fertilized for 28 years

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Mineralization and speciation of organic phosphorus in a sandy soil continuously cropped and phosphorus-fertilized for 28 years

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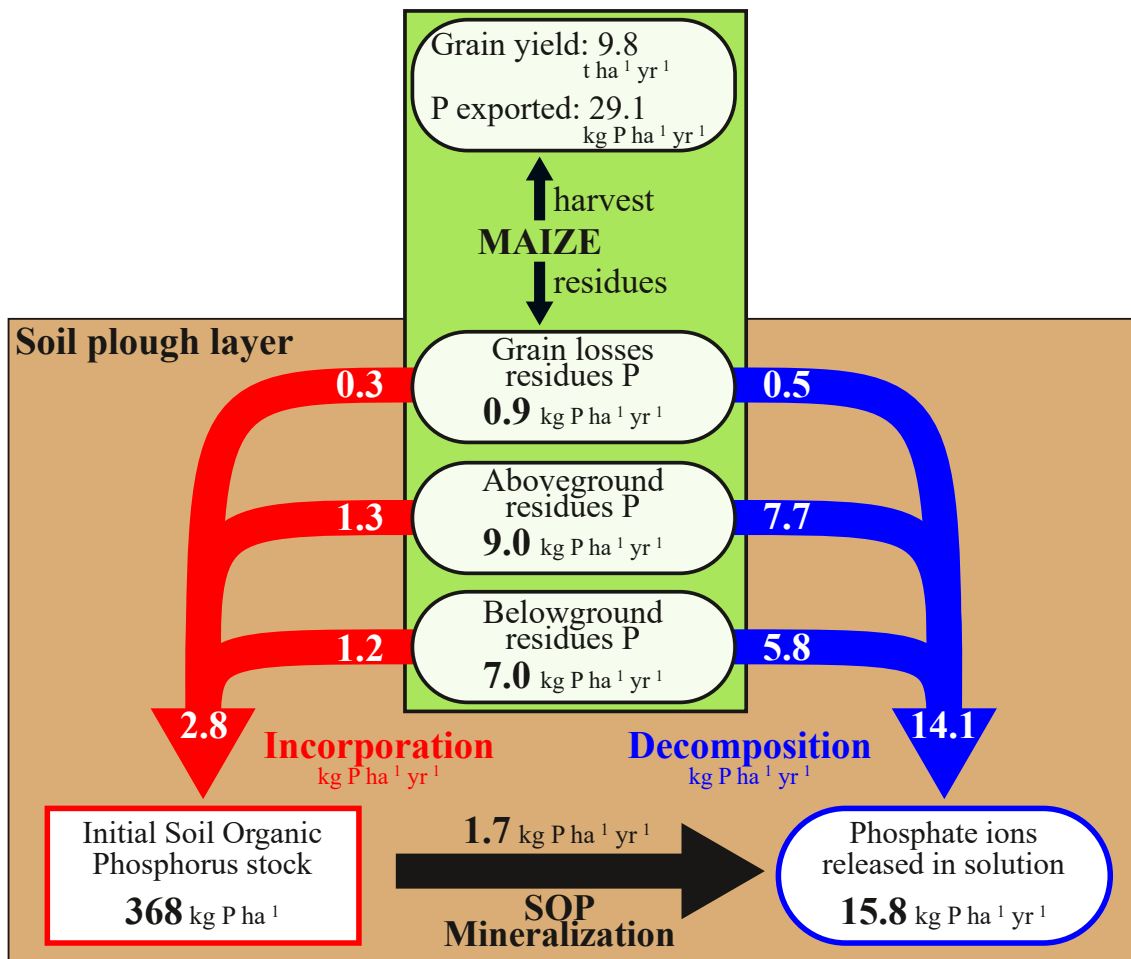
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Graphical abstract



Abstract

Phosphorus (P) is essential to plants and many crops require P fertilizers to optimize yields. However, there are concerns about future scarcity of the rock phosphates used to produce P chemical fertilizers. Soil organic phosphorus (SOP) might play a significant role in plant nutrition and soil P availability, reducing fertilizer requirements, but SOP mineralization is poorly understood. This study assessed rates of SOP mineralization and SOP speciation using a long-term field experiment in France, continuously cropped (1972-2000) and fertilized at three rates (triple superphosphate). The SOP concentration was determined every 2-3 years using the Saunders and Williams ignition method and converted to stock considering the soil mass per hectare; P speciation was determined using solution P nuclear magnetic resonance spectroscopy. The SOP stocks slightly increased with time, irrespective of P fertilization rates. Inorganic P stocks decreased without fertilization, but increased at the high P fertilization rate. By adapting a model describing soil organic carbon dynamics, the gross mineralization coefficient (k) was calculated with initial SOP stock (368 kg P ha^{-1}), P in maize residues (average of $17.0 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, differences across yields, plant parts and P fertilization rates) and their 17% incorporation rates into SOP (i.e. $2.9 \text{ kg P ha}^{-1} \text{ yr}^{-1}$). Irrespective of P fertilization rates, the model calibration using SOP time series gave a k-value of 0.0047 yr^{-1} (212 yr residence time) and a mineralization rate of $1.7 \pm 1.2 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. Speciation of SOP was 77% of orthophosphate monoesters, and 20% of orthophosphate diesters regardless of the P fertilization rates. The predominance of inositols hexakisphosphates, known to be strongly stabilized through sorption, might explain the low SOP mineralization rate. The results for these soils suggest that SOP may only play a minor role in soil P availability and crop nutrition.

Keywords:

Plant-available soil P, Crop management, Dynamics, Long-term field experiment, P-NMR.

Highlights:

- SOP dynamics were assessed by coupling 28-year data time series and modeling
- SOP stock and its speciation (P-NMR) changed very little with P application rate
- Phosphate ions was released from SOP by mineralization at $1.7 \pm 1.2 \text{ kg P ha}^{-1} \text{ yr}^{-1}$
- Low SOP mineralization may be due to high IHP concentrations

Résumé

L'objectif de ce chapitre est de modéliser la dynamique du POS en considérant que des régimes de fertilisation minérale phosphatée contrastés modifieraient la spéciation du P des résidus de culture et du POS, modifiant leurs capacités à libérer des ions phosphate dans la solution du sol. Grâce à un essai agronomique de 28 ans comprenant trois régimes de fertilisation minérale, nous avons montré que le stock de PIS augmente avec le taux de fertilisation et diminue en l'absence d'apport, alors que le POS reste stable. Le temps de résidence du POS calculé par modélisation était de 212 ans avec une faible vitesse de minéralisation, qui ne peut jouer qu'un rôle mineur dans la nutrition des plantes cultivées. La faible vitesse de minéralisation peut être expliquée par l'abondance des IHP, stabilisé par la phase solide du sol, minéralisé par des enzymes spécifiques (inhibées par une forte concentration d'ions phosphate en solution).

Mots clés :

P phytodisponible du sol, Gestion des cultures, Dynamique, Essai agronomique de longue durée, RMN du P.

Éléments clés :

- La dynamique du POS a été déterminée en couplant des séries chronologiques de données sur 28 ans et de la modélisation
- Le stock de POS et sa spéciation (RMN-P) ont très peu changé avec le taux d'application du P
- La minéralisation du POS a libéré $1.7 \pm 1.2 \text{ kg P ha}^{-1} \text{ an}^{-1}$
- La faible vitesse de minéralisation du POS peut être due à la forte concentration en IHP

1.1 Introduction

Phosphorus (P) is essential to biomass production, but its use in agricultural soils is affected by several crucial issues. One concern is the potential scarcity of P mineral fertilizers derived from rock phosphates, due to their limited reserves and their ever-increasing consumption by the agriculture sector to support the growing demand for food (Cordell and White 2011). Another concern is P enrichment of water bodies by agricultural activities, which can contribute to eutrophication and degradation of water quality (Sharpley et al. 2016; Pinay et al. 2018). Therefore, the management of plant-available soil P is a major agronomic, economic and environmental issue, requiring a full understanding of soil processes, compounds, and factors driving P cycling in agroecosystems.

Soil total P (TP) concentrations vary widely depending on soil types, P fertilizer sources, fertilizer application rates, and crop residue management (Ziadi et al. 2013; Johnston et al. 2014). Chemically, soil P compounds can be divided into two broad categories. One category is inorganic P, which includes phosphate ions (at the pH range of agricultural soils, H_2PO_4^- and HPO_4^{2-} are dominants; PO_4^{3-} only occurs at high pH) and polyphosphates (chains of phosphate; pyrophosphates are polyphosphates containing two phosphate groups). The other category is organic P, with compounds containing phosphate groups or P bonded to carbon (C) groups, including orthophosphate monoesters with one P-O-C bond [e.g. sugar phosphates, inositol hexakisphosphates (IHP) stereoisomers], orthophosphate diesters with one C-O-P-O-C bond (e.g., DNA, phospholipids) and phosphonates with a direct C-P bond (Condrón et al. 2005; Cade-Menun 2017). Land use affects soil inorganic and organic P compounds and concentrations (Liu et al. 2018; Perillo et al. 2021), including soils cultivated under annual crops (Cade-Menun 2017; Menezes-Blackburn et al. 2018), pastures (Liu et al. 2018; Menezes-Blackburn et al. 2018), olive and vineyards orchards (Recena et al. 2018) and forests (Achat et al. 2013; Perillo et al. 2021). Solution ^{31}P nuclear magnetic resonance spectroscopy (P-NMR) of NaOH-EDTA extracts has become the reference technique to identify and quantify organic P compounds in soils. In cultivated soils under annual crops, organic P compounds are present mainly as orthophosphate monoesters, to a lesser extent as orthophosphate diesters, and sometimes as phosphonates in small quantities (Cade-Menun 2017; Menezes-Blackburn et al. 2018).

In soils, inorganic and organic P compounds cycle geochemically and biochemically (Arai and Sparks 2007; Cade-Menun 2017). Geochemical processes include diffusion, sorption to and desorption from mineral surfaces, and precipitation with metals in the soil solution (Nriagu and Moore 1984; Barrow 1987; Arai and Sparks 2007; Cade-Menun 2017). Biochemically, phosphate ions (i.e. H_2PO_4^- / HPO_4^{2-}) are the main P compounds that can be directly taken up from the soil solution by plants or microorganisms. After uptake, phosphate ions can be converted to organic P compounds [e.g., phospholipids in

cell walls, storage compounds such *myo*-IHP (phytate) in seeds], or stored as inorganic P compounds including phosphates and polyphosphates (Noack et al. 2012, 2014). These inorganic and organic P compounds can be returned to the soil after cell death, where they will be affected by biogeochemical processes, sorbed to soil minerals, or be incorporated into the soil organic matter as organic P compounds recalcitrant to phosphatase hydrolysis (He et al. 2011; Giles et al. 2018). Phosphate ions are returned to the soil solution by mineralization of organic P compounds by phosphatases (e.g., phytate by phytase), by decomposition of soil organic matter, and decomposition of crop residues, which release inorganic P stored in plant cells, and by hydrolysis of polyphosphates (Condrón et al. 2005; Nannipieri et al. 2011). Here, the distinction is made between decomposition of crop residues and soil organic matter, which involve biological mineralization by enzymes targeting C and nitrogen, and biochemical mineralization of SOP and organic P compounds by enzymes specifically targeting the release of phosphate (e.g. phosphatases, diesterases, phytases; McGill and Cole 1981).

There is a consensus recognizing that soil organic P (SOP) could play a role in plant nutrition from the release of phosphate ions by mineralization of organic P compounds, and decomposition of organic matter and crop residues (Steffens et al. 2010; Dodd and Sharpley 2015). However, there is little information about the rate of phosphate ions release from SOP. This will be influenced by P speciation, because P compounds vary with respect to biogeochemical cycling and often require specific enzymes (e.g. phytases). Therefore, there is a need to study SOP dynamics and cycling in relation to P speciation to address the question (Cade-Menun 2017; Haygarth et al. 2018): is there a functional link between SOP mineralization and speciation?

The purpose of this study was to examine the long-term dynamics and transformations of SOP, using a 28-year field experiment in France under irrigated maize (*Zea mays L.*) monoculture fertilized with triple superphosphate at three rates, testing the hypothesis that repeated applications of mineral P fertilizers modify maize residue-derived P, affecting P speciation and the rate of release of phosphate ions from SOP. Three highly different P fertilization rates should lead to three contrasting situations. First, when P fertilization rate is higher than P exported in harvest, the SIP and plant-available P stocks will increase, improving P consumption by crops and P concentrations in maize organs as inorganic or organic P compounds. Therefore, the P in crop residues returned to the soil might slightly increase SOP stocks and change its speciation, with more storage P compounds resistant to mineralization. Second, when the P fertilization rate is equivalent to the P exported in harvest, changes in SIP and SOP speciation and stocks should be limited. Third, without any P added over a long period of cropping, the SIP stock would decrease to support crop needs. The P uptake by plants would be reduced, P concentrations in maize organs would be lower, and yield and P offtake decreases would be expected. Therefore, less P would be

returned in crop residues, which might increase SOP mineralization in order to replenish the soil plant-available phosphate ions. Soil organic P speciation would change, as easily degradable organic P compounds would be mineralized, leaving P compounds more likely to be tightly sorbed to soil minerals such as myo-IHP (Giles et al. 2018).

The SOP stock time series over several decades was analyzed, and then a model developed for soil organic C was adapted to describe SOP dynamics over decades at annual time steps (Hénin and Dupuis 1945). The specific objectives were to: (i) analyze crop responses to different mineral P fertilization rates; (ii) determine changes with time in TP, SIP and SOP stocks; (iii) use P-NMR analysis of NaOH-EDTA extracts to identify P compounds and assess their variability with P fertilizer application rates; (iv) estimate residue-derived phosphate ions returned to the soil in order to use a SOP dynamics model to calculate the rate of phosphate ions release from SOP mineralization; and finally (v) link phosphate ions release from SOP to P speciation.

1.2 Materials and methods

1.2.1 Site and long-term field experiment

This study used a 28-year maize monoculture (1972 to 2000) field experiment in Tartas, France (43°52' N, 0°44' W; altitude: 55 m). The experimental site was established on a farm with maize cultivation from the 1950s, with poultry litter applications to the end of the 1960s. The local climate is temperate subhumid (Cfb in the Köppen classification) with a mean annual temperature of 13.2°C and a mean annual rainfall of 950 mm during the study period. The soil is a Luvic Arenosol (FAO 2014) with 6% clay, 14% silt, 80% sand and a pH_{water} of 5.9 in the plough layer (0-25 cm). The soil organic C concentration was 10.3 g kg⁻¹, and the cation exchange capacity was 3.6 cmol_c kg⁻¹ (cobaltihexamine method), according to the NF X 31-130 standard procedure (AFNOR 1999) with 0.9, 0.1, and 0.2 cmol_c kg⁻¹ of exchangeable Ca, Mg, and K, respectively. Concentrations of oxalate-extractable iron (Fe) and aluminium (Al), 20.5 and 21.5 mmol kg⁻¹ respectively, were used as a proxy for poorly crystalline Fe- and Al-oxides (McKeague and Day 1966). The bulk density of the plough layer (0-25 cm) was 1.56 g cm⁻³ (3900 t of soil ha⁻¹) when determined in 1996, and was assumed to be unchanged for the duration of the study. Details of the analytical procedures are provided in Morel et al. (2021).

The experimental setup was a randomized complete block design with three P fertilizer application rates and four replicate plots (12 plots total), each 6 m wide and 30 m long. Phosphorus was applied early in spring before ploughing as commercial triple superphosphate (monocalcium phosphate [Ca(H₂PO₄)₂ H₂O, 20% P] at rates of 44 (TSP₄₄), and 96

(TSP₉₆) kg P ha⁻¹ yr⁻¹, and a control treatment (CON₀) receiving no P. All P fertilization rates were fertilized with N and K according to soil analysis and local recommendations for non-limiting conditions. This included annual applications of 100 kg K-KCl ha⁻¹ yr⁻¹ during early spring before ploughing, and NH₄NO₃ (33.5% N) at a sowing rate of 40-50 kg N ha⁻¹; at the end of May the rate was approximately 200 kg N ha⁻¹ in the interrows. Weeds were controlled by herbicide applications before maize emergence and at the 4-6 visible leaf stage. On average, 225 mm of irrigation was applied from May to September, and 5 t CaO ha⁻¹, was applied as dolomite (CaMg(CO₃)₂) every 4 or 5 years to maintain a soil pH of approximately 6.0. Aboveground residues of maize (chopped stover including the stalks, leaves, husks and tassels left in the field after harvesting the grain with a combine) were evenly distributed over the soil surface at harvest and then buried a few weeks later.

The plough layer (0-25 cm) was sampled for all experimental plots in 1976, 1977, 1978, 1980, 1983, 1986, 1988, 1992, 1995, 1998 and 2000 in March-April before P fertilization application, ploughing and seedling, except in 1998 (which was sampled in June). Each soil sample was obtained by manually mixing twelve cores randomly collected within each plot, avoiding edge effects. Each 1-kg soil sample was oven-dried at 40 °C and ground to pass through a 2-mm mesh sieve prior to storage at room temperature.

1.2.2 Soil P analyzes

Soil organic P (SOP) concentrations were determined in triplicate using the Saunders and Williams (1955) ignition method. Ignited (1 g, 550°C for 4 h), and non-ignited samples were extracted with 50 ml of 0.1 M H₂SO₄ for 16 h. After filtration, the P concentration in solution was determined using the green malachite colorimetric method (Van Veldhoven and Mannaerts 1987) with a spectrophotometer at 610 nm. The SOP concentration (mg P kg⁻¹) was calculated as the difference between the ignited and the non-ignited samples. The SOP stocks (kg P ha⁻¹) were then calculated by multiplying SOP concentration by soil mass per hectare (3900 t ha⁻¹).

Soil total P (TP_{HF}) concentrations were determined at the national laboratory of INRAE (French National Institute for Agriculture, Food and Environment) according to the NF X 31-147 standard procedure (AFNOR 1999), in which ground (<0.150 mm) and ignited soils (450°C for 4 hours) were digested in concentrated hydrofluoric (HF) and perchloric (HClO₄) acids. After filtration, P in the digested solutions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The analytical recoveries for TP_{HF} of Chinese certified soil reference materials GBW07401, GBW07402, GBW07404, and GBW07405 analyzed simultaneously were 106%, 100%, 94% and 89%, respectively. In addition, an internal control sample (named "Mons 2015") was also analyzed simul-

taneously. The TP_{HF} stocks were calculated as described for SOP stocks. The SIP was calculated as the difference between TP_{HF} minus SOP.

Soils sampled in 2000 were analyzed by solution P-NMR to identify and quantify P compounds. Using the modified (Cade-Menun and Preston 1996) procedure, 2.5 g of soil were shaken for 6 h with 25 mL of 0.25 mol L⁻¹ NaOH and 0.05 mol L⁻¹ Na₂EDTA solution, then centrifuged (20 min, 1500 × g). A 1-mL aliquot was removed and diluted to 10 mL with deionized water to determine P, Al, Fe, Ca, and Mn by ICP-OES for each sample, which was used to determine NMR delay times based on the ratio of P/(Fe + Mn) in the extracts (McDowell et al. 2006; Cade-Menun and Liu 2014). The remaining supernatants were frozen and freeze-dried. Freeze-dried samples were redissolved in 1.0 mL D₂O, 0.6 mL of 10 mol L⁻¹ NaOH, and 0.6 mL of the NaOH-EDTA extracting solution. The samples were centrifuged (1500 × g, 20 min) and transferred to 10-mm NMR tubes. Solution P-NMR spectra were acquired on a 600 MHz spectrometer (202.5 MHz for P; INOVA, Varian) equipped with a 10-mm broadband probe. The NMR experimental parameters were: pulse width, 18 μs (90°); acquisition 0.675 s, delay time 4.32 s; 2200 to 4300 scans (4–6 h); no proton decoupling. Chemical shifts were assigned to P compounds based on (Cade-Menun 2015) and by spiking with reference compounds. A table of chemical shifts of identified compounds and example spectra are shown in Supplementary information 1 (Table SI-1.1; Figure SI-1.1). Since some orthophosphate diesters (phospholipids, RNA) will degrade during extraction and P-NMR analysis to peaks that appear in the orthophosphate monoester region (Liu et al. 2015; Schneider et al. 2016; Recena et al. 2018), orthophosphate monoester and diester concentrations were corrected by subtracting degradation compounds (α- and β-glycerophosphate and the mononucleotides) from the total orthophosphate monoester area and adding them to the total diester area (Schneider et al. 2016).

1.2.3 Maize data

Every year, grain yield was measured at maturity on a 16-m² area corresponding to the two central rows on an 8-m length of each experimental plot. Five cobs were collected to measure P concentration in grain dry matter by ICP-OES after oven-drying (80°C, 72 h), grinding to <1 mm, ashing at 550°C, and digestion in concentrated nitric acid (HNO₃) solution. The P in harvested grain (P_{gr}) was calculated by multiplying the grain yield by the grain P concentration.

To estimate P in aboveground residues (P_{agr}), we established relationships between the measured P harvest index (HI_P) and cumulative P budget, i.e. the difference between P applied as superphosphate minus P exported in grain summed over the years of the experiment. Details are presented in Supplementary information 2. Both P_{agr} and P_{gr}

were determined five times over the duration of the study (annually in 1993, 1995, 1996, 1997, and 1998) and were used to calculate HI_P , as the amount of P in grains divided by the amount of P in all the aboveground biomass.

The linear regression between mean HI_P and mean cumulative P budget was:

$$HI_P = -6.85 \cdot 10^{-5} \times \text{cumulative P budget} + 0.78 \quad (\text{Eq. 1.1})$$

$(P < 0.001; R^2 = 0.61; n = 15)$

Then, the P_{agr} value was calculated for all years and P fertilization rates using the equation:

$$P_{agr} = \frac{P_{grr} - P_{grr} \times HI_P}{HI_P} \quad (\text{Eq. 1.2})$$

To estimate P in belowground residues (P_{bgr}), we used a root-to-shoot ratio of 0.18 for maize P (Yu et al. 2015). We considered the return to soil of maize grains lost during harvest by the combine harvester to be 3% of the harvested grain yield (Wang et al. 2021). The P_{grr} value was therefore calculated by multiplying the grain yield by its P concentration and by 3%.

1.2.4 Mineralization of soil organic P

The gross annual rate of SOP mineralization was calculated using the simple model presented in Figure 1.1, which was adapted from the model developed for soil organic C dynamics, initially proposed by (Hénin and Dupuis 1945) and then constantly improved (Andriulo et al. 1999; Clivot et al. 2019; Levavasseur et al. 2020). We assumed that the simplified theoretical framework used to describe, simulate and predict soil organic C dynamics in agricultural soils was also valid for SOP as it described dynamics by the balance between inputs and outputs of stocks, of soil organic C at the annual time step in the original model and SOP here.

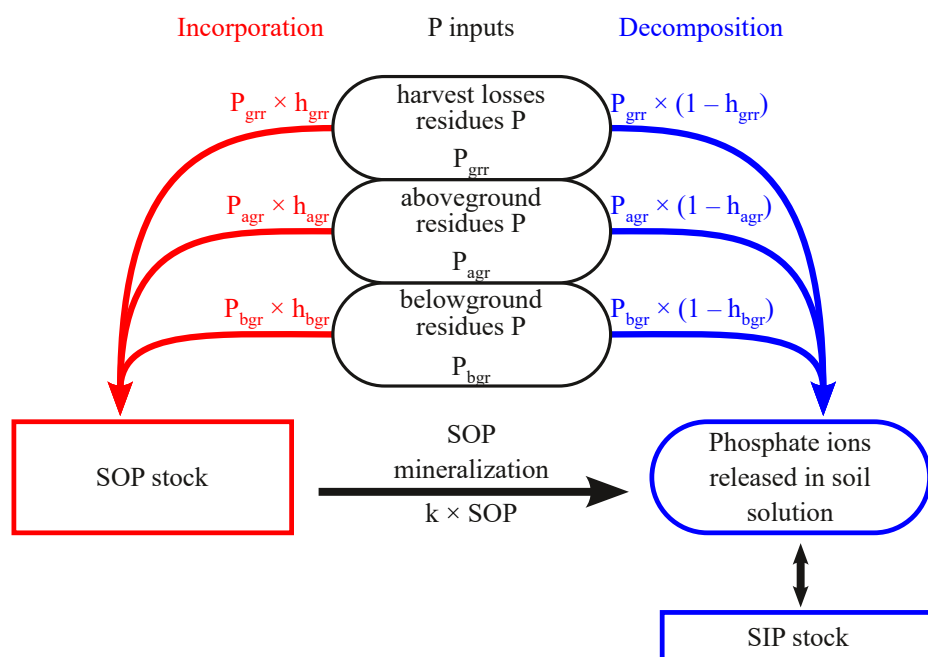


Figure 1.1 Conceptual diagram of the model describing soil organic phosphorus (SOP) dynamics.

During decomposition of maize residues (<1 yr), the h fraction of P in residues is incorporated into SOP and the remainder $(1-h)$ fraction is released in solution. Phosphate ions are released from SOP mineralization with the coefficient (k). We differentiate three categories of maize residues: grains lost at harvest (grr), aboveground (agr), and belowground (bgr) residues. Rounded forms are P fluxes ($\text{kg P ha}^{-1} \text{ yr}^{-1}$); rectangular forms are P stocks (kg P ha^{-1}).

SOP: total soil organic P (kg P ha^{-1})

P_{agr} : P amount that returns in the plough layer as aboveground residues ($\text{kg ha}^{-1} \text{ yr}^{-1}$)

P_{bgr} : P amount that remains in the plough layer as belowground residues ($\text{kg P ha}^{-1} \text{ yr}^{-1}$)

P_{grr} : P amount that returns annually to soil as fallen grains ($\text{kg P ha}^{-1} \text{ yr}^{-1}$)

k : coefficient of gross SOP mineralization (yr^{-1})

h_{agr} , h_{bgr} , h_{grr} (dimensionless): incorporation coefficients to SOP of P_{agr} , P_{bgr} , and P_{grr} , which returned to soil, respectively.

t = number of years of experimentation.

The model in Figure 1.1 considers SOP stock and several types of crop residues. Phosphate ions are released from SOP stock according to the coefficient k ($1/k$ is the residence time, i.e., the time that P stays in SOP). The SOP stock is annually supplied by P in crop residues. The residue-derived P supplies SOP according to the incorporation coefficient (h), i.e., the fraction of residue P that is incorporated into the SOP stock the year (the model time step) after harvest and return of crop residues to soil. During the year following residue return, a fraction $(1-h)$ of residue-derived P is released into the soil solution as phosphate ions, polyphosphates, and easily degradable organic P compounds. At this stage of our modeling approach, we neglected the contribution of microbial biomass to SOP dynamics by immobilization/(re)mineralization processes. The SOP leaching rate was also considered to be negligible.

The h parameter was determined in soil incubations studies using buried litterbags in pots and field conditions over several months (not part of this study). Those experiments gave h estimates of 0.14 [average of 0.20 (Linères and Lubet 1990), 0.12 (Buchanan and King 1993) and 0.11 (Mubarak et al. 2002)] for aboveground residues, 0.17 (Singh and Shekhar 1989) for belowground residues, and 0.4 for grains that are returned to soil (Doolette et al. 2010; Steffens et al. 2010). We assumed these incorporation coefficients did not vary with P fertilization. This assumption is probably acceptable for cereal crops, because studies suggest that plant P status had no effect on the proportion of P compounds detected in grains (Noack et al. 2014). However, for other annual crops, the distribution of P compounds could vary with plant P status (Noack et al. 2014). The k parameter was the only unknown parameter of the model and was estimated for each experimental plot by modeling. The optimization method used for this parameter is described in the next section.

The model is designed to monitor the kinetics of SOP stocks at an annual step in relation to k and h coefficients. Additional data were needed, including initial SOP stock and P inputs, which returned to the soil as maize residues. The output variables were yearly SOP stocks, annual amounts of phosphate ions released from SOP by mineralization ($= k \times SOP_t$, for the year t), the gross annual rate of SOP mineralization [$= \text{mean}(k \times SOP)$], maize residue decomposition during the year after grain harvest and return of crop residues [$= (\text{residues-derived P at year } t) \times (1-h)$], and P derived from residues incorporated into the SOP [$= (\text{residues-derived P at year } t) \times h$]. Therefore, two phosphate ions fluxes supply the plant-available P: the mineralized SOP according to k and the P from decomposed crop residues according to $1-h$ (on a time step inferior to the model). The model in Figure 1.1 calculates the SOP stock year by year according to the following set of equations:

$$\frac{dSOP}{dt} = \sum (P_j \times h_j) - k \times SOP_t \quad (\text{Eq. 1.3})$$

$$SOP_{t+1} = \frac{\sum (P_j \times h_j)}{k} \times (1 - e^{-k}) + SOP_t \times e^{-k} \quad (\text{Eq. 1.4})$$

Where:

- SOP_{t+1} is the SOP stock (kg P ha^{-1}) the year following the year t ;
- k is the coefficient of gross SOP mineralization (yr^{-1});
- j is a type of maize residue, either aboveground (agr), belowground (bgr) or grains return to soil (grr);
- P_j is the amount ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) of P input within maize residue j , with aboveground (P_{agr}), belowground (P_{bgr}) and grains return to soil (P_{grr});

- h is the incorporation coefficient (dimensionless) of maize residue j to SOP : above-ground (h_{agr}), belowground (h_{bgr}), and grain return to soil (h_{grr});
- The variable t is the elapsed time between two harvests, expressed in years.

Eq. 1.4 is used to estimate the SOP stock each year by iteratively adjusting k for each individual plot to optimize the fit between the simulated and the 11 values of the measured SOP stock time series. The model describing SOP dynamics was built using the free software R for statistics and its programming language (R Core Team 2021).

1.2.5 Statistical analysis

All statistics were carried out using R software, version 4.0.3 (R Core Team 2021). As soil P data are missing for two blocks in 1976, we removed data from 1976 for the linear mixed effect models to maintain a complete and balanced design. Data were tested for normality and variance homogeneity (Shapiro and Bartlett tests respectively).

Effects of P application rates on specific variables (i.e., grain yield, P in grains, P exported, P in residues, (R Core Team 2021), SIP) were tested using linear mixed effect models fitted by a restrictive maximum likelihood method with the *lme* function from the *nlme* R package (Pinheiro et al. 2022). Block was included as a random effect to account for spatial pseudoreplication (4 repetitions) and enable the comparisons among P fertilization rates. The continuous time variable (the year) was used to fit a first-order autoregressive variance structure and to account for non-independent measurements within plots across time. The yearly effects of variables were investigated with the same procedure, considering years as discrete values. To explore differences among P fertilization rates and years, linear mixed effect models results were investigated with a post-hoc Tukey test when the ANOVA showed a significant effect. Statistical tests were performed with a significance level of $\alpha = 0.05$.

Parameters of linear regressions that describe relationships of SIP, and SOP stocks with years (SOP: $n = 33$; SIP: $n = 27$) were estimated using the *lm* function. The k value was estimated iteratively for each experimental plot by minimizing residual sum of squares between observed vs simulated SOP stocks values. The optimization was performed with the *optim* function and the "L-BFGS-B" method. Several statistical criteria of agreement between observations and simulations were used, i.e., the coefficient of determination, the distribution of the residual of regression and the root mean squared deviation (RMSD), which is computed as follows:

$$RMSD = \sqrt{\frac{\sum_{i=1}^n (y_{sim,i} - y_{obs,i})^2}{n - 1}} \quad (\text{Eq. 1.5})$$

Where $y_{sim, i}$ and $y_{obs, i}$ are the simulated and observed SOP stocks values, respectively, for year i of sampling and n represents the number of data pairs. Centered log-ratio transformations (clr; compositional analysis) were used for the statistical analysis of P-NMR data (Abdi et al. 2015).

1.3 Results

1.3.1 Time series of maize data

Maize grain yields, grain P concentrations (g P kg⁻¹), and P exported in grains (kg P ha⁻¹) are shown in Figure 1.2 for the 28 years of cultivation and the three P fertilization rates. Maize grain yields (Figure 1.2a) varied significantly with the year of cultivation from a minimum of 7.4 t ha⁻¹ in 1977 to a maximum of 11.6 t ha⁻¹ in 1988 according to climate conditions, maize varieties, plant density, and protection against pests. The mean (\pm standard deviation) grain yield for all years and P fertilization rates was 9.9 ± 1.5 t ha⁻¹; mean grain yields were 9.4 ± 1.4 , 10.1 ± 1.5 , and 10.3 ± 1.5 t ha⁻¹ for the CON₀, TSP₄₄, and TSP₉₆ fertilization rates, respectively. Using an ANOVA per year, a significant yield decrease occurred systematically in the CON₀ fertilization rate after 1992, which accelerated with time during the last 15 years of the study, i.e., -4.8%, -7.2%, and -9.1% of the grain yield in the TSP₄₄ fertilization rate for the 1985-89, 1990-94, and 1995-2000 periods, respectively (results not shown). Grain P concentrations (Figure 1.2b) were significantly ($P < 0.0001$) influenced by P application rate and year. The overall mean grain P concentration was 3.0 ± 0.4 g P kg⁻¹, with values of 2.7 ± 0.4 , 2.9 ± 0.3 , and 3.2 ± 0.4 g P kg⁻¹ for the CON₀, TSP₄₄ and TSP₉₆ fertilization rates, respectively. The overall mean of P exported in harvested grain was 29.2 ± 6.0 kg P ha⁻¹ yr⁻¹, with means of 24.9 ± 4.5 , 29.6 ± 5.1 , and 33.1 ± 5.4 kg P ha⁻¹ on average for 28 years for the CON₀, TSP₄₄, and TSP₉₆ fertilization rates, respectively. The grain P concentration and the P exported in harvested grain were both significantly different ($P < 0.0001$) among all P fertilization rates.

The annual means of P_{agr} and P_{bgr} are shown in Figure 1.3 for the 28 years of cultivation and the three P application rates. There were significant differences ($P < 0.0001$) with fertilizer application rates for P_{agr} , and P_{bgr} (Table 1.1). Assuming a 3% return of harvested grains to soil, P_{grr} was much smaller for the CON₀, TSP₄₄, and TSP₉₆ fertilization rates, respectively (Table 1.1).

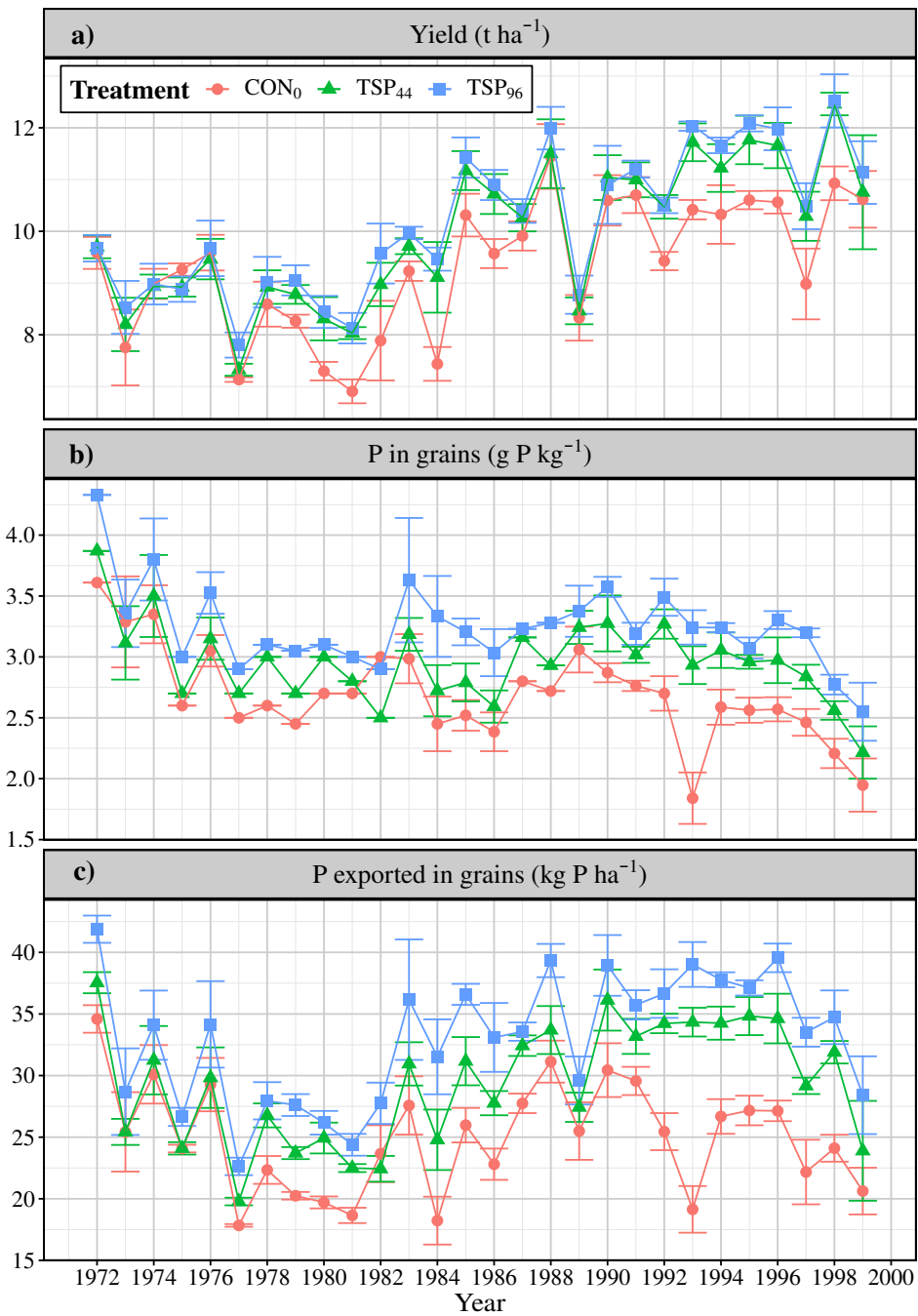


Figure 1.2 Annual grain yields (a), grain phosphorus (P) concentrations (b) and P exported in grain (c) over the 28 years of this long-term experiment, as affected by P fertilization rates.

Values are means ($n = 4$); error bars are standard deviations. CON₀, TSP₄₄ and TSP₉₆: 0, 44 and 96 kg P ha⁻¹ yr⁻¹ applied as triple superphosphate.

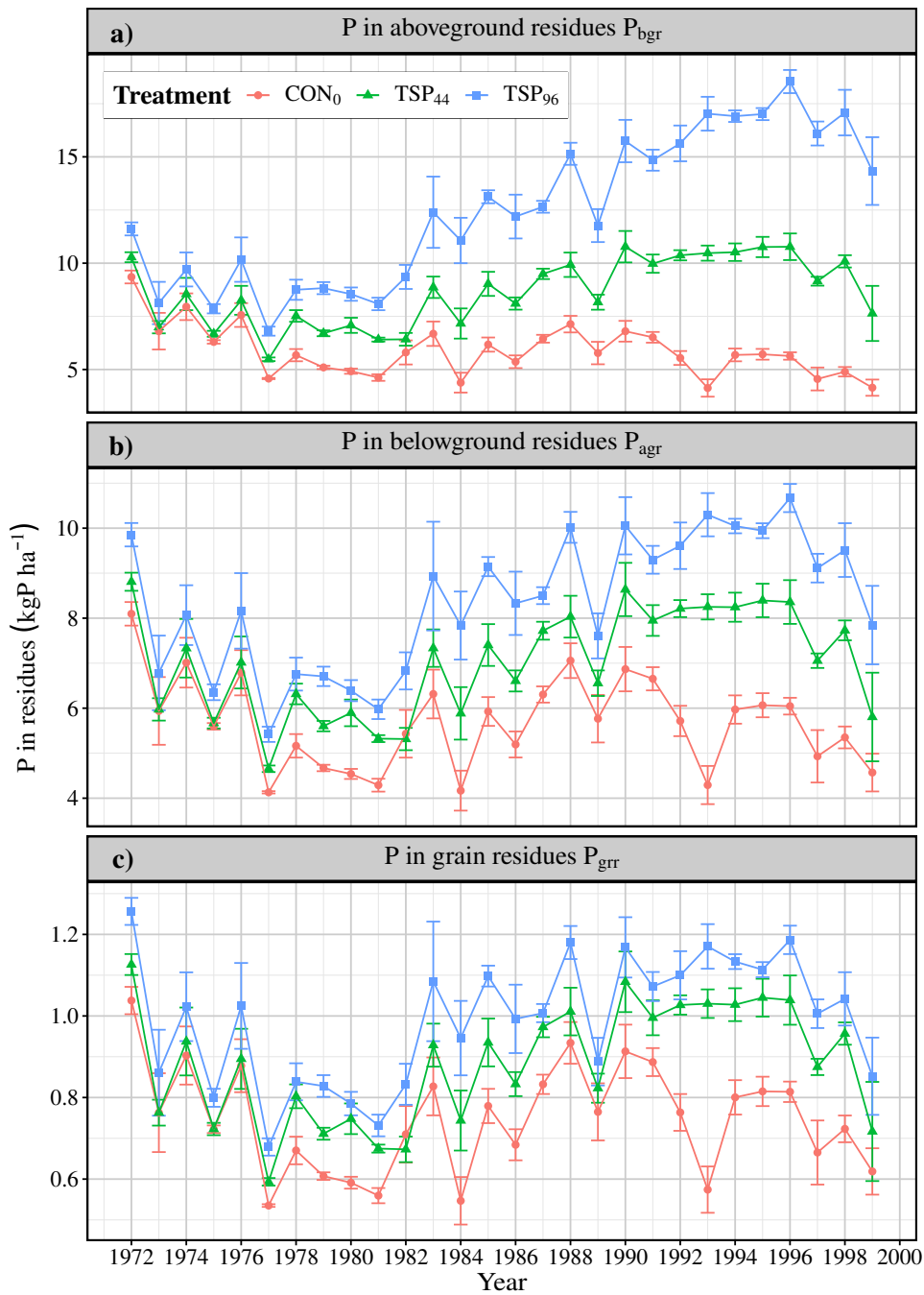


Figure 1.3 Annual estimated phosphorus (P) concentrations in aboveground (a, P_{agr}) and belowground (b, P_{bgr}) residues, and in fallen grains at harvest (c, P_{grr}) over 28 years. Values are means ($n = 4$); error bars are standard deviations. Aboveground residue P concentrations were calculated from the P harvest index (see Supplementary information 2), belowground residue P concentrations were calculated using a root-to-shoot ratio for P of 0.18. CON₀, TSP₄₄ and TSP₉₆: 0, 44 and 96 kg P ha⁻¹ yr⁻¹ applied as triple superphosphate.

Table 1.1 Average across all years of the experiment of phosphorus (P) fluxes from maize residues sampled annually ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) and the partitioning between P incorporated to soil organic P stock determined by the Saunders and Williams method (1955) (SOP) and P released in soil solution as phosphate ions during the post-harvest (<1yr) decomposition of maize residues, gross mineralization coefficient (k, yr^{-1}) and rate ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) of SOP.

Fertilization rates are CON_0 , TSP_{44} and TSP_{96} : 0, 44 and 96 $\text{kg P ha}^{-1} \text{ yr}^{-1}$ applied as triple superphosphate. Values are means \pm std. dev.; $n = 4$. Different letters (a, b, c) indicate significant differences among means ($\alpha = 0.05$).

	CON_0	TSP_{44}	TSP_{96}
P input from ($\text{kg P ha}^{-1} \text{ yr}^{-1}$):			
Aboveground residues, P_{agr}	5.9 ± 1.3 a	8.6 ± 1.7 b	12.5 ± 3.5 c
Belowground residues, P_{bgr}	5.7 ± 1.1 a	7.0 ± 1.2 b	8.4 ± 1.6 c
Grain return to soil, P_{grr}	0.7 ± 0.1 a	0.9 ± 0.2 b	1.0 ± 0.2 c
Sum	12.3 ± 2.4 a	16.5 ± 3.0 b	21.8 ± 5.1 c
Phosphate ions released into soil solution from ($\text{kg P ha}^{-1} \text{ yr}^{-1}$):			
Aboveground residues	5.0 ± 1.1 a	7.4 ± 1.4 b	10.7 ± 3.0 c
Belowground residues	4.7 ± 0.9 a	5.8 ± 1.0 b	6.9 ± 1.3 c
Grain residues	0.45 ± 0.08 a	0.53 ± 0.09 b	0.6 ± 0.1 c
Sum	10.2 ± 2.0 a	13.8 ± 2.5 b	18.3 ± 4.3 c
P from residues incorporated into SOP ($\text{kg P ha}^{-1} \text{ yr}^{-1}$):			
Aboveground residues	0.8 ± 0.2 a	1.2 ± 0.2 b	1.7 ± 0.5 c
Belowground residues	1.0 ± 0.2 a	1.2 ± 0.2 b	1.4 ± 0.3 c
Grain residues	0.3 ± 0.1 a	0.4 ± 0.1 b	0.4 ± 0.1 c
Sum	2.1 ± 0.4 a	2.8 ± 0.5 b	3.6 ± 0.8 c
Coefficient of gross SOP mineralization, k (yr^{-1})		0.0047 ± 0.0049	
Gross annual rate of SOP mineralization ($\text{kg P ha}^{-1} \text{ yr}^{-1}$)		0.9 ± 0.4	1.3 ± 1.4
			3.0 ± 1.8

1.3.2 Organic and inorganic P stocks time-series in the plough layer

The time series over 28 years of SOP assessed by the Saunders and Williams method and SIP are shown in Figure 1.4 for the eleven sampling dates and the three P application rates. The SOP stock did not change significantly among years or P rates. A linear regression described the measured SOP stock with years. Its intercept, i.e., the initial SOP, was 368 kg P ha^{-1} in the plough layer, and the SOP stock slightly increased by $+1.6 \pm 0.9 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ ($P = 0.08$; $R^2 = 0.03$; $n = 33$). In contrast, SIP stocks varied significantly with P fertilization (Figure 1.4), decreasing constantly with time for the CON_0 , slightly increasing for the TSP_{44} , and increasing more pronouncedly for the TSP_{96} fertilization rates (Figure 1.4).

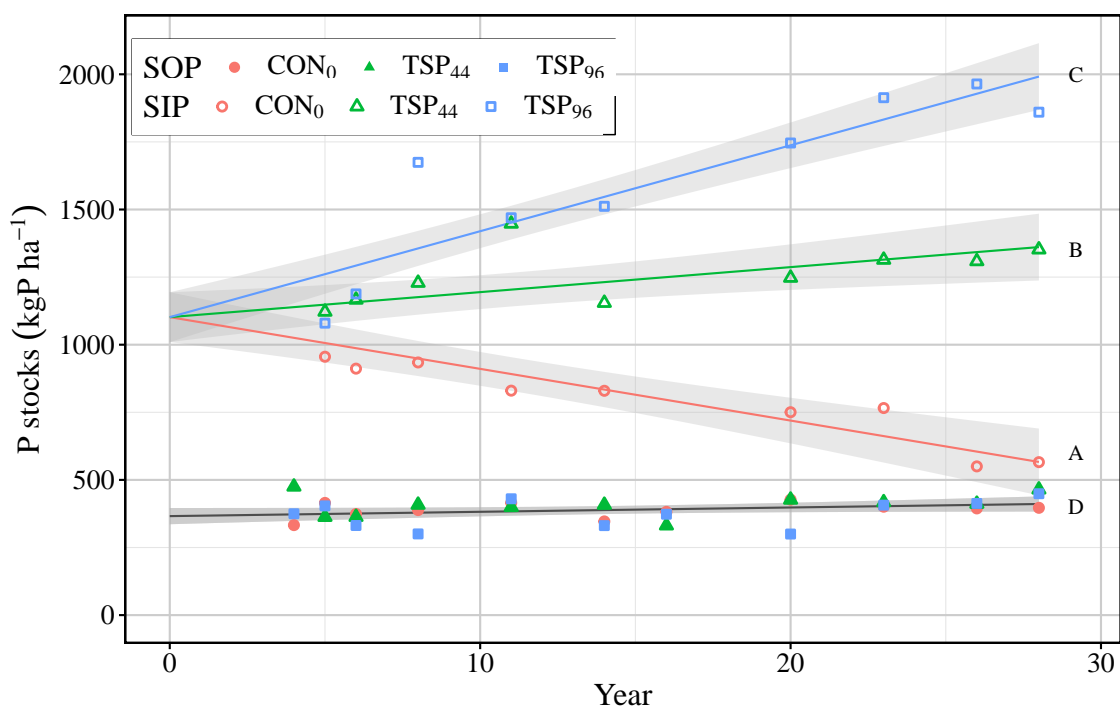


Figure 1.4 Soil organic P stocks (SOP) determined by the Saunders and Williams ignition method, and soil inorganic P (SIP) stocks, determined as the difference between total P_{HF} and SOP, for the 28-year study period.

Values are means ($n = 4$). Symbols: measured values. Lines: linear regressions. Grey area: standard error of the linear regressions. CON_0 , TSP_{44} and TSP_{96} : 0, 44, and 96 kg P $ha^{-1} yr^{-1}$ applied as triple superphosphate.

A (CON_0): $-19.1 \pm 3.0 \times Year + 1101 \pm 44$ ($P < 0.001$; $n = 9$; $R^2 = 0.93$)

B (TSP_{44}): $9.2 \pm 3.0 \times Year + 1101 \pm 44$ ($P = 0.005$; $n = 9$; $R^2 = 0.93$)

C (TSP_{96}): $31.8 \pm 3.0 \times Year + 1101 \pm 44$ ($P < 0.001$; $n = 9$; $R^2 = 0.93$)

D (all P fertilization rates): $y = 1.6 \pm 0.9 \times Year + 368 \pm 15$ ($P = 0.08$; $n = 33$; $R^2 = 0.10$)

1.3.3 Gross annual rate of SOP mineralization

From estimated amounts of maize residue-derived P (Figure 1.3), and their published coefficients of organic matter decomposition, we calculated for each type of residue the portion that is annually incorporated into the SOP, as well as the remainder fraction (1-h) that is released into the soil solution (Figure 1.1). On average over 28 years, the amount of P returned to the plough layer increased with fertilization rate, from 12.3 (CON_0) to 22.2 (TSP_{96}) kg P $ha^{-1} yr^{-1}$ (Table 1.1). The percentage of maize residue-derived P released in solution was 83% and the remaining 17% was incorporated into the SOP stock.

We ran Eq. 1.4 to iteratively determine the k coefficient, which is the unique unknown parameter of Eq. 1.4, minimizing the residual sum of squares of linear regression between measured and simulated SOP values. The k value did not differ significantly across the P

fertilization rates (Table 1.1). The overall mean was $0.0047 \pm 0.0049 \text{ yr}^{-1}$, corresponding to a residence time ($1/k$) of 212 years. The overall gross annual rate of SOP mineralization on average was $1.7 \pm 1.2 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ (significantly positive, one sample student t test $P < 0.0001$), which only amounted to 12% of the phosphate ions released into the soil solution by decomposition of maize residue. Averaging the three P fertilization rates (Table 1.1), decomposition of maize residues (aboveground, belowground and grain residues) released $14.2 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, which was eight-fold more phosphate ions than were released by the mineralization of SOP ($1.7 \text{ kg P ha}^{-1} \text{ yr}^{-1}$).

1.3.4 Identification and quantification of P compounds by P-NMR at the end of the experiment

Total P in the NaOH-EDTA extracts (P_{NE}) for P-NMR analysis accounted for 81% of the TP_{HF} regardless of P fertilization (Table 1.2). Both TP_{HF} and P_{NE} were significantly different among P fertilization rates. Inorganic P determined by solution P-NMR (NMR- P_i) was 84% of SIP. Within P_{NE} , NMR- P_i was the predominant fraction representing 66%, 79% and 82% of P_{NE} for the CON_0 , TSP_{44} , and TSP_{96} fertilization rates, respectively (data not shown, calculated from concentrations in Table 1.2). The NMR- P_i was 98% orthophosphate and 2% pyrophosphate and polyphosphate. Concentrations of orthophosphates were significantly different among P fertilization rates, and were lowest in the CON_0 and highest in the TSP_{96} fertilization rate, which was also seen for NMR- P_i concentrations (Table 1.2).

There were no significant differences among the three fertilization rates for total organic P concentrations determined by P-NMR (NMR- P_o ; Table 1.2). Within NMR- P_o , *myo*-IHP and phosphonates differed significantly among the P fertilization rates, generally increasing with P application rates (Table 1.2). However, the latter represented only a small proportion of the NMR- P_o . After correction for the degradation of orthophosphate diesters to orthophosphate monoesters during the different steps of P-NMR analysis, the dominant group was orthophosphate monoesters (77% of NMR- P_o on average for all P fertilization rates), of which 65% were IHP stereoisomers (including *myo*-, *scyllo*-, *neo*-, and *D-chiro*-IHP), and the remainder were unidentified peaks in the monoester region of P-NMR spectra (other orthophosphate monoesters, Table 1.2). Orthophosphate diesters represented 20%, and phosphonates represented 3%, of NMR- P_o .

Table 1.2 Soil total P determined by different analytical procedures, and P forms in NaOH-EDTA solutions analyzed by P-NMR in the soil plough layer sampled at the end of the experiment (2000).

Values are means \pm std. dev.; $n = 4$. Different letters (a, b, c) indicate significant differences among means ($\alpha = 0.05$). CON₀, TSP₄₄ and TSP₉₆: 0, 44 and 96 kg P ha⁻¹ yr⁻¹ applied as triple superphosphate. TP_{HF} and P_{NE}: soil total P in concentrated HF and HClO acids, and NaOH-EDTA extraction, respectively; SOP: soil organic P determined by the Saunders and Williams method; SIP: soil inorganic P. Unit for all variables is mg P kg⁻¹, except Recovery of TP_{HF}, in %.

	CON ₀	TSP ₄₄	TSP ₉₆
TP_{HF}	247 \pm 47 a	466 \pm 93 b	592 \pm 62 c
SOP	102 \pm 19	119 \pm 13	115 \pm 20
SIP= TP_{HF} – SOP	145 \pm 28 a	347 \pm 92 b	477 \pm 45 c
P_{NE}	207 \pm 9 a	368 \pm 86 b	476 \pm 29 c
Recovery of TP_{HF} (%)	86 \pm 16	79 \pm 7	81 \pm 5
Sum of NMR inorganic P	137 \pm 5 a	291 \pm 71 b	394 \pm 28 c
Orthophosphate	135 \pm 5 a	288 \pm 71 b	390 \pm 27 c
Polyphosphate	1.8 \pm 0.9	1.8 \pm 0.8	2.5 \pm 0.2
Pyrophosphate	0.7 \pm 0.4	0.8 \pm 0.2	0.8 \pm 0.3
Sum of NMR organic P	70 \pm 5	78 \pm 17	83 \pm 12
Sum of orthophosphate monoesters^w	56 \pm 4	59 \pm 13	63 \pm 9
Sum of IHP^x	37 \pm 3	38 \pm 7	41 \pm 5
<i>myo</i> -IHP	18 \pm 1 b	16 \pm 3 a	20 \pm 1 c
<i>scyllo</i> -IHP	9.6 \pm 0.8	10.5 \pm 2.3	10.8 \pm 1.7
<i>neo</i> -IHP	2.2 \pm 0.9	2.6 \pm 0.6	2.5 \pm 1.7
<i>D-chiro</i> -IHP	7.7 \pm 1.6	8.9 \pm 1.2	7.6 \pm 1.6
Phosphatidyl choline	1.4 \pm 0.1	2.6 \pm 0.6	2.9 \pm 1.0
Glucose 6-phosphate	1.4 \pm 0.1	2.1 \pm 1.0	1.3 \pm 0.9
Other orthophosphate monoesters ^y	16 \pm 2	16 \pm 5	18 \pm 4
Sum of orthophosphate diesters^w	12.5 \pm 1.8	16.3 \pm 3.9	16.8 \pm 4.3
DNA	0.4 \pm 0.3	0.5 \pm 0.3	0.5 \pm 0.4
Other orthophosphate diesters ^z	12.1 \pm 1.7	15.7 \pm 3.7	16.3 \pm 4.0
Phosphonates	1.4 \pm 0.1 a	2.6 \pm 0.6 b	3.0 \pm 0.4 c

^w Total orthophosphate monoesters and diesters corrected for degradation of diesters to monoesters during sample analysis;

^x Inositol hexakisphosphates (IHP): sum of *myo*-, *scyllo*-, *neo*-, *D-chiro*-IHP stereoisomers;

^y Other orthophosphate monoesters are peaks in the monoester region not specifically identified; See Supplemental information 2;

^z Other diesters include phospholipids, α and β glycerophosphates (products of phospholipid degradation), nucleotides and unidentified orthophosphate diester.

1.4 Discussion

1.4.1 Maize yield response between years and P fertilization rates

This field experiment was located on a slightly acidic sandy soil that was continuously cultivated for 28 years in an irrigated maize monoculture fertilized annually at three P application rates. The mean yield was 10.2 t ha⁻¹ for the TSP₄₄ and TSP₉₆ fertilization rates, and grain yields did not differ significantly between TSP₄₄ and TSP₉₆ (Figure 1.2). As expected in the CON₀ fertilization rate, grain yield was significantly reduced by 6.8% on average in comparison to TSP₄₄. However, this loss in yield without P fertilization varied over time. The yield decrease was systematic without P fertilization after 1992, and accelerated with time in the last 15 years of the experiment. Yield losses were commonly observed after variable cultivation periods in other long-term field experiments that included fertilization rate without P fertilization, although significant yield decreases were not seen until after several decades of cropping (Morel et al. 2000; Dodd and Mallarino 2005; Messiga et al. 2010), likely due to high concentrations of plant-available soil P at the onset of the experiments.

1.4.2 Soil total, inorganic and organic P concentrations

The total NaOH-EDTA-extractable P (P_{NE}) from the soil plough layer (0–25 cm depth) ranged from 247 to 592 mg kg⁻¹ for the three P fertilization rates (Table 1.2). The recovery of TP_{HF} was in the upper range of extraction efficiencies reported for other P-NMR studies. (Doolette et al. 2011) reported P_{NE} values of 21–89% of the total P in 18 Australian soils with a wide range of management, climate, chemical and physical properties, and soil orders. (Schneider et al. 2016) extracted on average 43% of the total P in soils of organic and conventional dairy farm forage fields on high-pH soils, while (Rheinheimer et al. 2019) reported considerably lower extraction efficiencies (14%) of P_{NE} in a Brazilian Oxisol, likely due to the clayey texture and mineralogy dominated by kaolinite and iron oxides.

Unlike TSP₄₄ and TSP₉₆ fertilization rates, the SIP stock declined constantly without any P addition (CON₀). An increasingly negative P budget caused by continuous P export over years without any P application determines the critical P threshold. For maize in this experiment, the critical P threshold was measured in a separate study, and was 1.24 mg P L⁻¹ for phosphate ions concentrations in solution of soil suspensions in water (1 g:10 ml ratio) and 22 mg P kg⁻¹ for Olsen (bicarbonate) extracts (Morel et al. 2021). These critical P thresholds were higher than published values for other studies (Tang et al. 2009; Messiga et al. 2010; Johnston et al. 2014), likely because the sandy texture of

the soil in this study poorly buffered phosphate ions concentrations in solution (Frossard et al. 2000; Morel et al. 2000). The close and positive correlations between SIP, NMR-P_i and orthophosphate concentrations (results not shown) suggest that all methods detected essentially equivalent pools of inorganic P (McLaren et al. 2015). In addition, it is useful to note that orthophosphate concentrations in the P-NMR extracts were positively linearly correlated with Olsen-P concentrations ($y = 5.75 \times x$; $R^2 = 0.99$; $P < 0.0001$; data not shown). These results confirm and extend published values for NMR-P-P_i (Abdi et al. 2014; Annaheim et al. 2015; Chen et al. 2021).

In contrast to expectations, the SOP (on average 112 mg P kg⁻¹) and NMR-P_o (on average 77 mg P kg⁻¹) concentrations did not vary significantly with P fertilization (Table 1.2). This result was in agreement with published results of other studies of the plough layer of continuously cropped soils under annual crops. In a Swiss field experiment, (Keller et al. 2012) studied the effects of 30 years of conventional and organic farming on soil P compounds, and found that SOP concentration did not change significantly in any farming system. In addition, repeated applications of farmyard manure for 52 years showed very limited effect on SOP stocks with a low mineralization rate (Ma et al. 2020). The NMR-P_o concentrations remained unchanged in soils that received for decades different rates of P applications of mineral fertilizer only (Zhang et al. 1999) or manure and mineral fertilizer together (Geisseler et al. 2011; Ahlgren et al. 2013). Additionally, the NMR-P_o concentration was 114 mg P kg⁻¹ on average in a slightly acidic Swiss Luvisol after 62 years of dairy manure, compost and dried sewage sludge applications (Annaheim et al. 2015). Concentrations of NMR-P_o were similar (225-257 mg P kg⁻¹) in a P-depleted sandy loam soil in Denmark fertilized for 20 years with mineral and organic P applications (van der Bom et al. 2019).

In our study, the NMR-P_o proportions were 34%, 21% and 18% of P_{NE} in the CON₀, TSP₄₄, and TSP₉₆ fertilization rates, respectively (calculated from concentrations in Table 1.2). As in (Chen et al. 2021), decreasing P fertilization significantly increased the NMR-P_o proportion, but did not affect its concentrations. The NMR-P_o proportions were even smaller (27%, 17% and 14% of the TP_{HF}) considering TP_{HF} instead of P_{NE} given that P_{NE} was 81% of TP_{HF} in the studied sandy soil (Table 1.2). However, comparisons to published NMR-P_o proportions are challenging, due to differing methods to determine TP among research groups.

1.4.3 Organic P compounds at the end of the experiment

In general, the concentrations of the main organic P compounds remained unchanged (Table 1.2) regardless of the rate of P fertilization. After correcting for partial orthophosphate diester degradation during P-NMR analysis, orthophosphate monoesters were 77%

of NMR-P_o, distributed among IHP (on average 50% of NMR-P_o) and unidentified orthophosphate monoester species (27%), whereas orthophosphate diesters and phosphonates were 20% and 3% of NMR-P_o, respectively. It is difficult to compare these values to many other studies in the literature because not every study has corrected for degradation. However, after correction, (Chen et al. 2021) reported comparable NMR-P_o proportions of 63%, 34%, and 3% of orthophosphate monoesters, orthophosphate diesters, and phosphonates, respectively, in the plough layer of soils cultivated in a wheat-fallow rotation in Saskatchewan Canada receiving either N and P fertilization or P only fertilization from 1967, or with P fertilizer cessation in subplots from 1995.

The IHP are generally the most abundant of the identifiable individual organic P compounds in the plough layer of cropped soils. In this study, IHP were 50% of NMR-P_o on average for all P fertilization rates, which was higher than other studies: 20% for wheat in (Chen et al. 2021) 30% in a corn-soybean rotation in Quebec, Canada (Abdi et al. 2014); 40% in a mixed crop rotation with different fertilizer types in Switzerland (Annaheim et al. 2015) and a wide range depending on the crop and residue management in a study in different parts of Sweden (Ahlgren et al. 2013). Although total IHP concentrations did not differ across P fertilization rates, the *myo*-IHP concentration showed significant differences among P rates with TSP₄₄ > TSP₉₆ > CON₀. The tendency of *myo*-IHP to increase with P rates was reported in another long-term field experiment of continuous wheat in Saskatchewan (Liu et al. 2015) with a significant difference of about 3 mg P kg⁻¹ between plots with continued P fertilization compared with plots where P fertilization stopped. Several reasons could explain the high IHP and *myo*-IHP concentrations in the current study. First, there is the high grain yield of maize with higher grain returns to the soil of *myo*-IHP (a storage compound in grains), with a small increase with higher fertilization rates (Abdi et al. 2014; Noack et al. 2014). Other studies also suggest that maize returns more *myo*-IHP to the soil than other plants (Perillo et al. 2021). Second, there is the possible loss of grains during wind and storm events, which can decrease yields by 10-20% in agricultural fields. Third, there were repeated applications of poultry droppings to these plots before the onset of this experiment. Untreated manure from monogastric such as chickens is generally high in *myo*-IHP because it is not hydrolyzed during digestion; this *myo*-IHP can accumulate in soils fertilized with poultry manure (Pointillart 1994; He et al. 2008). The persistence of IHP in soils may also be related to their greater affinity for Fe- and Al-oxides relative to other orthophosphate monoesters (e.g. glucose 6-phosphate) and diesters (nucleotides and phospholipids), as further discussed below.

1.4.4 Quantifying the mineralization of soil organic P with time series of SOP data

The SOP dynamics were analyzed with time series data over 28 years. The SOP stock tended to increase slightly over the years at $+1.6 \pm 0.9 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ regardless of P fertilization (Figure 1.4). This small increase indicates that slightly more P was incorporated into the SOP after residue decomposition than was being decreased by SOP mineralization. Among all studies that assessed long-term effects of different soil management on SOP stock and speciation, the large majority were performed after a single cultivation period. Only a few allowed the calculations of SOP dynamics with a variation of SOP stock across time. Chater and Mattingly (1980) reported any or small ($-1.0 \text{ kg P ha}^{-1} \text{ yr}^{-1}$) decreases in SOP for periods of 10-45 years in old arable soils of the historic experiments at Rothamsted and Saxmundham. Additionally, SOP stocks (ignition method) did not change significantly over time among P fertilization rates in a Chinese Mollisol after 14 years of maize–soybean–wheat rotation fertilized at three P rates (Song et al. 2011). In contrast, Zhang and MacKenzie (1997) found that SOP stocks (Hedley fractionation scheme) decreased at -16 to $-29 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ over 5 years in a Canadian clay (71%) soil cropped under continuous maize fertilization at 0, 44 and $132 \text{ kg P ha}^{-1} \text{ yr}^{-1}$.

To better understand and quantify SOP dynamics and their role in releasing phosphate ions into the soil solution to supply available P to plants, we used a simple model (Figure 1.1), derived from the Hénin-Dupuis model (Hénin and Dupuis 1945) for long-term predictions of organic C stock dynamics in different agricultural soils (Clivot et al. 2019; Levvasseur et al. 2020). This modeling approach considers that SOP stock is increased by an annual incorporation flow ($\sum h_j \times m_j$) of crop residues and decreased by an annual mineralization flow at the coefficient k (Figure 1.1). The model therefore includes the following parameters: the incorporation rates h_j , which vary according to the type of crop residues (with j : post-harvest below- and above-ground maize residues as well as the return of grains to soil), and the mineralization coefficient k , which likely depends on SOP speciation, soil and climatic conditions. Only the coefficient k was fitted for each individual plot using SOP stock time series over 28 years, since the initial SOP stock (Figure 1.4), the amounts of maize residues returned (Table 1.1), and their annual rates of incorporation to SOP stock were well known and fixed.

The residue fraction was incorporated annually into SOP according to the h parameter, based on literature. Plant residue decomposition (<1 year) and nutrient release are known to be affected by many factors, including chemical composition, climatic conditions and the soil microbial community (Parr and Papendick 2015; Grzyb et al. 2020). The total concentration of P and other nutrients in plant residues will decrease with time following simple exponential equations before equilibrating after several months. For maize, the

P fraction remaining after one year in the decomposed residues (i.e. the h parameter, P fraction incorporated to SOP) is 0.14 for aboveground residues, 0.17 for belowground residues, and 0.4 for grains that returned to soil. Thus, the P fluxes from maize residues were divided up during postharvest decomposition into P released into the soil solution, (10.2, 13.9, and 18.5 kg P ha⁻¹ yr⁻¹ for the CON₀, TSP₄₄ and TSP₉₆ fertilization rates), and P incorporated into the SOP stock (2.1, 2.8, and 3.6 kg P ha⁻¹ yr⁻¹; Table 1.1). The long-term cumulative effect of repeated cropping cycles led to a slight trend of SOP accumulation because the gross annual rate of SOP mineralization was 1.7 ± 1.2 kg P ha⁻¹ yr⁻¹, whereas P incorporation into the SOP stock was higher (2.8 ± 0.6 kg P ha⁻¹ yr⁻¹ on overall average). The SOP dynamic across the three P fertilization rates is explained by the small difference between the incorporated and the mineralized SOP.

The P-NMR results indicate that SOP is not a uniform pool; instead, it consists of many P compound classes and compounds in different proportions (77% orthophosphate monoesters with 50% IHP, 20% orthophosphate diesters and 3% phosphonates). The modeling approach was used to calculate an overall value of the k coefficient of SOP mineralization. Different P compounds (or different classes of organic P, Table 1.2) are expected to have different k coefficient values. However, there was no significant variation of the initial SOP stock of 368 kg ha⁻¹ over almost 30 years due to measurement variability (average variation coefficient: 23%) and residence time, i.e. 212 years. We expect that in other studies, SOP stocks and their mineralization could be significantly affected by factors such as: different annual P applications through crop residues (e.g. with or without crop residue retention); differences in organic P distribution within SOP from residues of different types of crops; or differences in organic P compounds applied within different organic fertilizer products (e.g. urban sewage sludge, farmyard manure, composts).

1.4.5 Agronomic analysis

On average, maize grain yields were 9.9 t ha⁻¹ yr⁻¹, with 29.2 kg P ha⁻¹ yr⁻¹ exported in grains (Figure 1.2) and 16.9 kg P ha⁻¹ yr⁻¹ in maize residues (Figure 1.3). Clearly, notable amounts of P are contained in residues, but they vary with time and P fertilization. Similar values have been reported for annual cereals (Noack et al. 2012). Lower results (0.4-5.4 kg P ha⁻¹) were reported in the southern Australian grain cropping regions by Damon et al. (2014) for lower biomasses of residues for common crops (1.8-5.4 t ha⁻¹) with lower residue P concentrations (0.2-1 g P kg⁻¹).

Using published values of incorporation coefficients of residue-derived P to SOP the first year after application, 17% of maize residue-derived P was incorporated on average into SOP. The remainder was released into the soil during decomposition of residues as phosphate ions or readily-degradable organic P compounds (He et al. 2009; Noack et al.

2014). When returned to the soil, crop residue decomposition contributed to the release of substantial amounts of phosphate ions in the soil solution, i.e., the P compound that is readily absorbed by plant roots and soil microorganisms, replenishing the compartment of plant-available soil P.

By running our model in such a way as to best fit the simulated SOP values to the measured values, the calculated gross annual rate of SOP mineralization was $1.7 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, regardless of the P fertilization rate. Assuming that 15-20% was recovered by the next crop (Johnston et al. 2014), the contribution of SOP gross mineralization to plant nutrition could therefore approximate $0.3 \text{ kg ha}^{-1} \text{ yr}^{-1}$, which represented less than 1% of the total P offtake [P in maize grains and residues ranged from $32\text{-}55 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ depending on P fertilization rates (Table 1.1)]. Conversely, with the same assumption, the contribution of maize residue decomposition to crop nutrition could represent $2.8 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, i.e. up to 9% of the total P offtake. In addition, the SIP variation (slope) according to the cumulative P budget (i.e. P input in fertilization minus P output in harvest) explained almost 100% of the TP_{HF} stock variations in the soil plough layer, whereas the SOP remained stable regardless of the P budget and with no significant differences among P fertilization rates. Thus, SIP is the main pool contributing to crop nutrition.

The minor contribution of SOP in these soils despite a substantial SOP stock may be linked to the dominance of IHP compounds, which were 50% of NMR-Po (Table 1.2). Research in calcareous soils showed that *myo*-IHP could be rapidly mineralized over the months following its addition to soils, making the efficiency of phosphate ions release from *myo*-IHP almost equivalent to superphosphate (Doolette et al. 2010; Steffens et al. 2010). However, similar results have not been reported for non-calcareous soils, where IHP compounds strongly react with soil colloids and constituents, stabilizing them and protecting against microbial degradation (Cade-Menun 2017; Menezes-Blackburn et al. 2018). The IHP can bind tightly to the soil solid phase because sorption is favored by the six phosphate groups in IHP (McKercher and Anderson 1989), i.e., sorption is greater for IHP > inositol-triphosphate > inositol-monophosphate > α -glycero-P = glucose-P. Ognalaga et al. (1994) proposed that the adsorption mechanism formed inner-sphere surface complexes between the surface hydroxyls of Fe oxide (goethite) and IHP phosphate groups. The sorption of IHP compounds is related to poorly crystalline Fe oxides, unlike other organic P compounds (Recena et al. 2018; Celi et al. 2020). In addition to being strongly stabilized in soils, IHP compounds require specialized enzymes (phytases) for mineralization. Thus, to be mineralized, tightly sorbed IHP compounds need to be desorbed before they can be degraded by phytases. Giles et al. (2018) demonstrated that organic anions (e.g. citrate) and phytase must be present together; if they are not, mineralization rates will be low. In addition, the small contribution of SOP mineralization to plant nutrition could also be explained by the high stock of SIP, as previous studies have shown that mineral fertilization

and soil phosphate ions concentrations can inhibit phosphatase synthesis and activity and thus limit organic P mineralization (Olander and Vitousek 2000; Nannipieri et al. 2011). Sorption, enzyme activity and the production of organic anions were not measured for this study, so no specific conclusions about the low mineralization rates can be made. However, it is clear that incorporating those measurements in future modeling studies would be very beneficial.

1.5 Conclusion

In this study, inorganic P stocks in the soil plough layer significantly varied with rates of P fertilization whereas organic P stocks did not. Major organic P compound classes were orthophosphate monoesters (77% with 50% IHP, where *myo*-IHP was affected by P application rate) and orthophosphate diesters (20%). The SOP stock tended to slightly and constantly increase with time ($+1.6 \pm 0.9 \text{ kg P ha}^{-1} \text{ yr}^{-1}$) indicating that the organic P flux incorporated into SOP by decomposition of maize residues was slightly higher than the P flux released by SOP mineralization. Using a modeling approach, the SOP residence time was 212 years with a gross annual rate of SOP mineralization value of $1.7 \pm 1.2 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, irrespective of the P fertilization rate. This low rate (less than 1% of the SOP stock), which can only play a minor role in plant nutrition and soil P availability, was ascribed to: i) the abundance of IHP compounds in these soils, which can be strongly stabilized by sorption/precipitation reactions at the surface of the soil solid phase and which require specialized enzymes (phytases) for mineralization; ii) the inhibition of phosphatases by high phosphate ions concentrations in soil solution. Further studies are required to confirm this first assessment of SOP mineralization and residence time in relation to speciation in other agroecosystems. Additionally, to refine our mechanistic assessment of plant-available soil P and the modeling of its long-term dynamics in sustainable cropping systems, it would be informative to assess the role of mineralization and diffusion processes supply phosphate ions into the soil solution over time.

SI-1.1 Supplementary information 1: Soil P-NMR spectra and chemical shifts of peaks detected

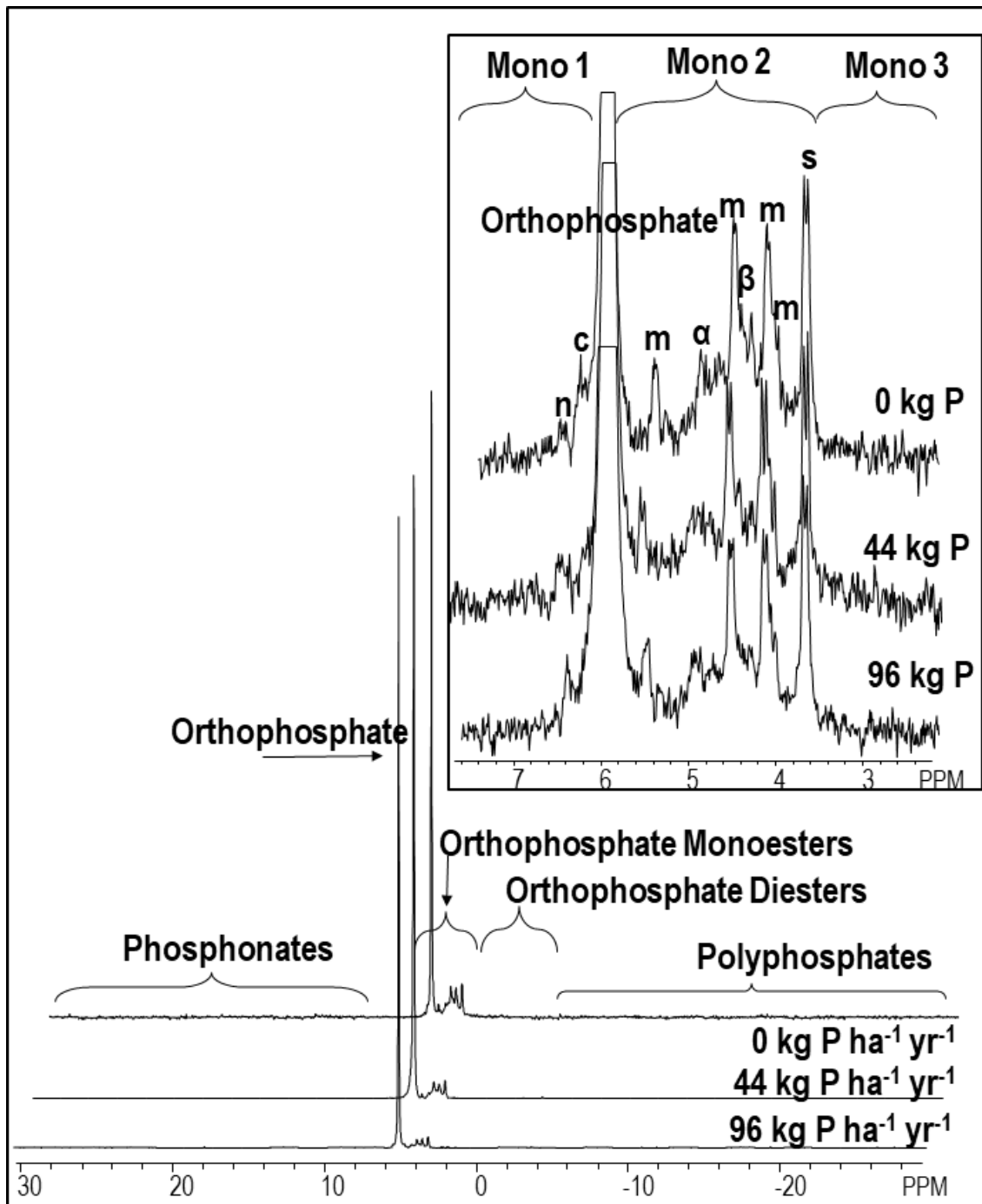


Figure SI-1.1 Sample P-NMR spectra of NaOH-EDTA extracts for the soils sampled in 2000 from the three fertilization treatments. Spectra were analyzed without proton decoupling. The full spectra were processed with 7 Hz line-broadening and were scaled to the height of the orthophosphate peak; the insets were processed with 7 Hz line-broadening and were scaled to the height of the *scyllo*-IHP peak. P species abbreviations: n = *neo*-IHP, c = *D-chiro*-IHP, m = *myo*-IHP, s = *scyllo*-IHP, IHP = inositol hexakisphosphate, α = alpha glycerophosphate, β = beta glycerophosphate.

Table SI-1.1 Chemical shifts of peaks detected in P-NMR spectra of Tartas soils, present in six or more of the twelve samples.

Category	P Form	Chemical Shift (ppm)
Inorganic P		
	Orthophosphate	6.00 ±0.00
	Pyrophosphate	-4.03 ±0.17
	Polyphosphates	-3.93 ±0.30, -6.76 ±0.53, -9.00 ±0.53, -11.33 ±0.39, -16.45 ±0.60, -19.29 ±0.74, -22.07 ±0.87, -24.09 ±0.59, -25.68 ±0.65
Organic P		
	Phosponates	33.12 ±0.48, 28.25 ±0.97, 24.57 ±0.81, 22.35 ±0.48, 19.81 ±0.86, 10.55 ±0.67, 7.75 ±0.29
Orthophosphate Monoesters		
	<i>myo</i> -IHP	5.48 ±0.12, 4.53 ±0.10, 4.14 ±0.11, 4.04 ±0.11
	<i>scyllo</i> -IHP	3.68 ±0.10
	<i>neo</i> -IHP	6.40 ±0.09, 4.25 ±0.10
	<i>D-chiro</i> -IHP 4e/2a	6.55 ±0.09, 5.28 ±0.10, 3.96 ±0.12
	<i>D-chiro</i> -IHP 4a/2e	6.24 ±0.04, 4.73 ±0.09, 4.34 ±0.21
	Glucose 6-phosphate	5.17 ±0.09
	α-glycerophosphate	4.80 ±0.07
	β-glycerophosphate	4.46 ±0.10
	Mononucleotides	4.35 ±0.05, 4.28 ±0.03, 4.23 ±0.04, 4.11 ±0.03
	Choline phosphate	3.82 ±0.12
	Monoester 1	6.93 ±0.02, 6.79 ±0.07, 6.63 ±0.09, 6.38 ±0.08, 6.21 ±0.06
	Monoester 2	5.85 ±0.04, 5.74 ±0.05, 5.62 ±0.06, 5.39 ±0.08, 4.99 ±0.07, 4.88 ±0.05, 4.70 ±0.05
	Monoester 3	3.65 ±0.09, 3.49 ±0.06, 3.34 ±0.07, 3.09 ±0.08, 2.90 ±0.10, 2.67 ±0.17
Orthophosphate Diesters		
	Other Diester 1	2.36 ±0.08, 2.10 ±0.08, 1.67 ±0.08, 0.58 ±0.21, -0.04 ±0.20, -0.51 ±0.13
	DNA	-0.82 ±0.16, -1.02 ±0.16
	Other Diester 2	-1.28 ±0.09, -1.57 ±0.12, -1.97 ±0.12, -3.27 ±0.16

SI-1.2 Supplementary information 2: Calculation of the phosphorus harvest index (HI_P) for all years of the field experiment

SI-1.2.1 Introduction

To perform modelling of soil organic P dynamics over decades, the annual P flux returning to the soil as aboveground residue (P_{agr}) is indispensable data. The P_{agr} values were not measured every year over the 28 years of the experiment but only five times, in 1993, 1995, 1996, 1997, and 1998.

We calculated the P_{agr} value using the P harvest index (HI_P), i.e., the ratio of P in grains to the sum of P in aboveground residue and P in grains (P_{grr}):

$$HI_P = \frac{P_{grr}}{P_{grr} + P_{agr}} \quad (\text{SI-Eq. 1.1})$$

Which allows us to calculate P_{agr} values:

$$P_{agr} = \frac{P_{grr} - P_{grr} \times HI_P}{HI_P} \quad (\text{SI-Eq. 1.2})$$

The objective of this supplemental information is to establish relationships between the measured HI_P values and cumulative P budget (Bcum), i.e., difference between P applied as superphosphate minus P exported in grain summed over the years of the experiment. Knowing the HI_P values for all years of experimentation and treatments, P_{agr} values can be calculated yearly for all P treatments.

SI-1.2.2 Materials and methods

Maize grain yield at harvest were determined every year for all experimental plots (see materials and method section). The annual P budget was calculated as the difference between P applied and P exported in harvested grains. The cumulative P budget (Bcum, kg P ha⁻¹) was the annual P budget summed year after year over the duration of the experiment.

Maize aboveground residue that returned to the soil at harvest (chopped stover including the stalks, leaves, husks and tassels) were weighed in 1993, 1995, 1997, and 1998, and analyzed for P concentration. The HI_P values was calculated for each of these 5 years using the SI-Eq. 1.1.

Parameters of the linear regression that describes relationships of the HI_P values with $Bcum$ values were estimated using R software (R Core Team 2021).

SI-1.2.3 Results and discussion

The $Bcum$ values over the 28 years of maize monoculture are shown in Figure SI-1.2 for the three P fertilization rates. The mean $Bcum$ at the end of the experiment were 723 ± 5 , 411 ± 5 , and $1829 \pm 8 \text{ kg P ha}^{-1}$ for the CON_0 , TSP_{44} , and TSP_{96} treatments, respectively.

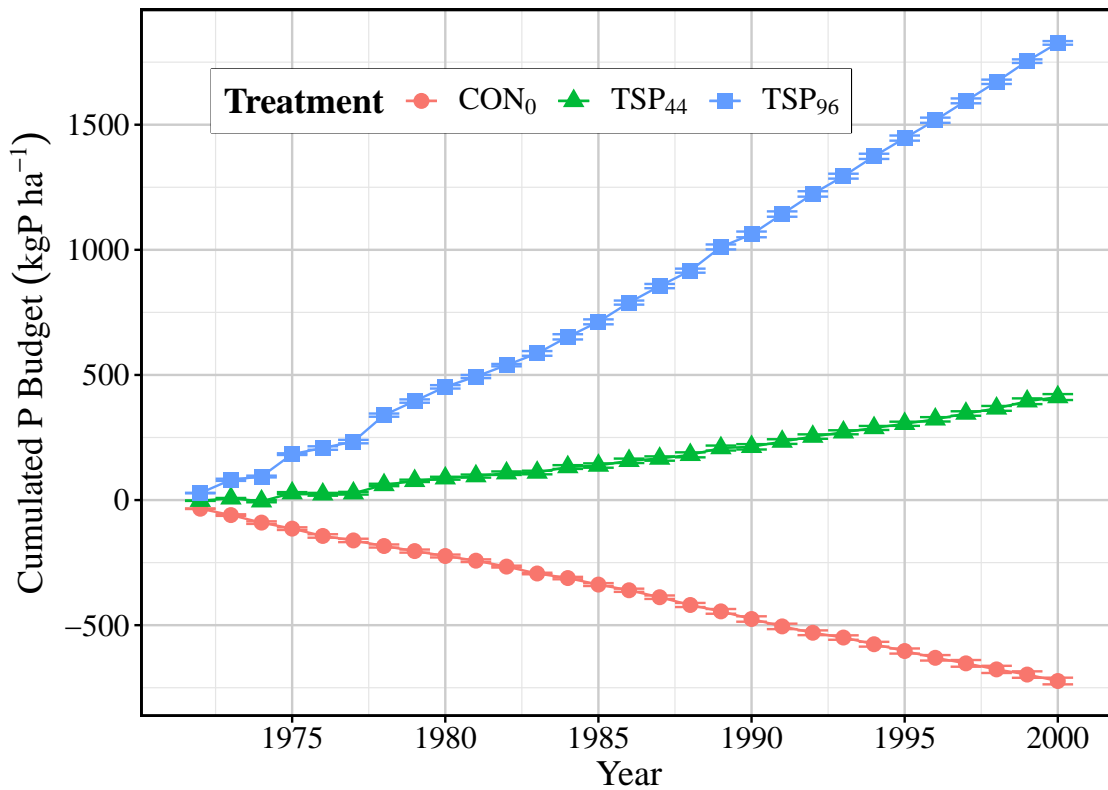


Figure SI-1.2 Cumulative P budget over 28 successive years of cultivation for the CON_0 , TSP_{44} , and TSP_{96} treatments. Values are means \pm standard deviation.

The HI_P values, measured in 1993, 1995, 1996, 1997, and 1998, are presented as a function of the $Bcum$ values in Figure SI-1.3. The following linear regression fitted significantly ($P < 0.0001$, $R^2 = 0.61$) to the 15 experimental data:

$$HI_P = 0.78 - 6.8510^{-5} \times Bcum \quad (\text{SI-Eq. 1.3})$$

The relation between both variables shows that HI_P values decrease for positive $Bcum$ values whereas HI_P values increases for negative $Bcum$ values. Calculated HI_P values for all years and P treatments using SI-Eq. 1.3 ranged from 0.83 to 0.66. The HI_P value at the

onset of the experiment, which corresponds to the null Bcum value, was 0.78, i.e., 78% of P in total aboveground biomass was in harvested grains. These values are rather inferior to the median HI_P value of 0.89 (minimum value of 0.47 and maximum value of 0.98) found by Wortmann et al. (2009) analyzing 34 field irrigated maize trials conducted in diverse situations across Nebraska.

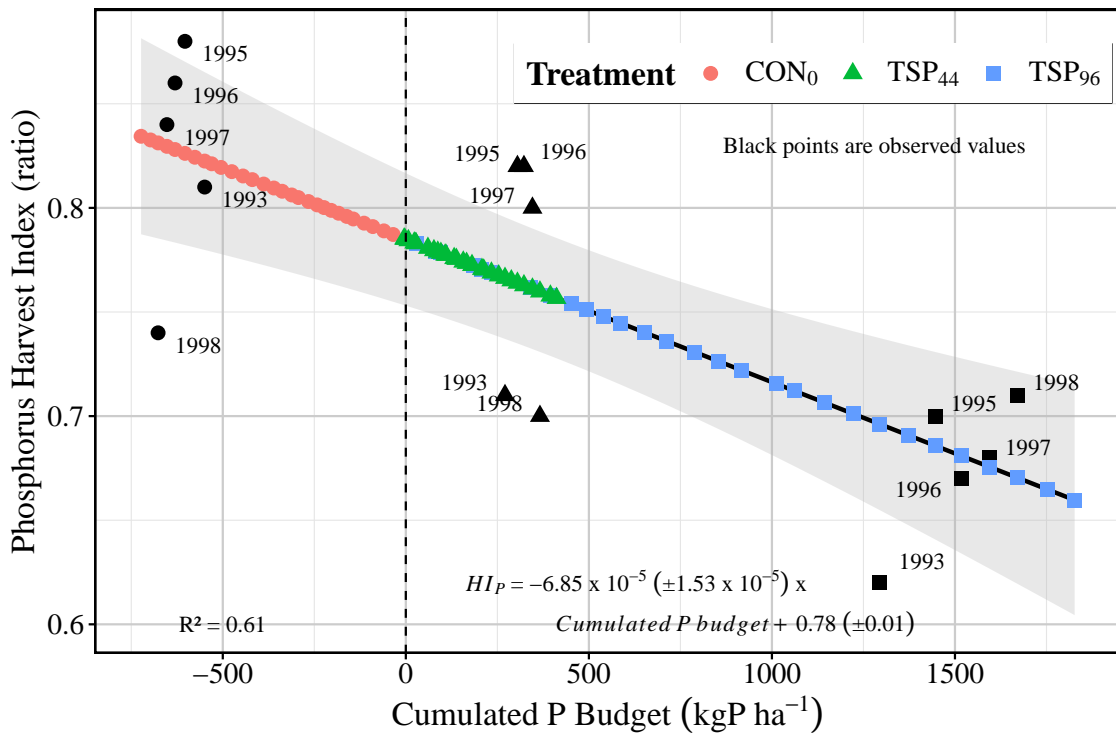


Figure SI-1.3 Relationship between the P harvest index and cumulative P budget over 28 years of the experiment for the three P application rates. Black symbols: measured HI_P values; colored symbols: calculated HI_P values. Grey area: 95% confidence interval.

This study shows that changes in the cumulative P budget, which drives gradients of plant-available P in soils (Messiga et al. 2010), significantly affects the accumulation and partitioning of P between the vegetative and reproductive stages. There were no significant differences in grain yield between the TSP_{44} and TSP_{96} treatments indicating that field conditions allowed optimal plant growth and development for maize cultivars. The partitioning of P between vegetative and reproductive organs was in favor of aboveground residue. On the other hand, small loss of grain yield occurred in the CON_0 treatment mainly during the last decades of cultivation. In that particular case, partitioning of P between aboveground residues and grains is in favor of grains. The HI_P value which corresponds to 95% of the maximum yield was approximately 0.80. It seems that P in the aboveground residues plays the role of P source for grains when plant-available soil P decreases thus avoiding, delaying or even minimizing yield losses.

In conclusion, the decrease in the HI_P with the positive B_{cum} values and the increase in the HI_P values with the negative B_{cum} values fitted to the same linear regression. Slope and intercept of this linear regression likely depend on the plant-available soil P. Further studies based on several long-term field experiments on P fertilization, for which time series of HI_P values have been determined, are required to test this hypothesis.

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CHAPTER 2

Organic phosphorus mineralization in cropped soils fertilized by different P sources. Results from three field experiments

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Dynamic of organic phosphorus in the plough soil layer of three contrasting long-term field experiments

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Abstract

Phosphorus (P) is a major nutrient for crops and its application to agricultural soils is crucial to optimize the P availability to plants for sustaining and ensuring food production. Mineralization of soil organic P (SOP) might play a significant role to supplying plant-available P. This study aimed to determine SOP mineralization rate in soils cropped with contrasting agropedoclimatic conditions. We determined this rate using and applying the modelling approach described in Raguet et al. (2023). We used databases of three French long-term field experiments (LTFE) on P fertilization combining different P rates (range of 0 to 112 kg P ha⁻¹ yr⁻¹), applied for decades as superphosphate or organic wastes (OW) (urban composts, urban sewage sludge, or farmyard manure), different soil types (luvic arenosol, glosic luvisol, calcareic cambisol), and different annual crops successions. These databases consisted of long time series on SOP and inorganic P (SIP) concentrations of topsoils, and annual crops measurements (yield, biomass of aboveground and belowground residues at harvest, their P concentration). For the three LTFE, initial SOP stock was 446, 595, and 1145 kg P ha⁻¹, P exported in harvest was 26.5, 26.6, and 25.3 kg P ha⁻¹ yr⁻¹, and P restituted to topsoil as crop residues were 15.0, 14.4, and 11.5 kg P ha⁻¹ yr⁻¹ with significant differences across yields, plant parts and fertilization treatments. Rates of 2.5, 7.9, and 11.0 kg P ha⁻¹ yr⁻¹ were incorporated to SOP by the decomposition of crop residues and OWP during the post-harvest year. Rates of SOP mineralization, 2.1, 5.4, and 11.2 kg P ha⁻¹ yr⁻¹, differed significantly across LTFE. As a result, SOP stocks did not change significantly with years of cropping and fertilization, irrespective of P fertilization (types and rates). At the same time, close correspondences fitted SIP stocks vs cumulative budget of (applied P – exported P by harvests).

Keywords:

Agroecosystems, fertilizers, field experiment, manures, organic waste, phosphorus, productivity, soil-plant cycling.

Highlights:

- Analysis by modelling of time series data on soil organic P (SOP) of three fertilization trials
- SOP mineralization rate differed among soils (2.1 - 11.3 kg P ha⁻¹ yr⁻¹) irrespective of applied fertilizer types (superphosphate, urban composts, farmyard manure)
- SOP stocks did not change (or few) although (applied - crop removed) P budget varied considerably
- By contrast, evolution of soil inorganic P stocks closely fitted to P budget changes

Résumé

L'objectif de ce chapitre est de déterminer la vitesse de minéralisation du POS (V_m -POS) dans différentes situations agropédoclimatiques. L'approche par modélisation, proposée par Raguet et al. (2023), a été utilisée. Pour tester l'hypothèse que la nature (organique et/ou minérale) de la fertilisation, de même que les conditions agropédoclimatiques pourraient affecter différemment V_m -POS, trois essais de longue durée, menés sur la fertilisation, ont été sélectionnés de manière à couvrir différentes situations de types de sol, cultivés selon diverses successions de cultures, et fertilisés par des engrais de nature différente (superphosphate ou PRO). Les résultats de la modélisation montrent que V_m -POS est faible (0.8% du stock de POS) et varie entre essais. Pour un essai donné, elle n'est pas affectée par la nature et la dose de P apporté et ne varie pas avec le bilan P, malgré des valeurs considérablement différentes entre les traitements. En revanche, l'évolution du stock de PIS suit exactement ce bilan.

Mots clés :

Agroecosystemes, Fertilisants, Essai agronomique au champ, Fumier, Résidus organiques, Phosphore, Productivité, Cycle plante-sol.

Éléments clés :

- Analyse par modélisation des séries chronologiques de données sur le P organique du sol (POS) de trois essais agronomiques
- Les vitesses de minéralisation du POS diffèrent entre les sols (2.1 - 11.3 kg P ha⁻¹ an⁻¹) indépendamment du type de fertilisant apporté
- Les stocks de POS ne changent pas (ou peu) malgré les différentes valeurs de bilan phosphaté
- Les stocks de P inorganique du sol suivent fidèlement les variations de bilan phosphaté des parcelles

2.1 Introduction

Agricultural systems are facing crucial issue regarding phosphorus (P) management. Previous studies highlighted i) the risk of shortage of rock phosphates reserves, raw materials used to produce synthetic P fertilizers, because of an increasing consumption over next decades due to growing demand for food, and ii) the risk of geopolitical tension on this resource (Tilman et al. 2002; Cordell et al. 2009; Cordell and White 2011). Alternative P sources to mineral P fertilizers, such as organic waste products (OWP) (urban composts) and animal manures, can help to avoid a possible future shortage of P fertilizers. The environmental risk is another major issue facing P management in agricultural soils (Némery and Garnier 2007; Sharpley et al. 2016; Pinay et al. 2018). Runoff of particulate and dissolved P from fields towards water bodies can contribute to alter water quality in case of eutrophication. It is therefore crucial to improve the management of plant-available soil P and our understanding of soil processes of P cycling in agroecosystems.

The use of OWP in place of synthetic fertilizer is a common practice and can replenish soil P pools and potentially replace industrial inorganic fertilizers (Diacono and Montemurro 2011). Indeed, repeated OWP applications in agriculture are used according to add carbon (C) or nitrogen (N) to agricultural soils, or their role to improve soil stability, C storage or organic matter storage (Annabi et al. 2007; Gopinath et al. 2008; Paetsch et al. 2016). However, the C/N/P ratio of OWP is highly variable because of their origin, composting parameters and storage methods. Thus, the use of these products could lead to highly variable P supply (Fuchs et al. 2014).

Phosphates ions in solution (H_2PO_4^- and HPO_4^{2-} for the range of cropped soil pH) are the P compounds absorbed by plants and microorganisms. The absorbed ions by plants can be either converted to organic P compounds or stored as inorganic P compounds (Noack et al. 2012, 2014). Thus, crop residues and OWP contain organic and inorganic P forms. Their decomposition in soils by biogeochemical processes (He et al. 2011; Giles et al. 2018; Arenberg and Arai 2019), supplied both soil inorganic P (SIP) and soil organic P (SOP) stock. There is general agreement that mineralization of SOP can be a potential source of phosphate ions for plants and so might play a significant role in plant nutrition. The same is true for crop residues and OWP: their decomposition and mineralization of their organic P compounds by enzymatic hydrolysis (i.e. by phosphatases; Nannipieri et al. 2011; Dodd and Sharpley 2015) released phosphate ions in solution, which increase inorganic P pool. However, limited information exists on the mineralization rate of SOP and on the incorporation P rate to SOP during decomposition of crop residues and OWP as well as phosphate ions release in SIP pool.

The purpose of this study was to determine the SOP mineralization rate in different soil types, under various management practices and climates. Recently, Raguét et al. (2023) (see chapter 1), adapted to the SOP dynamic, the two-compartments model often used to describe long-term dynamic of soil organic C, to assess SOP mineralization rate and its residence time. We used and applied this modelling approach using databases, containing time series of data on soils and plants, of three field experiments, conducted in France for 18, 14 and 17 years on superphosphate or OWP applications, in contrasting agropedoclimatic situations characterized by various soil types and soil textures, different cropping systems, and climatic conditions.

2.2 Materials and methods

2.2.1 Description of the long-term field experiments

Each field experiment was organized as a complete randomized block design (4 replicates per treatment).

One (LTFE1), was located close to the Mant village (43°35' N, 0°30' W; altitude: 188 m; Landes, Nouvelle Aquitaine) was part of the *Institut National de Recherche pour l'Agriculture, l'Alimentation et l'Environnement* (INRAE) network on P fertilization (Boniface and Trocmé 1988). The local climate is oceanic (sub-humid Cfb in Köppen classification), with 917 mm annual rainfall and 13.2°C annual temperature on average. The experiment (12 plots of 6 m × 30 m) was conducted from 1975 to 1992 on a silt loam luvisol (FAO 2014 classification) under maize (*Zea mays* L.) monoculture, annually fertilized at 0 (CON₀), 27 (TSP₂₇), and 79 (TSP₇₉) kg P ha⁻¹ yr⁻¹, applied as triple superphosphate. Supplemental information including N and K fertilization, irrigation, and lime management were in Morel et al. (2021).

Another LTFE, called QualiAgro (LTFE2), located close of Feucherolles village (48°53' N, 1°58' E; altitude: 177 m; Yvelines, Île-de-France) was one of the long-term field experiments of the *SOERE-PRO* (*Système d'Observations et d'Expérimentations pour la Recherche en Environnement sur les Produits Résiduaux Organiques*) network. The local climate is oceanic sub-humid but degraded, with a mean annual rainfall of 572 mm and mean annual temperature of 11°C. QualiAgro was conducted for 17 years (1998 – 2015) on a glossic luvisol (FAO, 2014), with a silt loam texture under a maize-wheat (*Triticum spp.*) succession except in 2007 (spring barley due to local infestation by chrysomela). The following five treatments were studied in QualiAgro (20 plots of 10 m × 45 m): three composts with a municipal solid waste compost (MSW), a biowaste compost (BIOW), a green waste and a dehydrated urban sewage sludge compost (GWS); a cattle dairy

farmyard manure (FYM); and the control without applied any OWP (CON). All OWP were spread every two years at 4 t C ha⁻¹ from 1998 to 2013 and at 2 t C ha⁻¹ yr⁻¹ in 2015 (total of 10 applications). Up 2013, optimal rate (80-140 kg N ha⁻¹ yr⁻¹ depending on years) of N fertilizer was applied as the 1:1 urea and ammo-nitrate solution (39% N). From 2014 corresponding to the conversion of QualiAgro to organic farming practices, new source for applying optimal N rate was used: a mixture of meat and bone powder and blood flour (commercial name: AXE-NP-BIO; AFNOR standardized product according to NF U42-001, containing 6% of N and 2.2% of P). As a result, the CON treatment received 47 kg P ha⁻¹ in 2014, and all plots received 16 kg P ha⁻¹ in 2015. Early 2016, the average of annual P applied (mainly as OWP and a little as organic fertilizers) was 3, 24, 40, 46, 112 for CON₃, MSW₂₄, FYM₄₀, BIOW₄₆, and GWS₁₁₂, respectively. Further details on OWP origin and composting parameters can be found in supplementary information (Table SI-2.1) and (Annabi et al. 2007, 2011). Plots were not fertilized for synthetic mineral P or K fertilizers. In 2006, 2007, 2009, 2011, and 2013, 71%, 75%, 70%, 75% and 84% of wheat and barley straw were exported, respectively. The remaining aboveground residues were returned to soil, as for the entire maize stem. Details on crop succession and management were described in Chalhoub et al. (2013) and Paetsch et al. (2016).

The third field trial (LTFE3), called PROspective, was also a part, as QualiAgro, of the SOERE-PRO network. It was set up in 2001 at the Colmar experimental research centre of INRAE (48°04' N, 7°21' E; altitude: 205 m; Haut-Rhin, Alsace) on a silt loam calcareous cambisol under maize/wheat/barley (*Hordeum vulgare* L.)/sugar beet (*Beta vulgaris* L.) rotation. The local climate is semi-continental (also Cfb in Köppen classification) with a mean annual rainfall of 556 mm and mean annual temperature of 10.9°C. We used one of the four experimental set-up among 4 (Chen et al. 2022), including a control (CON) without any OWP application (CON) and five different types of OWP with supplementation of mineral N fertilization (24 experimental plots of 9 m × 10 m). OWP were applied every two years at 170 kg N ha⁻¹ since 2001, which is twice lower than the European Nitrates Directive, adopted to reduce water pollution by nitrates from agricultural sources and improve water quality. The OWP types were: a biowaste compost (BIOW); a dairy farmyard manure (FYM); the FYM after composting (FYMC); a dehydrated urban sewage sludge (SLU); The SLU after composting with green waste (GWS). The OWP applied to soil were buried the day after their application. Before sugar beets cropping, 46 kg P-TSP ha⁻¹ were applied in 2007 to all plots, and 11, 31 and 72 kg P-TSP ha⁻¹ were applied in 2011 to FYMC, BIOW and CON, respectively. On average of the 7 OWP applications and two TSP applications, the annual P rate added was 17, 21, 21, 36, and 45 kg P ha⁻¹ yr⁻¹ for BIOW₁₇, FYM₂₁, FYMC₂₁, SLU₃₆, and GWS₄₅, respectively. Details on OWP, crop species, soil sampling dates, dates of OWP and N fertilizer applications, amounts of applied OWP, and mineral fertilizer are in Chen et al. (2022). Further information on OWP origin and composting parameters are in supplementary information (Table SI-2.2).

2.2.2 Characteristics of OWP

The main characteristics of compost, farmyard manure and dehydrated sewage sludge in LTFE2 and LTFE3 are presented in Table 2.1. The OWP were sampled before application, air-dried and grounded ($<250\ \mu\text{m}$) for analyses. Samples were analyzed at the *Laboratoire d'Analyses des Sols*, INRAE (LAS, Arras, France) with normalized techniques (AFNOR, 1999). Dry matter was determined after heating at 105°C . According to NF ISO 10390, the pH_{water} was measured in a soil:water suspension of volumetric ratio 1:5. Both total N and organic C concentration were determined by combustion according to NF ISO 10694 and NF ISO 13878, respectively. CaCO_3 was determined by measuring CO_2 from HCl (NF ISO 10693) sample digestion. Total P concentrations (TP_{HF}) were determined after wet digestion by concentrated fluorhydric (HF) and perchloric (HClO_4) acids (NF X 31-147). Organic P concentrations in OWP were determined by the Saunders and Williams (1955) ignition method. The inorganic P concentrations were calculated as the difference between TP_{HF} and organic P in OWP.

2.2.3 Plant analysis

In LTFE1, plants were collected each year from two central row of maize to avoid edge effect. Grains were dried at 105°C to determine crop yield (t DM ha^{-1}). The P concentration in harvested grains was measured each year by colorimetric method after digestion in H_2SO_4 and H_2O_2 solution, according to Murphy and Riley (1962). The amount of P restituted to soil laying maize aboveground residues was not measured in this long-term field experiment. We computed it for all years cropping using the equation proposed for maize monoculture by Raguet et al. (2023) in which P in belowground depended on P in harvested grain, on P harvest index and on cumulative P budget (Bcum).

In both LTFE2 and LTFE3, grains and aboveground residues were sampled each year. Samples were weighted and oven-dried at 40°C . The grains and aboveground residues P concentrations were analyzed at the central plant-testing laboratory (USRAVE) of INRAE. Plant sub-samples were ground and then calcinated at 480°C for 5 h, then solubilized in nitric and hydrofluoric acids to determine total P concentration by radial ICP-OES (Masson et al. 2010). The annual exported P in harvests was calculated by multiplying grain yield or biomass of aboveground residues by their respective P concentration.

Table 2.1 Main properties of OWP, applied repeatedly at LTFE2 and LTFE3. Values are means \pm std. err. of 10 and 7 applications, sampled over years, at LTFE2 and LTFE3, respectively. MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; GWS: compost of green waste and SLU; SLU: dehydrated urban sewage sludge; BIOW: bio-waste compost. Subscript values in treatment abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{yr}^{-1}$. Values between parentheses are organic P proportions within total P (TP_{HF}). Different lower case letters (a, b, c) indicate significant differences among treatments within LTFE ($\alpha = 0.05$).

LTFE	Organic products	Dry matter (%)	pH water	Organic C	Total N	TP_{HF} ($\text{g kg}^{-1} \text{DM}$)	Organic P
LTFE2	MSW₂₄	87 \pm 4	7.6 \pm 0.2 b	311 \pm 13 a	17 \pm 1 c	3.6 \pm 0.2 b	0.32 \pm 0.03 (9) b
	FYM₄₀	78 \pm 8	9.1 \pm 0.1 a	324 \pm 20 a	22 \pm 1 ab	5.8 \pm 0.4 b	2.08 \pm 0.15 (34) a
	BIOW₄₆	90 \pm 3	8.1 \pm 0.2 b	219 \pm 17 b	18 \pm 1 bc	4.7 \pm 0.5 b	0.35 \pm 0.05 (8) b
	GWS₁₁₂	86 \pm 4	7.5 \pm 0.2 b	267 \pm 13 ab	23 \pm 1 a	12.8 \pm 1.0 a	2.10 \pm 0.17 (16) a
P-value	0.45	< 0.0001	0.0002	0.0002	< 0.0001	< 0.0001	< 0.0001
LTFE3	BIOW₁₇	60 \pm 5 a	8.5 \pm 0.1 b	245 \pm 20 b	20 \pm 1 c	4.4 \pm 0.3 d	0.31 \pm 0.02 (7) c
	FYM₂₁	19 \pm 1 b	9.5 \pm 0.1 a	395 \pm 21 a	26 \pm 1 b	6.6 \pm 0.7 cd	2.39 \pm 0.24 (36) b
	FYMC₂₁	19 \pm 1 b	9.4 \pm 0.1 a	356 \pm 30 a	26 \pm 1 b	7.5 \pm 0.5 c	2.71 \pm 0.17 (36) b
	SLU₃₆	18 \pm 1 b	7.2 \pm 0.3 c	371 \pm 33 a	61 \pm 2 a	29.2 \pm 0.6 a	4.96 \pm 0.10 (17) a
P-value	56 \pm 3 a	7.6 \pm 0.2 c	294 \pm 55 b	25 \pm 1 bc	13.6 \pm 1.3 b	2.17 \pm 0.17 (16) b	< 0.0001

For all LTFE, the annual P budget was calculated as the difference between P applied as TSP or OWP, and annual P exported, cumulative P budget (Bcum) by adding up over years successive annual budgets. Amount of P in roots residues (except sugar beet cropped at LTFE3) was calculated considering P amount in aboveground residues and published values of root-to-shoot parameters at harvest, i.e. 0.18, 0.38, and 0.49 for maize, wheat, and barley, respectively (Bolinder et al. 1997; Rajala and Peltonen-Sainio 2001; Amanullah 2014; Amanullah et al. 2015). We considered that 3% of grain yield were lost at harvest and returned to soil (Wang et al. 2021).

2.2.4 Main soil properties

The main soil properties (Table 2.2) were assessed according to French AFNOR and ISO standards (AFNOR 1999). Sedimentation analyses to determine soil particle size were carried out according to standard NF X 31-107 and ISO 11277. The pH_{water} was measured in a soil suspension with a soil-to-water ratio of 1:2.5 (m:v) (ISO 10390). Soil total carbonate concentration was determined according to NF ISO 10693. In LTFE1, soil organic carbon was determined sulfochromic oxidation using excess potassium dichromate solution and sulphuric acid (ISO 14235). Total nitrogen was measured by a modified Kjeldahl method (ISO 11261). In LTFE2, soil organic carbon was determined by combustion (ISO 10694). Total nitrogen was measured by total elemental analysis CN (ISO 13878). In LTFE3, soil organic carbon was also determined according to ISO 14235 and the total nitrogen was also measured according to ISO 13878. For all LTFE, the cation exchange capacity and exchangeable cations were evaluated by the cobaltihexamine (NF ISO 23470).

2.2.5 Soil P analysis

Soil ploughed layer were sampled using the NF X 31-100 standard in each experimental plot after crop harvest and before OWP applications. At LTFE1, soils (0-0.25 m) were sampled (0-0.25 m) in 1975 (before the onset of the experiment), 1982, 1987, and 1992. At LTFE2, soils (0-0.25 m) were sampled (0-0.25 depth) in 1998 (before the onset of the experiment), 2002, 2004, 2006, 2009, 2011, 2013, and 2016. At the LTFE3, soils (0-28 cm) were sampled (0-28 cm depth) in 2000 (before the onset of the experiment), 2002, 2004, 2008, 2010, 2012, and 2014. Each soil sample was obtained by mixing 10-12 randomly collected cores within each plot avoiding edge effect. Mixed samples were air-dried at 40°C before grounding to pass to the 2 mm mesh sieving. Soil organic P (SOP) concentrations were determined for each sample using the ignition and acid extraction method of Saunders and Williams (1955). Briefly, one gram of soil was ignited at 550°C. Phosphorus from both ignited and non-ignited samples were extracted with H₂SO₄. The P

concentration in solution was determined using the green malachite colorimetric method (Van Veldhoven and Mannaerts 1987) with a spectrophotometer at 610 nm. The SOP value was calculated as the difference in P concentrations between ignited and non-ignited samples. Soil TP_{HF} in all soil samples was determined at the National laboratory of INRAE according to the NF X 31-147 standard. Soils were ground (<0.150 mm) and ignited (450°C), then digested in concentrated fluorhydric (HF) and perchloric ($HClO_4$) acids. After filtration, P in digested solution was determined by ICP-OES. The SIP value was the difference between TP_{HF} and SOP.

Table 2.2 Main soil physicochemical properties of the plough layer at the three studied LTFE. Values are means \pm std. dev. For LTFE1, values are means ($n = 4$) for soils sampled in TSP₂₇ treatment in March 1992. For LTFE2 and LTFE3, values are means for all experimental plots and years of soil sampling ($n = 140$ and $n = 144$, for LTFE2 and LTFE3 respectively).

LTFE	LTFE1	LTFE2	LTFE3
Bulk density (g cm⁻³)	1.40	1.32	1.34
Plough layer depth (cm)	25	25	28
Clay (%)	12 \pm 1	15 \pm 7	21 \pm 1
Silt (%)	52 \pm 1	78 \pm 5	70 \pm 1
Sand (%)	36 \pm 1	7 \pm 4	9 \pm 1
CaCO₃ (g kg⁻¹)	< 1	< 1	114 \pm 13
TP_{HF} (mg kg⁻¹)	429 \pm 78	697 \pm 135	1148 \pm 51
SOP (mg kg⁻¹)	129 \pm 13	172 \pm 42	322 \pm 35
Total N (g kg⁻¹)	1.0 \pm 0.1	1.2 \pm 0.2	1.4 \pm 0.1
Organic C (g kg⁻¹)	9.3 \pm 0.9	12.5 \pm 2.0	14.6 \pm 1.0
Water pH	7.3 \pm 0.4	7.2 \pm 0.3	8.3 \pm 0.1
CEC (cmolc kg⁻¹)	5.9 \pm 0.8	9.8 \pm 0.9	16.9 \pm 0.5
Ca (cmolc kg⁻¹)	7.1 \pm 1.5	9.1 \pm 1.0	16.7 \pm 0.6
Mg (cmolc kg⁻¹)	0.4 \pm 0.1	0.59 \pm 0.15	0.98 \pm 0.10
K (cmolc kg⁻¹)	0.3 \pm 0.1	0.50 \pm 0.21	0.63 \pm 0.14

2.2.6 Modelling soil organic P dynamics

Raguet et al. (2023) proposed to describe long-term SOP dynamics in cropped soils using and adapting the two-compartment model, developed by Hénin and Dupuis (1945) to simulate soil organic carbon dynamics. They applied this modelling approach to determine the coefficient k of SOP mineralization in one long-term field experiment on superphosphate applications for 28 years. Here, we applied the same modelling approach to determine the k coefficient, and to assess the resulting rate of SOP mineralization, in three other agropedoclimatic situations (the three LTFE), which cover a wider range of fertilizer applications (superphosphate or OWP), soil types, climates, and crop rotations.

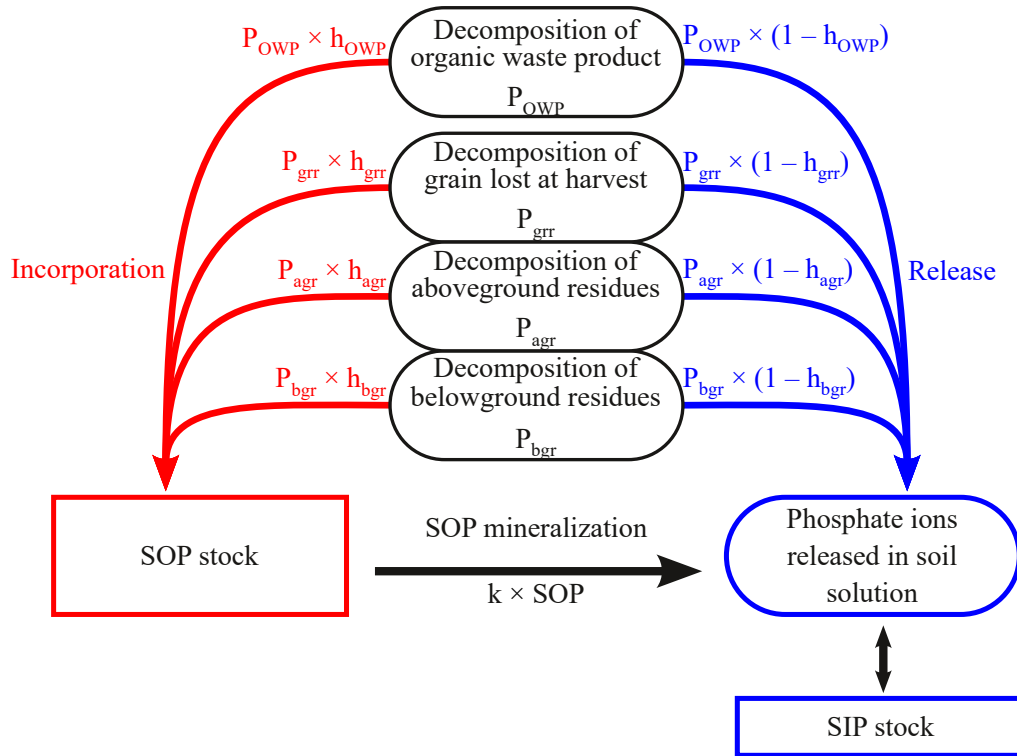


Figure 2.1 Conceptual diagram of the model describing soil organic P stock and P fluxes and processes that drives its dynamics. The P inputs as crop residues and total P in OWP are either released ($1-h$ fraction) in solution as phosphate ions or incorporated (h fraction) into the soil organic P stock (SOP). The SOP stock mineralizes according to the k mineralization constant.

SOP and SIP: stock of soil organic and inorganic P, respectively (kg P ha^{-1});
 P_{agr} and P_{grr} : annual P amount ($\text{kg ha}^{-1} \text{ yr}^{-1}$) that return to the soil ploughed layer as aboveground (except grains) and grains residues at grain harvest, respectively;
 P_{bgr} : annual P amount ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) that remained in the soil ploughed layer as belowground (roots) residues at grain harvest;
 P_{OWP} : total P applied as OWP ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) k : coefficient of SOP mineralization (yr^{-1});
 h_{agr} , h_{bgr} , h_{grr} , h_{OWP} . (dimensionless): incorporation coefficients to SOP of P in aboveground, belowground, grains residues, and total P in OWP.

The SOP dynamic model considers only two P compartments (Figure 2.1): P applied as organic materials (i.e. aboveground residues including grains lost at harvest, belowground residues, or OWP), and SOP compartment. This SOP compartment is supplied by a fraction (incorporation coefficient h , dimensionless) of organic inputs and is subjected to mineralization according to first-order kinetics with the k (yr^{-1}) decay constant (with $1/k$ the residence time in years). The remaining ($1-h$) fraction is released into the solution as phosphate ions and easily degradable inorganic and organic P compounds. The SOP dynamic model computes at the time step of the year SOP stock with this equation:

$$SOP_{t+1} = \frac{\sum(P_j \times h_j)}{k} \times (1 - e^{-k}) + SOP_t \times e^{-k} \quad (\text{Eq. 2.1})$$

where, SOP_t and SOP_{t+1} stocks were SOP stock ($kg\ ha^{-1}$) the year t and the following year the experiment, respectively; P_j ($kg\ P\ ha^{-1}\ yr^{-1}$) was the annual P input j as crop residues and OWP; h_j (dimensionless) represented the fraction of P_j incorporated to SOP over one year. The set of input data needed to run the model was: P_j and h_j (Table 2.3) from plants residues and OWP applications, initial SOP stock and k value. As P_j and initial SOP stock has been determined experimentally, and h_j assessed from literature (Table 2.3), the Eq. 2.1 is used to calculate iteratively at the annual time step the k value for each experimental plot by minimizing the residual sum of squares between simulated SOP stocks and time series of field-observed SOP stocks.

Table 2.3 Average of published values of the h incorporation coefficient (dimensionless) of crop residues to the stock of soil organic phosphorus across crops and types of organic products.

The h coefficients were set for each plant part, each crop, and each OWP according to literature on crops residues and urban composts, farmyard manure or dehydrated urban sewage sludge decomposition. When data were not available for P, data on N and C decomposition were used.

Parameter	Value	Reference(s)
Maize		
h_{ag}	0.14	Linères and Lubet 1990; Buchanan and King 1993; Mubarak et al. 2002
h_{bg}	0.17	Singh and Shekhar 1989
h_{gr}	0.40	Doolette et al. 2010; Steffens et al. 2010; Noack et al. 2012, 2014
Root-to-Shoot	0.18	Raguet et al. 2023
Wheat		
h_{ag}	0.40	Soon and Arshad 2002; Lupwayi et al. 2007; Jalali and Ranjbar 2009
h_{bg}	0.38	Martin and Cunningham 1973; Soon and Arshad 2002
h_{gr}	0.19	Doolette et al. 2010; Steffens et al. 2010; Noack et al. 2012, 2014
Root-to-Shoot	0.38	Bolinder et al. 1997; Rajala and Peltonen-Sainio 2001; Amanullah 2014; Amanullah et al. 2015
Barley		
h_{ag}	0.15	Christensen 1986; Gioacchini et al. 2016; from publication on N
h_{bg}	0.38	supposed similar to wheat

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Table 2.3 – Continued from previous page

Parameter	Value	Reference(s)
h_{gr}	0.22	Doolette et al. 2010; Steffens et al. 2010; Noack et al. 2012, 2014
Root-to-Shoot	0.49	Bolinder et al. 1997; Rajala and Peltonen-Sainio 2001; Amanullah 2014
Sugar beet		
h_{ag}	0.77	Thomsen and Christensen 1996; Thomsen and Christensen 1998; based on nitrogen residues decomposition
Dehydrated urban sewage sludge		
h_{OWP}	0.46	Levvasseur et al. 2020, based on h values of carbon incorporation determined with AMG model
Compost of green waste and urban sewage sludge		
h_{OWP}	1	Levvasseur et al. 2020, based on h values of carbon incorporation determined with AMG model
Biowaste compost		
h_{OWP}	1	Levvasseur et al. 2020, based on h values of carbon incorporation determined with AMG model
Cattle dairy farmyard manure		
h_{OWP}	0.99	Levvasseur et al. 2020, based on h values of carbon incorporation determined with AMG model
Compost of cattle dairy farmyard manure		
h_{OWP}	0.71	Levvasseur et al. 2020, based on h values of carbon incorporation determined with AMG model
Municipal solid waste compost		
h_{OWP}	0.81	Levvasseur et al. 2020, based on h values of carbon incorporation determined with AMG model

2.2.7 Statistical analysis

All statistics and modelling were carried out using the free software R version 4.1.2 (R Core Team 2021).

Data residues normality and variance homogeneity were tested beforehand by Shapiro and Bartlett tests, respectively. Effects of fertilization treatments on yield, P exported, P applied (as crop residues and OWP), and P incorporated to SOP were investigated with one-way ANOVA for a given LTFE and tested using linear mixed effect models fitted by a restrictive maximum likelihood method, with the *lme* function from the *nlme* R package

(Pinheiro et al. 2022). The fertilization treatment, years and their interaction were the fixed effect tested. Random effects were the block, to account for spatial pseudoreplication (4 repetitions). The year was also the continuous time variable we used in order to fit a first-order auto-regressive variance structure to consider non-independent measurements within plots across time. When results showed a significant effect, differences between treatments or years were investigated with a post-hoc Tukey test at a significance level of $\alpha = 0.05$.

The coefficients (intercept and slope) of linear regressions describing SOP and SIP stocks vs Bcum values were estimated using the *lm* function.

The k values were determined iteratively for each experimental plot with the *optim* function and the "L-BFGS-B" method to minimize residual sum of squares of time series of simulated vs observed SOP values. We used the standardized major axis regression (SMA), proposed by Correndo et al. (2021a), to evaluate adequacy between observed and predicted datasets, since they showed that SMA is the most appropriate approach to fit a symmetric-line describing the predicted-observed scatter. Several statistical criteria of adequacy between observations and simulations were used: the coefficient of determination (R^2) and the root mean squared error (RMSE). The relative root mean squared error (RRMSE) was used to compared simulated values dispersion to observed values coefficient of variation. In addition, SMA procedure allows decomposition of the model error into the percentage lack of precision (PLP) and the percentage lack of accuracy (PLA). Here are the equations for R^2 , RMSE, RRMSE, PLP, and PLA:

$$R^2 = \left[\frac{\sum_{i=1}^n (S_i - \bar{S})(O_i - \bar{O})}{\sigma_S \sigma_O} \right]^2 \quad (\text{Eq. 2.2})$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (S_i - \bar{S})^2}{n}} \quad (\text{Eq. 2.3})$$

$$RRMSE = 100 \times \frac{RMSE}{\bar{O}} \quad (\text{Eq. 2.4})$$

$$PLA = 100 \times \frac{\frac{1}{n} \times \sum_{i=1}^n (S_i - \hat{O}_i)^2}{\frac{1}{n} \times \sum_{i=1}^n (O_i - S_i)^2} \quad (\text{Eq. 2.5})$$

$$PLP = 100 \times \frac{\frac{1}{n} \times \sum_{i=1}^n (|S_i - \hat{S}_i|)(|O_i - \hat{O}_i|)}{\frac{1}{n} \times \sum_{i=1}^n (O_i - S_i)^2} \quad (\text{Eq. 2.6})$$

With:

S_i and O_i : simulated and observed values; \bar{S} and \bar{O} : mean of simulated and observed values;

$\sum_{i=1}^n (S_i - \hat{O}_i)^2$: the sum of systematic differences; $\sum_{i=1}^n (|S_i - \hat{S}_i|)(|O_i - \hat{O}_i|)$: the sum of unsystematic differences; \hat{S}_i and \hat{O}_i : deriving from the linear regression of simulated vs. observed values; n : number of simulated-observed pairs, $\sigma_S = \frac{1}{n} \times \sum_{i=1}^n (S_i - \bar{S})^2$ and $\sigma_O = \frac{1}{n} \times \sum_{i=1}^n (O_i - \bar{O})^2$ standard deviations of the simulated and observed values. These error metrics were calculated using R-code tutorial proposed by Correndo et al. (2021b).

In supplementary information, we used Pearson pairwise correlations and principal component analysis (PCA) to analyze relations of some soil and LTFE characteristics with k coefficient, initial SOP stock, and SOP mineralization rate. We selected SOC, organic matter C/N, CaCO₃, clay, silt (clay+silt), mean annual T°C, and mean annual water inputs (rainfall + irrigation), which were identified as relevant in soil organic matter and/or N mineralization (Clivot et al. 2017). The SIP stock were also included as relevant LTFE characteristic.

2.3 Results

2.3.1 The OWP main composition

On average, OWP applied at LTFE2 contained 280 ± 10 g C kg⁻¹, 20 ± 1 g N kg⁻¹ and 6.7 ± 0.6 g P kg⁻¹. In LTFE3, OWP were in the same range of concentration with 332 ± 11 g C kg⁻¹, 32 ± 3 g N kg⁻¹, and 12.3 ± 1.6 g P kg⁻¹. In both LTFE, C, N and P concentrations were significantly different among OWP (Table 2.2).

The C/P ratios of the OWP applied at LTFE2 were 1060 (MSW₂₄), 117 (FYM₄₀), 706 (BIOW₄₆), and 135 (GSW₁₁₂). At LTFE3, the N/P ratios were 65 (BIOW₁₇), 11 (FYM₂₁), 10 (FYMC₂₁), 12 (SLU₃₆) and 12 (GWS₄₅). Due to highly different C/N/P ratio and due to fertilization reasoning based on C or N, P inputs were highly variable among OWP. Cumulated over 17 years of trial (LTFE2) with ten OWP applications, 420, 699, 819 and 2008 kg P ha⁻¹ were added to soil for MSW₂₄, FYM₄₀, BIOW₄₆, and GSW₁₁₂ (Figure 2.2). Cumulative organic P inputs (% of TP_{HF}) were respectively 37 (9%), 241 (34%), 64 (8%), and 325 (16%) kg P ha⁻¹ (Figure 2.2). In LTFE3, cumulative TP_{HF} inputs were 250, 317, 317, 545 and 667 kg P ha⁻¹ for BIOW₁₇, FYM₂₁, FYMC₂₁, SLU₃₆ and GWS₄₅, respectively, including were 18 (7%), 114 (36%), 114 (36%), 93 (17%), and 107 (16%) kg P ha⁻¹ of organic P (Figure 2.2).

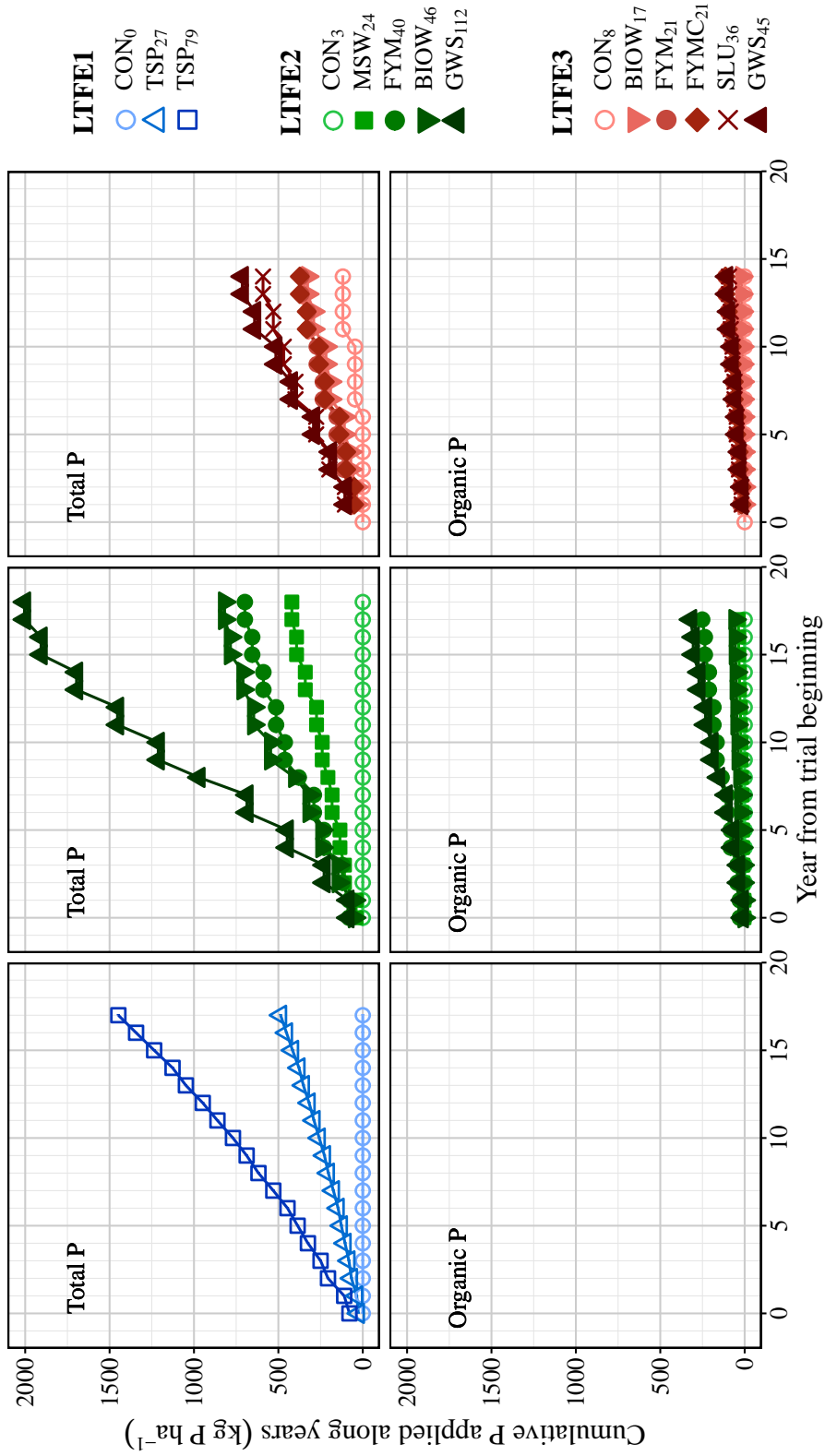


Figure 2.2 Cumulated P applied as OWP and triple superphosphate (TSP) for all years and treatments in the three LTFE. Organic P input through OWP is also specified. Values are means ($n = 4$). CON: no P input; MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; SLU: dehydrated urban sewage sludge; GWS: compost of green waste and SLU; BIOW: bio-waste compost, TSP: triple superphosphate. Subscript values in treatments abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{ yr}^{-1}$.

2.3.2 Crop yields, harvest P concentration and exported P

Annual means of the P concentration in harvested biomass were depicted over all years and treatments for the studied experiments in Figure 2.3. The average yield over all sites were $8.5 \pm 0.2 \text{ t ha}^{-1}$ with small but significant differences between experiments (Table 2.4). In LTFE1, maize grain yield ranged from a minimum of $4.8 \pm 0.1 \text{ t P ha}^{-1}$ in 1977 to a maximum of $11.4 \pm 0.3 \text{ t P ha}^{-1}$ in 1989 (Figure 2.3). Under OWP fertilization, yields in LTFE2 did not show significant differences, despite the discrepancies in P inputs along the different organic products ($P = 0.65$). Without adding P fertilization (except a low rate in 2014), yields ($7.5 \pm 0.4 \text{ t ha}^{-1} \text{ yr}^{-1}$) have decreased significantly than those in the other treatments ($8.4 \pm 0.1 \text{ t ha}^{-1} \text{ yr}^{-1}$). In LTFE3, crop yields were $8.8 \pm 0.4 \text{ t ha}^{-1} \text{ yr}^{-1}$. Despite the difference in P input through OWP and control, no difference was observed on yields among treatment.

The overall mean for all experiments, years and treatments of the P concentration in harvested biomass was $3.1 \pm 0.1 \text{ g P kg}^{-1}$. There were no significant differences among sites (Table 2.4). For the LTFE1 experiment, maize grains P concentration was significantly affected by P rate, with a maximum for TSP₇₉ in 1984 (4.0 g P kg^{-1}) and a minimum for CON₀ in 1992 (2.6 g P kg^{-1}). The control treatment started to differentiate from the two TSP in 1988 and remain significantly lower after that date ($P = 0.003$; Figure 2.3). In both LTFE2 and LTFE3, no discrepancies were observed among treatments (Table 2.4).

On average over sites, treatments and years, exported P in harvest represent $26 \pm 1 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. The exported P in harvest were significantly higher in LTFE1 and LTFE2 than in LTFE3 ($P = 0.008$), with on average $26.5 \pm 0.5 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. In LTFE1, all treatments presented a positive increase in exported P, but this increase was lower for CON₀, which start to differentiate from the two other treatments in 1984 (Figure 2.2). In LTFE2, the exported P in CON₃ were slightly lower than the four other treatments. Conversely, no difference among treatments were observed in LTFE3 (Table 2.4).

Table 2.4 Annual yield ($\text{t ha}^{-1} \text{ yr}^{-1}$), P concentration (g P kg^{-1}) and annual exported P in harvests (include grains or beetroot, and exported residues) ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) for all treatments of the three LTFE. Values are mean \pm std. err. of years of experiments (LTFE1: $n = 18$; LTFE2: $n = 17$; LTFE3: $n = 14$). Different upper case letters (A, B, C) indicate significant differences between LTFE. Different lower case letters (a, b, c) indicate significant differences among treatments within LTFE ($\alpha = 0.05$). CON: no P input; MWS: municipal solid waste compost; FYM: cattle dairy farmyard manure; FYMC: FYM compost; GWS: compost of green waste and SLU; SLU: dehydrated urban sewage sludge; BIOW: bio-waste compost, TSP: triple superphosphate. Subscript values in treatment abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{ yr}^{-1}$.

Treatment	Yield ($\text{t ha}^{-1} \text{ yr}^{-1}$)	P content in harvest (g P kg^{-1})	Exported P in harvest ($\text{kg P ha}^{-1} \text{ yr}^{-1}$)
LTFE1			
CON ₀	8.2 \pm 0.4	3.0 \pm 0.1 b	24.1 \pm 0.9
TSP ₂₇	8.5 \pm 0.5	3.2 \pm 0.1 ab	27.1 \pm 1.4
TSP ₇₉	8.5 \pm 0.5	3.3 \pm 0.1 a	28.3 \pm 1.6
Treatment effect ANOVA	<i>0.85</i>	<i>0.02</i>	<i>0.11</i>
Mean over Treatments	8.4 \pm 0.3 AB	3.2 \pm 0.1	26.5 \pm 0.6 A
LTFE2			
CON ₃	7.5 \pm 0.4 b	3.0 \pm 0.1	23.0 \pm 1.2 b
MSW ₂₄	8.3 \pm 0.3 a	3.0 \pm 0.1	26.2 \pm 1.2 a
FYM ₄₀	8.5 \pm 0.3 a	3.2 \pm 0.1	28.5 \pm 1.4 a
BIOW ₄₆	8.3 \pm 0.2 a	3.1 \pm 0.1	27.2 \pm 1.1 a
GWS ₁₁₂	8.4 \pm 0.2 a	3.1 \pm 0.2	28.0 \pm 1.7 a
Treatment effect ANOVA	<i>0.002</i>	<i>0.43</i>	<i><0.0001</i>
Mean over Treatments	8.2 \pm 0.3 B	3.1 \pm 0.1	26.6 \pm 0.8 A
LTFE3			
CON ₀	8.6 \pm 0.9	3.0 \pm 0.3	24.4 \pm 1.8
BIOW ₁₇	8.8 \pm 1.0	3.0 \pm 0.3	24.7 \pm 1.4
FYM ₂₁	8.9 \pm 1.1	3.1 \pm 0.3	25.8 \pm 1.5
FYMC ₂₁	8.9 \pm 1.0	3.1 \pm 0.3	25.9 \pm 1.7
SLU ₃₆	9.0 \pm 1.1	3.1 \pm 0.3	25.4 \pm 1.2
GWS ₄₅	8.9 \pm 1.1	3.1 \pm 0.3	25.4 \pm 1.5
Treatment effect ANOVA	<i>0.99</i>	<i>0.99</i>	<i>0.70</i>
Mean over Treatments	8.8 \pm 0.4 A	3.1 \pm 0.1	25.3 \pm 0.6 B
LTFE effect ANOVA	<i>0.006</i>	<i>0.082</i>	<i>0.008</i>

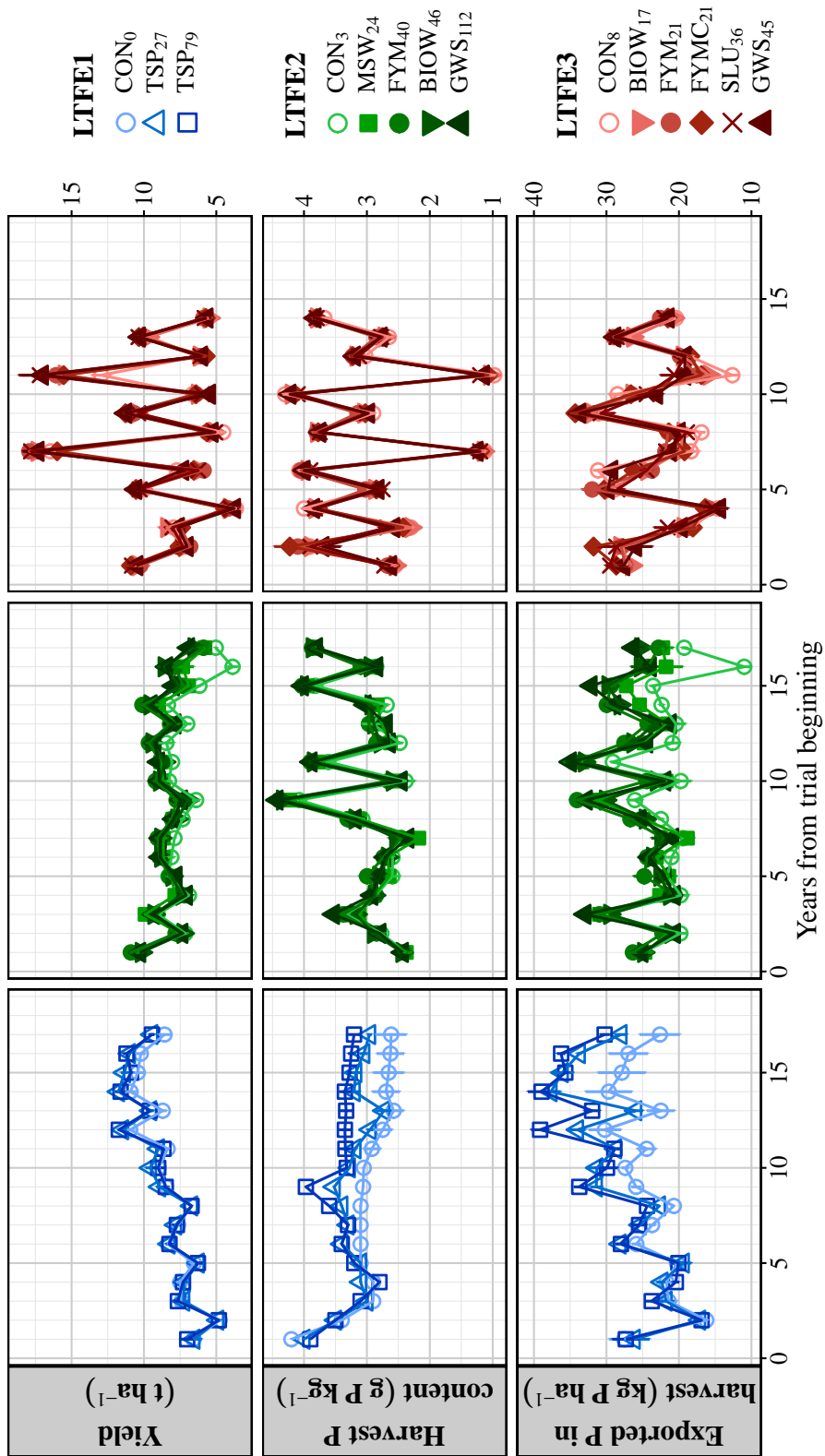


Figure 2.3 Annual yield, its P concentration and annual P exported as affected by fertilization treatments and years for the three studied LTFE. Values are means \pm std. err. ($n = 4$). CON: no P applied; MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; SLU: dehydrated urban sewage sludge; GWS: compost of green waste and SLU; BIOW: bio-waste compost; TSP: triple superphosphate. Subscript values in treatment abbreviations are the average annual rate of P application, in kg P ha⁻¹ yr⁻¹.

2.3.3 Rates of incorporation to SOP and release of phosphate ions in solution from OWP and crop residues

Crop residues and OWP P inputs across LTFE, treatments and years are in Figure 2.4. Averages overall years of experiment and significant differences across treatments are presented in Tables 5, 6, 7 for the LTFE1, LTFE2 and LTFE3, respectively. On average for all sites, years and treatments, 39 ± 2 kg P ha⁻¹ was applied to soil through crop residues and OWP, with significant differences between sites ($P < 0.0001$), i.e. 15 ± 1 (LTFE1), 57 ± 7 (LTFE2), and 35 ± 4 (LTFE3) kg P ha⁻¹ yr⁻¹. In all sites, the sum of all P inputs (i.e. aboveground, belowground and grain residues and total P in OWP) were significantly different among treatments (LTFE1 $P = 0.02$ (Table 2.5); LTFE2 $P < 0.00001$ (Table 2.6); LTFE3 $P < 0.0001$ (Table 2.7)).

Table 2.5 Amount of P in crop residues (kg P ha⁻¹ yr⁻¹) and its partition between P incorporated to SOP and phosphate ions released in soil solution during the post-harvest (<1 yr) decomposition at the LTFE1. Values are means \pm std. err. ($n = 18$). Different lower case letters (a, b, c) indicate significant differences among treatments ($\alpha = 0.05$). CON: no P input; TSP: triple superphosphate. Subscript values in treatment abbreviations are the average annual rate of P application, in kg P ha⁻¹ yr⁻¹.

P fluxes (kg P ha ⁻¹ yr ⁻¹)	CON ₀	TSP ₂₇	TSP ₇₉	P-Value
Phosphate ions released to soil solution by residues decomposition				
aboveground residues	5.3 \pm 0.2 b	6.6 \pm 0.3 ab	8.3 \pm 0.6 a	0.01
belowground residues	4.6 \pm 0.2 b	5.3 \pm 0.3 ab	5.8 \pm 0.4 a	0.04
harvest losses	0.4 \pm 0.1	0.5 \pm 0.1	0.5 \pm 0.1	0.11
Sum	10.4 \pm 0.4 b	12.4 \pm 0.7 ab	14.6 \pm 1.0 a	0.02
P incorporated to SOP				
aboveground residues	0.9 \pm 0.1 b	1.1 \pm 0.1 ab	1.4 \pm 0.1 a	0.01
belowground residues	0.9 \pm 0.1 b	1.1 \pm 0.1 ab	1.2 \pm 0.1 a	0.04
harvest losses	0.29 \pm 0.01	0.33 \pm 0.02	0.34 \pm 0.02	0.11
Sum	2.1 \pm 0.1 b	2.5 \pm 0.1 ab	2.9 \pm 0.2 a	0.02
Sum of the two above P fluxes				
aboveground residues	6.2 \pm 0.2 b	7.6 \pm 0.4 ab	9.7 \pm 0.7 a	0.01
belowground residues	5.6 \pm 0.2 b	6.4 \pm 0.3 ab	7.0 \pm 0.4 a	0.04
harvest losses	0.7 \pm 0.1	0.8 \pm 0.1	0.8 \pm 0.1	0.11
Sum	12.5 \pm 0.4 b	14.9 \pm 0.8 ab	17.5 \pm 1.2 a	0.02

In LTFE1, aboveground residues represented the most important P flux from maize returned to soil. P in belowground and aboveground residues were affected by contrasting P addition, while grains residues was homogeneous among P fertilization rates (Table 2.5). Therefore, cumulative P return within TSP₇₉ crop residues was higher than in TSP₂₇ and CON₀ (315 ± 2 , 267 ± 5 , 224 ± 9 kg P ha⁻¹, respectively).

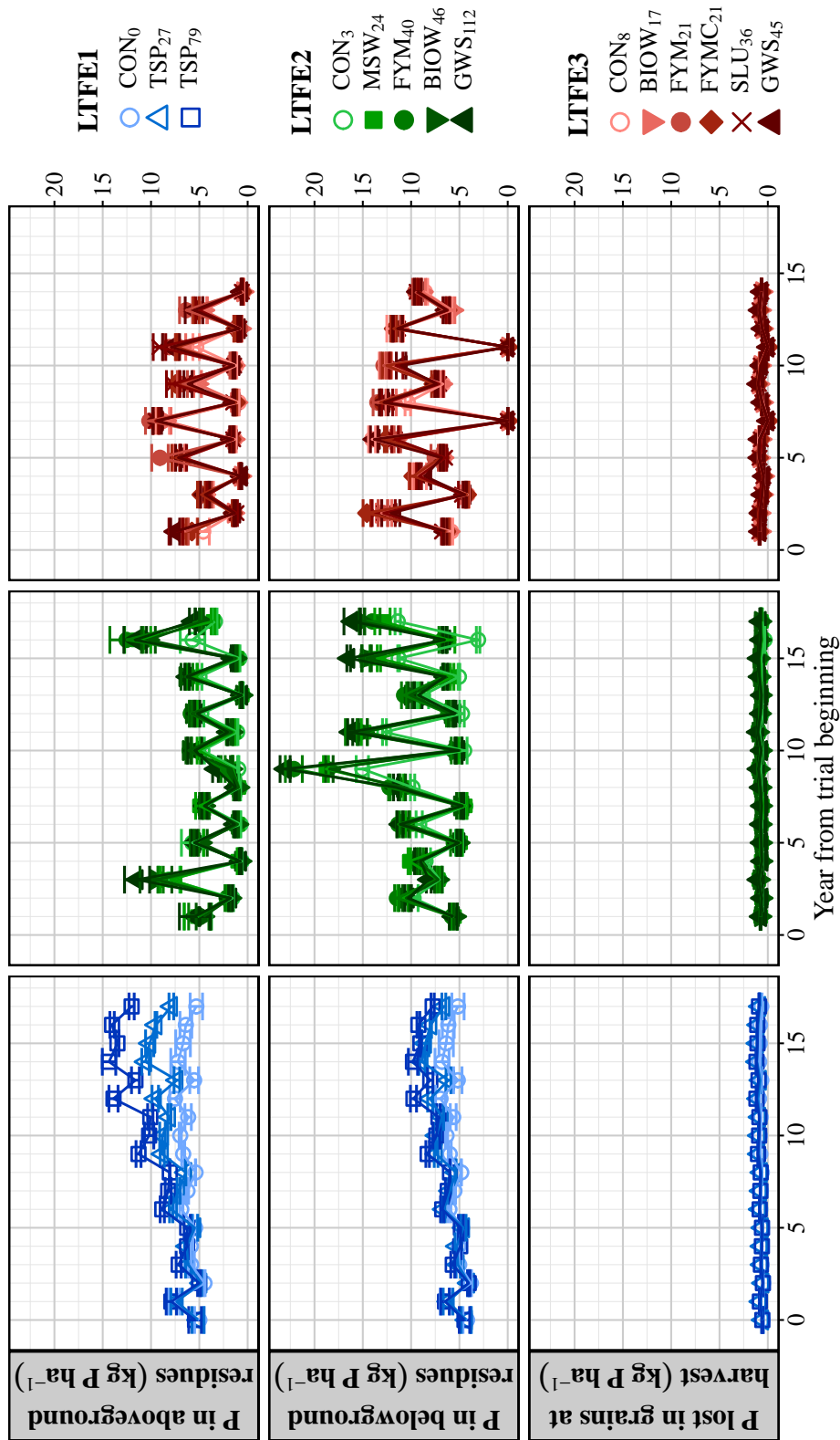


Figure 2.4 Annual amount of P in aboveground, belowground and grains residues in relation to years of experiment, as affected by P fertilization treatments for the three studied LTFE. Values are means \pm std. err. ($n = 4$). CON: no P applied; MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; GWS: green waste and SLU compost; SLU: dehydrated urban sewage sludge; BIOW: biowaste compost, TSP: triple superphosphate. Subscript values in treatments abbreviations are the average annual rate of P application, in kg P ha⁻¹ yr⁻¹.

Table 2.6 Amount of P applied as OWP and crop residues ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) and its partition between P incorporated to SOP and phosphate ions released in soil solution during the post-harvest (<1 yr) decomposition at LTFE2. Values are means \pm std. err. ($n = 17$). Different lower case letters (a, b, c) indicate significant differences among treatments ($\alpha = 0.05$). CON: no P input; MSW: municipal solid waste compost; FYM: farmyard manure; GWS: compost of green waste and urban sewage sludge; BIOW: bio-waste compost. Subscript values in treatment abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{ yr}^{-1}$.

P fluxes ($\text{kg P ha}^{-1} \text{ yr}^{-1}$)	CON₃	MSW₂₄	FYM₄₀	BIOW₄₆	GWS₁₁₂	P-value
Phosphate ions released to soil solution by residues decomposition						
aboveground residues	2.5 \pm 0.5	2.9 \pm 0.6	3.3 \pm 0.7	3.1 \pm 0.7	3.4 \pm 0.7	0.38
belowground residues	5.1 \pm 5.1	5.9 \pm 0.6	6.4 \pm 0.7	6.1 \pm 0.6	6.4 \pm 0.7	0.07
harvest losses	0.4 \pm 0.1	0.5 \pm 0.1	0.5 \pm 0.1	0.5 \pm 0.1	0.5 \pm 0.1	0.06
OWP		22 \pm 5 b	25 \pm 6 b	42 \pm 10 b	94 \pm 22 a	<0.0001
Sum	8 \pm 1 c	31 \pm 5 bc	35 \pm 6 b	52 \pm 10 b	104 \pm 22 a	<0.0001
P incorporated to SOP						
aboveground residues	0.51 \pm 0.07 b	0.61 \pm 0.08 ab	0.71 \pm 0.09 ab	0.64 \pm 0.09 ab	0.72 \pm 0.0.9 a	0.04
belowground residues	2.4 \pm 0.4	2.8 \pm 0.5	3.0 \pm 0.6	2.9 \pm 0.5	3.0 \pm 0.6	0.45
harvest losses	0.18 \pm 0.02	0.20 \pm 0.02	0.22 \pm 0.02	0.21 \pm 0.02	0.21 \pm 0.02	0.17
OWP		1.7 \pm 0.4 b	13.8 \pm 3.3 a	3.2 \pm 0.8 b	17.8 \pm 4.3 a	<0.0001
Sum	3.1 \pm 0.4 b	5.3 \pm 0.8 b	17.8 \pm 3.6 a	6.9 \pm 1.2 b	21.8 \pm 4.7 a	<0.0001
Sum of the two above P fluxes						
aboveground residues	3.0 \pm 0.6	3.5 \pm 0.7	4.0 \pm 0.8	3.7 \pm 0.7	4.1 \pm 0.8	0.30
belowground residues	7.5 \pm 0.9	8.7 \pm 1.1	9.5 \pm 1.2	9.0 \pm 1.1	9.5 \pm 1.3	0.16
harvest losses	0.62 \pm 0.05 b	0.70 \pm 0.05 ab	0.75 \pm 0.05 a	0.72 \pm 0.05 ab	0.73 \pm 0.05 ab	0.02
OWP		23 \pm 6 b	39 \pm 9 b	45 \pm 11 b	111 \pm 27 a	<0.0001
Sum	11 \pm 1 c	36 \pm 6 bc	53 \pm 9 b	59 \pm 11 b	126 \pm 27 a	<0.0001

Table 2.7 Amount of P applied as crop residues ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) and its partition between P incorporated to SOP and phosphate ions released in soil solution during the post-harvest (<1 yr) decomposition at the LTFE3. Values are means \pm std. err. ($n = 14$). Different lower case letters (a, b, c) indicate significant differences among treatments ($\alpha = 0.05$). CON: no P input; FYM: farmyard manure; FYMC: FYM compost; GWS: compost of green waste and SLU, SLU: dehydrated urban sewage sludge, BIOW: bio-waste compost. Subscript values in treatment abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{ yr}^{-1}$.

P fluxes ($\text{kg P ha}^{-1} \text{ yr}^{-1}$)	CON₈	BIOW₁₇	FYM₂₁	FYMC₂₁	SLU₃₆	GWS₄₅	P-value
Phosphate ions released to soil solution by residues decomposition							
aboveground residues	2.0 \pm 0.5	2.2 \pm 0.5	2.5 \pm 0.6	2.4 \pm 0.6	2.4 \pm 0.6	2.4 \pm 0.6	0.79
belowground residues	4.9 \pm 0.7	4.9 \pm 0.7	5.1 \pm 0.8	5.2 \pm 0.8	5.0 \pm 0.7	5.0 \pm 0.7	0.99
harvest losses	0.4 \pm 0.1	0.4 \pm 0.1	0.4 \pm 0.1	0.4 \pm 0.1	0.4 \pm 0.1	0.4 \pm 0.1	0.99
OWP		16 \pm 5 b	14 \pm 4 b	16 \pm 5 b	34 \pm 10 a	37 \pm 11 a	<0.0001
Sum	7 \pm 1 c	23 \pm 5 b	22 \pm 4 bc	24 \pm 5 b	41 \pm 10 a	45 \pm 11 a	<0.0001
P incorporated to SOP							
aboveground residues	1.1 \pm 0.5	1.2 \pm 0.5	1.4 \pm 0.6	1.3 \pm 0.6	1.4 \pm 0.6	1.3 \pm 0.6	0.96
belowground residues	2.3 \pm 0.5	2.3 \pm 0.5	2.4 \pm 0.5	2.5 \pm 0.5	2.3 \pm 0.5	2.4 \pm 0.5	0.99
harvest losses	0.17 \pm 0.03	0.17 \pm 0.03	0.18 \pm 0.03	0.18 \pm 0.03	0.17 \pm 0.03	0.17 \pm 0.03	0.99
OWP		1.2 \pm 0.3 c	7.6 \pm 2.3 a	5.4 \pm 1.6 ab	2.8 \pm 0.8 bc	7.1 \pm 2.1 a	<0.0001
Sum	3.6 \pm 0.5 c	4.9 \pm 0.5 c	11.6 \pm 2.3 a	9.4 \pm 1.6 ab	6.8 \pm 0.9 bc	11.0 \pm 2.1 a	<0.0001
Sum of the two above P fluxes							
aboveground residues	3.1 \pm 0.7	3.4 \pm 0.7	4.0 \pm 0.9	3.7 \pm 0.8	3.8 \pm 0.9	3.7 \pm 0.8	0.70
belowground residues	7.2 \pm 1.2	7.2 \pm 1.2	7.6 \pm 1.2	7.7 \pm 1.3	7.3 \pm 1.2	7.4 \pm 1.2	0.99
harvest losses	0.6 \pm 0.1	0.6 \pm 0.1	0.6 \pm 0.1	0.6 \pm 0.1	0.6 \pm 0.1	0.6 \pm 0.1	0.99
OWP		17 \pm 5 c	21 \pm 7 bc	21 \pm 6 bc	36 \pm 11 ab	45 \pm 13 a	0.003
Sum	11 \pm 1 d	28 \pm 5 cd	33 \pm 7 bc	33 \pm 6 bc	48 \pm 11 ab	56 \pm 13 a	<0.0001

In both LTFE2 and LTFE3, the most important P input was P applied as OWP (Table 2.62.7). Within crop residues, belowground residues represented the main P input flux. In LTFE2 grains residues, FYM₄₀ were slightly higher than CON₃, otherwise, no discrepancies were observed among treatments regardless of site or residue type. Therefore, cumulative crop residues P input in LTFE2 were 201 ±6 (CON₃), 232 ±6 (MSW₂₄), 256 ±3 (FYM₄₀), 241 ±6 (BIOW₄₆), and 257 ±5 (GWS₁₁₂). In LTFE3, cumulative crop residues P input were 164 ±3 (CON₈), 168 ±1 (BIOW₁₇), 182 ±4 (FYM₂₁), 180 ±1 (FYMC₂₁), 176 ±2 (SLU₃₆), and 175 ±1 (GWS₄₅). Cumulative P inputs in OWP were presented in section 2.3.1.

On average, decomposition of crop residues and OWP over one year released 12.5 ±0.5, 46 ±6, and 27 ±3 kg P ha⁻¹ yr⁻¹ as phosphate ions in solution for LTFE1, LTFE2, and LTFE3, respectively, i.e., 83% (LTFE1), 80% (LTFE2) and 71% (LTFE3) of P applied as OWP and crop residues. Rates of P incorporated to SOP stock were 2.5 ±0.1, 11.0 ±1.4, and 7.9 ±0.7 kg P ha⁻¹ yr⁻¹ for LTFE1, LTFE2 and LTFE3, respectively (Tables 2.5, 2.6, 2.7).

2.3.4 Multiannual evolution of SOP and SIP stocks vs cumulative P budget

On average over treatments and years, TP_{HF} stocks were 1500 ±74, 2577 ±89, 4307 ±27 kg P ha⁻¹ in LTFE1, LTFE2 and LTFE3, respectively, whose 451 ±7, 635 ±14, 1209 ±16 kg P ha⁻¹ were SOP stocks and the remainder were SIP stocks (1048 ±73, 1941 ±85, 3104 ±30 kg P ha⁻¹).

The section 2.3.1 highlighted the discrepancies on cumulative P applied among OWP in LTFE2 and LTFE3. In LTFE1, cumulative 487 and 1448 kg P ha⁻¹ were applied in TSP₂₇ and TSP₇₉, respectively. Therefore, SIP stock dynamics were significantly affected by treatments in all sites (Figure 2.5; Table SI-2.5): SIP stock decrease without applying P, while it increased significantly in LTFE1 and LTFE2 for treatments with the highest P inputs.

The Figure SI-2.1 represent observed SOP stocks dynamics with years and its linear regression according to years for all sites. The initial SOP stocks varied significantly between sites ($P < 0.0001$, Table 2.8). In LTFE1, the SOP stocks remain stable over 17 years of cropping (Figure SI-2.2) since there is not significantly differences among treatments and years (ANOVA: treatment $P = 0.64$; year $P = 0.97$). The SOP stocks in LTFE2 increased significantly (Figure SI-2.2) regardless of OWP treatments ($P = 0.30$). As for LTFE2, LTFE3 presented a significant positive increase on SOP stocks (Figure SI-2.2). No treatments difference was observed either ($P = 0.13$).

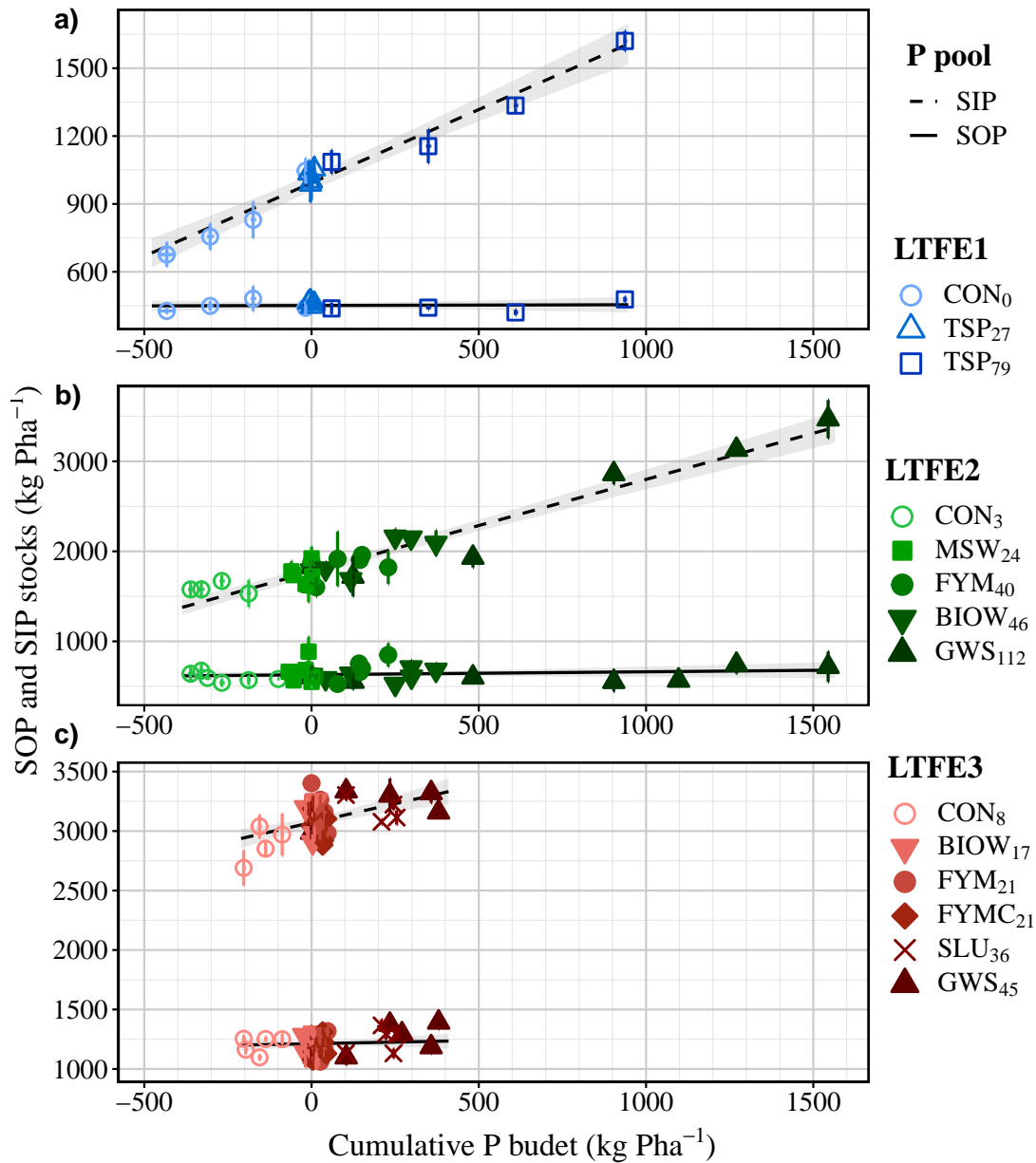


Figure 2.5 Evolution of soil inorganic P (SIP, dotted line) and soil organic P (SOP, solid line) stocks in the ploughed layer as affected by plot cumulative P budget (Bcum). Values are means \pm std. err. ($n = 4$). Lines are linear regressions and grey areas are confidence interval (95%) of the linear regressions. CON: no P input; MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; SLU: dehydrated urban sewage sludge; GWS: compost of green waste and SLU; BIOW: biowaste compost; TSP: triple superphosphate. Subscript values in treatments abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{yr}^{-1}$.

LTFE	P stocks	Regressions equations	P-value	R ²	n
LTFE1	SIP	$0.65 \pm 0.05 \times Bcum + 993 \pm 18$	<0.0001	0.80	12
	SOP	$0.003 \pm 0.018 \times Bcum + 451 \pm 7$	0.85	0.001	
LTFE2	SIP	$1.0 \pm 0.1 \times Bcum + 1774 \pm 27$	<0.0001	0.72	35
	SOP	$0.032 \pm 0.031 \times Bcum + 629 \pm 14$	0.29	0.01	
LTFE3	SIP	$0.62 \pm 0.14 \times Bcum + 3072 \pm 20$	<0.0001	0.14	36
	SOP	$0.05 \pm 0.08 \times Bcum + 1213 \pm 12$	0.51	0.003	

Table 2.8 Main features of the mineralization of soil organic P (SOP) stocks ($\text{kg P ha}^{-1} \text{ yr}^{-1}$) in the plough layer of the three studied LTFE. Parameters (\pm std. dev.) of initial stock; coefficient of SOP mineralization: k (yr^{-1}); $1/k$: residence time (yr); annual rates of SOP mineralization and incorporation ($\text{kg P ha}^{-1} \text{ yr}^{-1}$). Values are means \pm std. err. Different lower case letters (a, b, c) indicate significant ($\alpha = 0.05$) differences between treatments within a given LTFE. Different upper case letters (A, B, C) indicate significant ($\alpha = 0.05$) differences between LTFE. CON: no P input; MWS: municipal solid waste compost; FYM: cattle dairy farmyard manure; FYMC: FYM compost; GWS: compost of green waste and SLU; SLU: dehydrated urban sewage sludge; BIOW: biowaste compost, TSP: triple superphosphate. Subscript values in treatment abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{ yr}^{-1}$.

Treatment	Initial SOP stock kg P ha^{-1}	Coefficient k yr^{-1}	$1/k$ yr	Mineralization rate $\text{kg P ha}^{-1} \text{ yr}^{-1}$	Incorporation rate (OWP and residues) $\text{kg P ha}^{-1} \text{ yr}^{-1}$	Decomposition rate (OWP and residues) $\text{kg P ha}^{-1} \text{ yr}^{-1}$
LTFE1						
CON ₀						
TSP ₂₇	446 \pm 13 B	0.0046 \pm 0.0011 B	217	2.1 \pm 0.1 C	2.1 \pm 0.1 b	10.4 \pm 0.4 b
TSP ₇₉	0.59	0.81		0.81	2.5 \pm 0.2 a	12.4 \pm 0.7 ab
Treatment effect P-value					0.02	0.02
Mean over Treatments					2.5 \pm 0.1 C	12.5 \pm 0.5 C
LTFE2						
CON ₃		0.011 \pm 0.006 ab	91		3.1 \pm 0.4 b	8 \pm 1 c
MSW ₂₄		0.001 \pm 0 b	1000		5.3 \pm 0.8 b	31 \pm 5 bc
FYM ₄₀	595 \pm 28 B	0.030 \pm 0.003 a	33	11.2 \pm 0.5 A	17.8 \pm 3.6 a	35 \pm 6 b
BIOW ₄₆		0.015 \pm 0.008 ab	67		6.9 \pm 1.2 b	52 \pm 10 b
GWS ₁₁₂		0.031 \pm 0.011 a	32		21.8 \pm 4.7 a	104 \pm 22 a
Treatment effect P-value	0.93	0.03		0.10	<0.0001	<0.0001
Mean over Treatments		0.018 \pm 0.004 A	56		11.0 \pm 1 A	46 \pm 6 A
LTFE3						
CON ₈					3.6 \pm 0.5 c	7 \pm 1 c
BIOW ₁₇					4.9 \pm 0.5 c	23 \pm 5 b
FYM ₂₁	1145 \pm 22 A	0.0044 \pm 0.0009 B	227	5.4 \pm 0.3 B	11.6 \pm 2.3 a	22 \pm 4 bc
FYMC ₂₁					9.4 \pm 1.6 ab	24 \pm 5 b
SLU ₃₆					6.8 \pm 0.9 bc	41 \pm 10 a
GWS ₄₅					11.0 \pm 2.1 a	45 \pm 11 a
Treatment effect P-value	0.22	0.48		0.52	<0.0001	<0.0001
Mean over Treatments	<0.0001	0.0009		<0.0001	7.9 \pm 0.7 B	27 \pm 3 B
LTFE effect P-value					<0.0001	<0.0001

The average SOP mineralization k coefficient, was $0.005 \pm 0.001 \text{ yr}^{-1}$, $0.018 \pm 0.004 \text{ yr}^{-1}$ and $0.004 \pm 0.001 \text{ yr}^{-1}$ for LTFE1, LTFE2 and LTFE3, respectively. The corresponding SOP residence time $1/k$ were 217, 56 and 227 yr, on average. The k value in LTFE2 was significantly higher than the two other sites ($P < 0.0001$) with residence time below 100 years. LTFE2 was also the only site where fertilization treatment has affected the k optimization, with MSW_{24} at the lower limit set for optimization, significantly lower than FYM_{40} and GWS_{112} (Table 2.8). Thus, SOP residence time in GWS_{112} treatment was much shorter than in other treatments (about 30 years). However, k differences in LTFE2 was not reflected in the gross annual rate of SOP mineralization, none of the sites has treatment effect on this variable. On average, rates of SOP mineralization were 2.1 ± 0.1 , 11.2 ± 0.5 and $5.4 \pm 0.3 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, for LTFE1, LTFE2, LTFE3 respectively with significant differences between sites (Table 2.8).

2.4 Discussion

2.4.1 Crop yields response to fertilizations across several decades

The observed yields in all sites were in the same range as the yields recorded in annual report on France agronomy (Agreste 2022). Comparable yields were also reported in normalized reference on maize (Denoroy et al. 2004) and in previous studies (Eghball et al. 2004; Herencia et al. 2007; Dodd and Sharpley 2015). In both LTFE2 and LTFE3, no effect was found on annual yields after applying OWP. However, in LTFE2, yield decrease in control compare to other treatments were significant and represented -10.7% losses on average of yield under OWP. This loss was consistent with previous studies, where yield decline only after several decades without no P applied (Gallet et al. 2003; Dodd and Mallarino 2005).

Our results on P concentration in crop harvests were consistent with literature in different experiments but similar situations (Tang et al. 2008; Cadot et al. 2018). In both LTFE2 and LTFE3, no significant differences were observed in grain P concentrations across OWP, regardless of the different crops. Contrariwise, in LTFE1, maize grain P concentration were significantly affected by the absence of TSP fertilization, as reported in another long-term field experiment (Raguet et al. 2023). Without P application, maize grains contained less P than in optimal and excessive fertilization.

2.4.2 Multiannual dynamics of SOP

The multiannual dynamics of SOP were analyzed on time series data from the three sites, over 18 years for LTFE1, 17 years in LTFE2, and 14 years for LTFE3.

In LTFE1, SOP remain stable over almost two decades. Additionally, P return in maize residues (on average: $14.9 \text{ kg P ha}^{-1} \text{ yr}^{-1}$) was in the same magnitude as SOP standard deviation ($13 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, with SOP coefficient of variation of 10%). Raguét et al. (2023) had also reported no significant SOP variation over 28 years of cropping in close long-term field experiment. However, while a small tendency to increase have emerged in Raguét et al. (2023), any trend could be highlighted in the present study, probably because of not long enough experimentation (28 years against 18).

Despite the variable SOP data (coefficient of variation: 24% in LTFE2; 11% in LTFE3), both LTFE2 and LTFE3 presented significant SOP stock increased according to years of cropping. Such dynamic can be due to a higher P incorporation to SOP through crop residues and OWP than SOP gross mineralization. However, the control treatments, without P applied, were not different from fertilized treatments and SOP also increase significantly over almost two decades.

Additionally, it is hard to compare our SOP dynamic results overs years as only few studies have calculated SOP dynamics in field conditions over several years or decades by monitoring SOP stocks across time. However, results were highly variable among those studies. Song et al. (2011) reported no significant change of SOP stock after 14 cropping (maize–soybean–wheat rotation) under three P fertilization rates. In the same way, Chater and Mattingly (1980) reported small or no stock decrease over 10-45 years of cropping (Rothamsted and Saxmundham experiments). On the other hand, Zhang and MacKenzie (1997) highlight significant SOP decreases from -16 up to $-29 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ over five years of continuous maize cropping on a Canadian clayed soil (71% of clay).

2.4.3 Calculation of annual rate of SOP mineralization at the studied sites

During postharvest decomposition ($<1 \text{ yr}$), the P contained in crop were split according to the h parameter (Table 2.3) between P incorporated to SOP and P released in soil solution as phosphate ions, or easily degradable organic compounds which can supply the plant-available P pool in soils (He et al. 2009; Noack et al. 2014). Thus, 17%, 37%, 35% and 77% of maize, wheat, barley and sugar beet residues P were incorporated to SOP. Considering a maximum of 20% of released P was recovered by the next crop (Johnston et al. 2014), the remaining crop residues P could represent a maximum of 6% (2.5 kg

P ha⁻¹ yr⁻¹), 5% (1.9 kg P ha⁻¹ yr⁻¹), and 4% (1.5 kg P ha⁻¹ yr⁻¹) of absorbed P (sum of exported P and P return in residues) in LTFE1, LTFE2 and LTFE3, respectively.

In our study, the P in OWP were 93%, 91%, 84%, 83% and 64% inorganic for BIO, MSW, GWS, SLU, and the two FYM and FYMC, respectively. These results were in accordance with previous studies: the majority of P in applied products is inorganic and can directly contribute to plant-available P supply (Cabeza et al. 2011; Glæsner et al. 2019). For certain OWP, some studies have reported a similar fertilization capacity as industrial inorganic fertilizers, especially for dehydrated sewage sludge (Morel et al. 2002). With the same assumptions as for crop residues, the crop absorbed P from OWP decomposition were 7.3 kg P ha⁻¹ yr⁻¹ (17%) in LTFE2 and 3.9 kg P ha⁻¹ yr⁻¹ (12%) in LTFE3.

As there are few studies on crop residues or OWP P decomposition, some h values were set according to N or C results based on literature (Table 2.3). Using those parameters suppose a homogeneous and coupling dynamic between C and N and P, which is altered by intensive management (Recous et al. 2019).

By running the model and fitting simulated to observed SOP values, the annual rates of mineralization were 2.1 (LTFE1), 11.2 (LTFE2), and 5.4 (LTFE3) kg P ha⁻¹ yr⁻¹. SOP mineralization rate in LTFE1 were comparable to the results on another long-term field experiment, which obtained 1.7 kg P ha⁻¹ yr⁻¹ (Raguét et al. 2023). In addition, for all LTFE and treatments, phosphate ions release through OWP and crop residues decomposition was higher than phosphate ions release through SOP mineralization by 6 times for LTFE1, 4 time for LTFE2, and 5 times for LTFE3. Considering again a maximum of 20% of released P recovered by the next crop, SOP could contribute to the absorbed P up to 0.4 (1%), 3.4 (6%) and 2.1 (3%) kg P ha⁻¹ yr⁻¹ for LTFE1, LTFE2, LTFE3, respectively. Therefore, SOP can only play a minor role in plant P nutrition while OWP could represent 1/5 of the absorbed P with this calculation.

Although gross annual rates of SOP mineralization did not differ significantly among treatments for a given site, the SOP residence time was affected by OWP in LTFE2 and range from 30 years (FYM₄₀ and GWS₁₁₂) to more than a millennium (MSW₂₄). The shortest residence time was greater to residences times found on SOC using the AMG model, derived from the Hénin-Dupuis model. In deed, Clivot et al. (2019) used a k default value of 0.29 yr⁻¹ (i.e. residence time of 3.4 years), which is far different our results. The observed difference in calculated k values could be due to the amount and speciation of P applied. P inputs represented 325 kg ha⁻¹ of cumulative organic P incorporation for GWS₁₁₂ while MSW₂₄ represented a cumulative incorporation of 30 kg P ha⁻¹. Thus, as the SOP stock were not different, the P under GWS₁₁₂ fertilization should cycle faster than in MSW₂₄.

The low annual rate of mineralization, the long residence time, and thus the low contribution of SOP to plant nutrition despite substantial stocks can be linked to several factors. First, the composition and speciation of added P in crop residues and OWP. Organic P contains a wide range of compounds of which orthophosphate monoesters the most important group and mainly include the *myo*-inositolhexakisphosphate (i.e. phytate) (Condrón et al. 2005; Cade-Menun 2017; Menezes-Blackburn et al. 2018). This compound is known to be a compound storage in plant seeds and is likely to be released to soil after residues return (Noack et al. 2012, 2014). Although phytate can be rapidly mineralized after addition, it can also bind tightly to the soil solid phase by sorption and remain unavailable for enzymatic mineralization (McKercher and Anderson 1989; Steffens et al. 2010). Second, the high phosphate ions concentration in soil solution (0.86, 1.03 and 0.52 mg P L⁻¹ in LTFE1, LTFE2 and LTFE3, respectively) can inhibit phosphatase synthesis and activity. As a result, SOP mineralization would be limited (Olander and Vitousek 2000; Nannipieri et al. 2011).

With the present set of long-term field experiments, where SOP mineralization were significantly different among LTFE, determining drivers of SOP mineralization was possible. For SOC, it decomposes according to first-order kinetics with a rate constant k affected by the climate (mean annual water balance, and air temperature) and soil characteristics (clay and carbonate concentrations, pH and C/N ratio of the total soil organic matter) (Clivot et al. 2017). An exploratory approach is presented in supplementary information (Section SI-2.1.4). Extend the application of this model to a wide range of agroecosystems with different soils, management practices and climates would contribute to improve our understanding of SOP dynamics and its control drivers. Additionally, including insight on SOP and OWP speciation, and soil enzymatic assay would bring a useful tool for this approach.

2.4.4 Model precision and accuracy

Over the three studied sites, the model precision and accuracy seems pretty high, with a regression slope of the symmetric regression line of simulated versus observed SOP close to 1 (Figure SI-2.3; $R^2 = 0.86$), and with a RMSE of 129 kg P ha⁻¹. Percentage lack of accuracy was 7%, and percentage lack of precision was (93%). Therefore, the apparent model low precision and high accuracy is attributed to the initial SOP stocks, highly variable among sites (Table 2.8), but also within sites which limits model precision. This statement was supported by a RRMSE (15%) twice lower than the coefficient of variation of observed SOP (over all sites: 40%), but higher than AMG model applied to C (about 5%) (Clivot et al. 2019). However, the model still accurate as its predicted SOP values remain in the same magnitude as observed SOP values. The origin and difference among

initial SOP stock could be explained by the management history of plots, but information was not available, making it difficult to conclude.

2.5 Conclusion

Three long-term field experiments were investigated in order to determine the SOP stock mineralization over almost two decades in contrasting agroecosystems. According to the model calculations, the SOP residence time were over two centuries for LTFE1 and LTFE3 while it was variable in LTFE2, from 30 years (GWS_{112}) to more than a millennium (MSW_{24}). With these values, SOP can only contribute to a maximum of 1% (LTFE1), 6% (LTFE2) and 3% (LTFE3) of the absorbed plant, which is relatively low in comparison to crop residues and OWP contribution (LTFE1: 6%; LTFE2: 24%; LTFE3: 15%). OWP in LTFE2 and LTFE3 have brought highly variable amount of P, essentially as inorganic forms. The OWP are more likely to behave as inorganic fertilizers than SOP supply source. Further studies are required to extend the range of application of the model in order to determine SOP mineralization driving factor, taking into account the SOP, crop residues P and OWP P speciation as well as phosphatase enzymatic assay.

SI-2.1 Supplementary information

SI-2.1.1 Organic waste product composting process and parameters

Table SI-2.1 Synthesis of organic waste products composting process in LTFE2.

OWP	Year	Origin: City (French department)	Product input	Refining	Fermentation		Maturation	
				mm	Process	Duration	Process	Duration
GWS	1998	Nantes (44)	Green wastes of wood chips + sewage sludge	20	Sheltered swath	3 months	Sheltered	2 months
	2000				Outside	1 month	Outside	1 month
	2002	Cernay (68)	Green wastes of wood chips + sewage sludge (Colmar) + grounded pallets	40	Forced ventilation under shelter	6 weeks	Outside	3 months
	2004					4 weeks		4 months
	2006			20				3 months
	2007					2011		
2009	2011	2013	2015					
2011				2013	2015			
2013	2015							
2015								
BIOW	1998	Cergy (95)	Fermentable fraction of municipal waste + Green wastes	20	SILODA Sheltered	1 month	Sheltered	2 months
	2000	Sim le Noble (59)			Forced ventilation under tarpaulin	26 days	Outside swath	4 months
	2002	Marbache (54)		25	Slowly composted (turning)	3 months	Outside swath	3 months
	2004							
	2006	Caudan (56)		15	Accelerated fermentation in compost tunnel	5 weeks	Sheltered (with 2 weeks with forced ventilation)	6 months
	2007						Sheltered (with 2 weeks with forced ventilation)	3 months
2009								
2011								
2013								
2015								
MSW	1998	Murianette (38)	Residual municipal wastes ²	10-12	SILODA Sheltered	22 days	Sheltered	5 days
	2000							
	2002	Lantic (22)	Mixed	30	BRS 3d	Swath 1 month		
	2004							
	2006	Vatteville la rue (76)	12,5	Forced ventilation (no turning)	1 month	Outside	5 days	
	2007	St-Pérvay-la-Colombe (45)	40	Forced ventilation + 1 turning	3 weeks	Sheltered	3 weeks	
2009								
2011	Ecorpain (72)	Residual municipal wastes ²	6	3 weeks	Sheltered	3 weeks		
2013								
2015								
FYM	1998	Grignon (78)	Dairy cattle manure from the Grignon experimental farm					
	2000							
	2002							
	2004							
	2006							
	2007							
	2009							
	2011							
	2013							
	2015							

² Residual municipal wastes: the waste remaining after sorting the recyclable waste (used paper, plastic packaging, metal packaging, beverage containers, biodegradable waste, glass and textiles)

Table SI-2.2 Synthesis of organic waste products composting process in LTFE3.

Compost	Year	Provenance	Waste input	Refining	Fermentation		Maturation	
				mm	Process	Duration	Process	Duration
SLU	2001 2003 2005 2007 2009 2011 2013	Colmar (68)	Urban sewage sludge activated by prolonged aeration and dried by centrifugation					
DVB	2001	Cernay (68)	Urban sewage sludge + Bark, green waste, wood chips	25	Forced ventilation (not turned)	6 weeks	sheltered	2 months
	2003 2005		Urban sewage sludge + green waste, wood chips, grounded pallets					
	2007		Urban sewage sludge + green waste, wood chips, maize cobs	17.5		4-5 weeks		
	2009		Urban sewage sludge + green waste, maize cobs					
	2011		Urban sewage sludge + green waste					
	2013	Réguisheim (68)	Urban sewage sludge (Colmar) + green waste, maize cobs, screening rejects	20				
BIOW	2001	Aspach (68)	Fermentable fraction of municipal waste + Green wastes	12	Turning with worm screw + forced ventilation	15-20 days	sheltered	3 months
	2003 2005 2007	Marbache (54)		25	Outside windrows + turning	3 months	outside	
				20				
	2009 2011 2013	Lorient (56)		15	Accelerated fermentation in composting tunnels	1 month	sheltered (including 1 weeks of forced suction)	
FYM	2001 2003 2005	INRAE station of Mirecourt (88)	Dairy cattle farmyard manure					
	2007 2009	Hymont (88)						
	2011 2013	Holtzwhir (68)						
FYMC	2001 2003 2005	INRAE station of Mirecourt (88)	Dairy cattle farmyard manure		Outside windrows + turning	2 months		
	2007 2009	Hymont (88)						
	2011 2013	Holtzwhir (68)						

SI-2.1.2 Crops successions in LTFE2 and LTFE3

Table SI-2.3 Crops succession in LTFE2.

1999	2000	2001	2002	2003	2004	2005	2006	2007
maize	wheat	maize	wheat	maize	wheat	maize	wheat	barley

2008	2009	2010	2011	2012	2013	2014	2015
maize	wheat	maize	wheat	maize	wheat	maize	barley

Table SI-2.4 Crops succession in LTFE3.

2001	2002	2003	2004	2005	2006	2007
maize	wheat	maize	barley	maize	wheat	sugar beet

2008	2009	2010	2011	2012	2013	2014
barley	maize	wheat	sugar beet	barley	maize	wheat

SI-2.1.3 Dynamic of SIP and SOP with years of experimentation

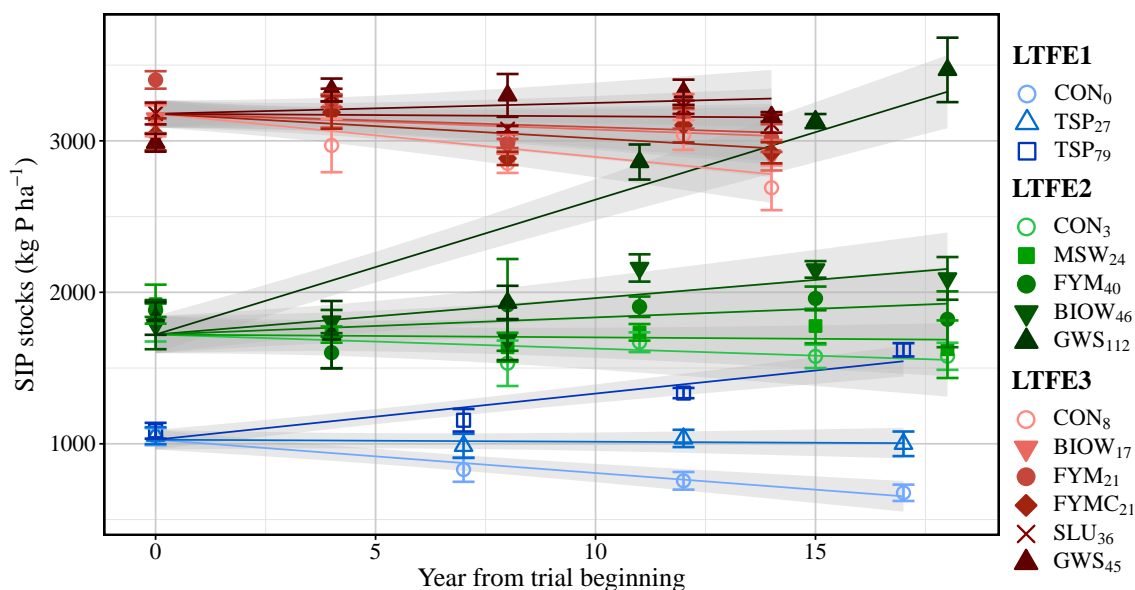


Figure SI-2.1 Evolution of stocks over years of soil inorganic P (SIP) in the ploughed layer as affected by P fertilization treatments in the three studied LTFE. Values are means \pm std. err. ($n = 4$). Lines are linear regressions and grey areas are confidence interval (95%) of the linear regressions. Linear regressions equations are presented in supplementary information. CON: no P input; MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; SLU: dehydrated urban sewage sludge; GWS: compost of green waste and SLU; BIOW: biowaste compost; TSP: triple superphosphate. Subscript values in treatments abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{ yr}^{-1}$. Linear regressions equations are presented in Table SI-2.5.

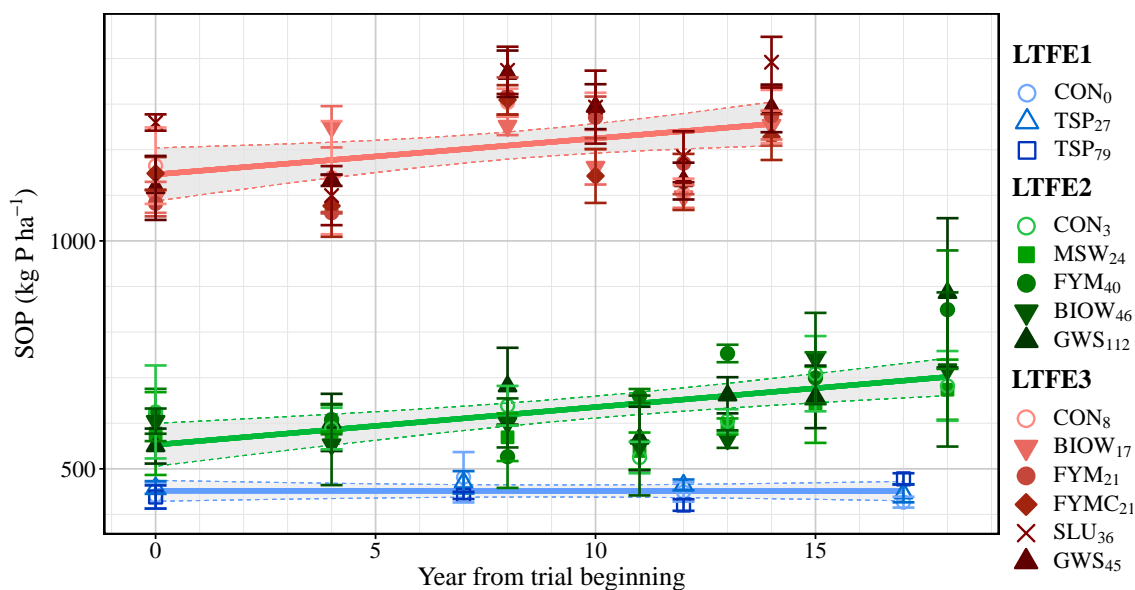


Figure SI-2.2 Stocks of soil organic P (SOP) in the ploughed layer in relation to years of experiment as affected by P fertilization treatments of the three studied LTFE. Values are means \pm std. err. ($n = 4$). Lines are linear regressions. Grey areas are linear regression confidence interval at 95%. CON: control with no P input; MWS: municipal solid waste compost; FYM farmyard manure; FYMC: FYM compost, GWS: compost of green waste and SLU; SLU: dehydrated sewage sludge; BIOW: biowaste compost; TSP: triple superphosphate. Subscript values in treatments abbreviations are the average annual rate of P application, in $\text{kg P ha}^{-1} \text{ yr}^{-1}$.

LTFE1: $\text{SOP} = -0.04 \pm 0.94 \times \text{Year} + 452 \pm 10$ (P -value = 0.97; $R^2 = 0.00$; $n = 12$)

LTFE2: $\text{SOP} = 8.3 \pm 2.0 \times \text{Year} + 553 \pm 21$ (P -value = 0.0002; $R^2 = 0.34$; $n = 35$)

LTFE3: $\text{SOP} = 7.9 \pm 3.1 \times \text{Year} + 1146 \pm 29$ (P -value = 0.015; $R^2 = 0.16$; $n = 36$)

Table SI-2.5 Linear regression of soil inorganic P (SIP) stock in relation to years of experiment as affected by P fertilization rates of the three LTFE. CON: no P input; MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; SLU: dehydrated urban sewage sludge; GWS: compost of green waste and SLU; BIOW: biowaste compost; TSP: triple superphosphate. Subscript values in treatment abbreviations are the average annual rate of P application, in kg P ha⁻¹ yr⁻¹.

Treatments	Regressions equations	Slope <i>P</i> -value	Regression statistics
LTFE1			
CON ₀	$-22.0 \pm 3.3 \times Year + 1027$	0.0002	$R^2 = 0.96; n = 12$
TSP ₂₇	$-1.3 \pm 3.3 \times Year + 1027$	0.70	
TSP ₇₉	$30.5 \pm 3.3 \times Year + 1027$	<0.0001	
LTFE2			
CON ₃	$-9.3 \pm 7.7 \times Year + 1721$	0.24	$R^2 = 0.88; n = 30$
MSW ₂₄	$-1.9 \pm 7.8 \times Year + 1721$	0.81	
FYM ₄₀	$11.3 \pm 7.8 \times Year + 1721$	0.16	
BIOW ₄₆	$24.0 \pm 7.8 \times Year + 1721$	0.005	
GWS ₁₁₂	$89.1 \pm 7.8 \times Year + 1721$	<0.0001	
LTFE3			
CON ₀	$-28.5 \pm 7.8 \times Year + 3179$	0.001	$R^2 = 0.47; n = 30$
BIOW ₁₇	$-10.4 \pm 7.8 \times Year + 3179$	0.19	
FYM ₂₁	$-8.8 \pm 7.8 \times Year + 3179$	0.27	
FYMC ₂₁	$-16.3 \pm 7.8 \times Year + 3179$	0.05	
SLU ₃₆	$1.0 \pm 7.8 \times Year + 3179$	0.89	
GWS ₄₅	$4.5 \pm 7.8 \times Year + 3179$	0.57	

SI-2.1.4 Simulated and observed SOP comparison

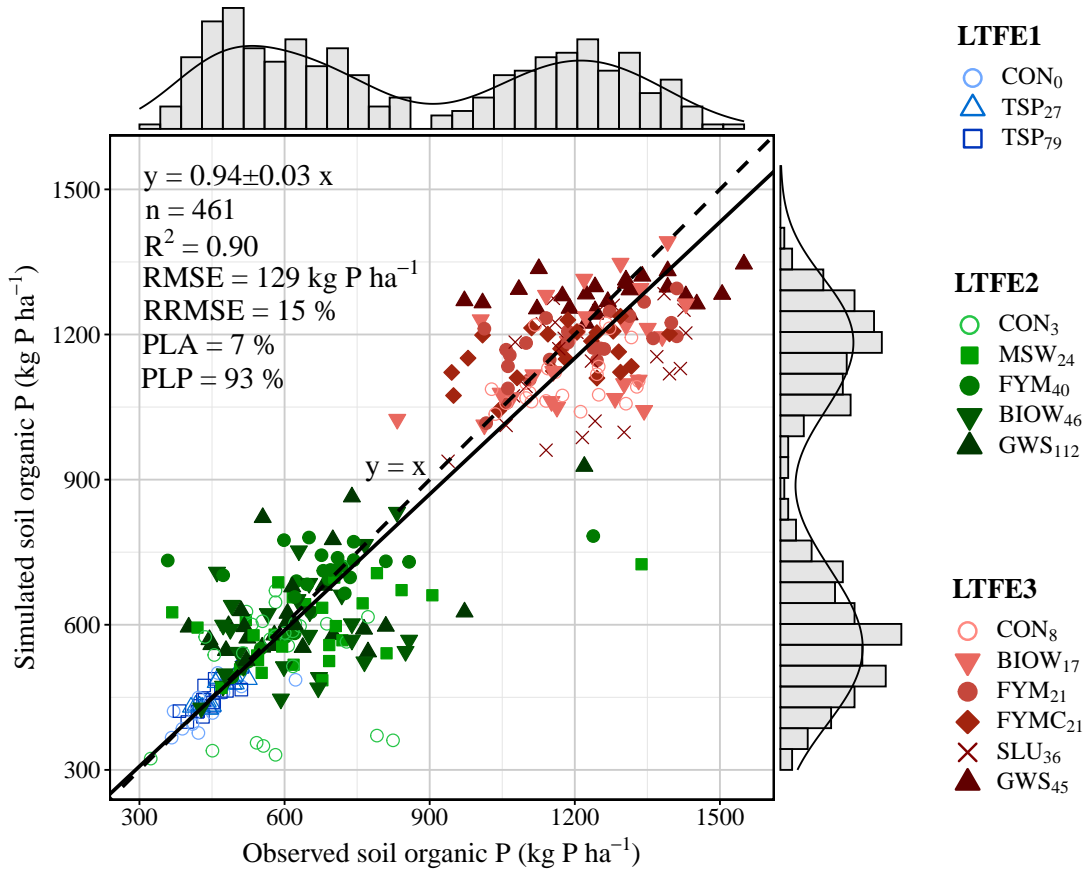


Figure SI-2.3 Simulated vs observed SOP stocks in the ploughed soil layer by the Hénin and Dupuis (1945) model transposed to SOP.

The solid line is the symmetric regression line (Correndo et al. 2021a). CON: no P input, MWS: municipal solid waste compost, FYM farmyard manure, FYMC: FYM compost; GWS: compost of green waste and SLU: SLU: dehydrated urban sewage sludge; BIOW: bio-waste compost; TSP: triple superphosphate. Numbers in treatments names are P annually applied on average (kg P ha⁻¹ yr⁻¹). Numbers in treatments names are P annually applied on average (kg P ha⁻¹ yr⁻¹). LTFE1: $n = 48$, LTFE2: $n = 140$, LTFE3: $n = 144$.

SI-2.1.5 Multivariate analysis

Either the coefficient of mineralization k , the initial SOP stock, or SOP mineralization rate were slightly but significantly different among LTFE (analysis includes the LTFE0). Therefore, it is possible to explore the potential effect of some environmental and soil variables on SOP mineralization rate, k , and SOP initial stock by correlation or multivariate analysis. Previous results have studied and highlight the relation of such variables on soil organic C (SOC) and soil N (Clivot et al. 2017; Basile-Doelsch et al. 2020). We selected SOC, organic matter C/N, CaCO₃, clay, silt, mean annual T°C, and mean annual water inputs (rainfall + irrigation), as well as SIP. Data were averaged over years for each

treatment and bloc within LTFE (LTFE0: $n = 12$; LTFE1: $n = 12$; LTFE2: $n = 30$; LTFE3: $n = 36$).

Mineralized SOP correlation with climatic and edaphic variables

Table SI-2.6 Pearson correlation coefficient and P-values between either Initial SOP stock, coefficient k, or SOP mineralization flux, and explanatory variables selected.

Variable	Initial SOP		Coefficient k		Mineralized SOP	
	Corr.	P-value	Corr.	P-value	Corr.	P-value
pH	0.85	< 0.001	-0.12	0.33	0.07	0.56
SIP (mg P ha ⁻¹)	0.89	< 0.001	0.03	0.81	0.21	0.084
SOC (g kg ⁻¹)	0.82	< 0.001	0.15	0.21	0.34	0.004
C/N	-0.31	0.010	-0.16	0.18	-0.22	0.070
CEC (cmol _c kg ⁻¹)	0.84	< 0.001	-0.05	0.67	0.16	0.20
CaCO ₃ (g kg ⁻¹)	0.92	< 0.001	-0.25	0.036	-0.04	0.72
Clay (g kg ⁻¹)	0.92	< 0.001	-0.07	0.53	0.13	0.31
Silt (g kg ⁻¹)	0.52	< 0.001	0.28	0.020	0.39	0.001
Annual temperature (°C)	-0.25	0.041	-0.08	0.50	-0.13	0.29
Annual water input (mm)	-0.81	< 0.001	-0.15	0.24	-0.32	0.009

Principal component analysis

A principal component analysis was performed on the selected variables in Table 4-SI and considering the three studied variables as response variable (initial SOP stock, coefficient k, and SOP mineralization flux). This approach provides an insight of variables relation, how SOP mineralization is affected by those variables, and how the three LTFE are discriminated according to those variables.

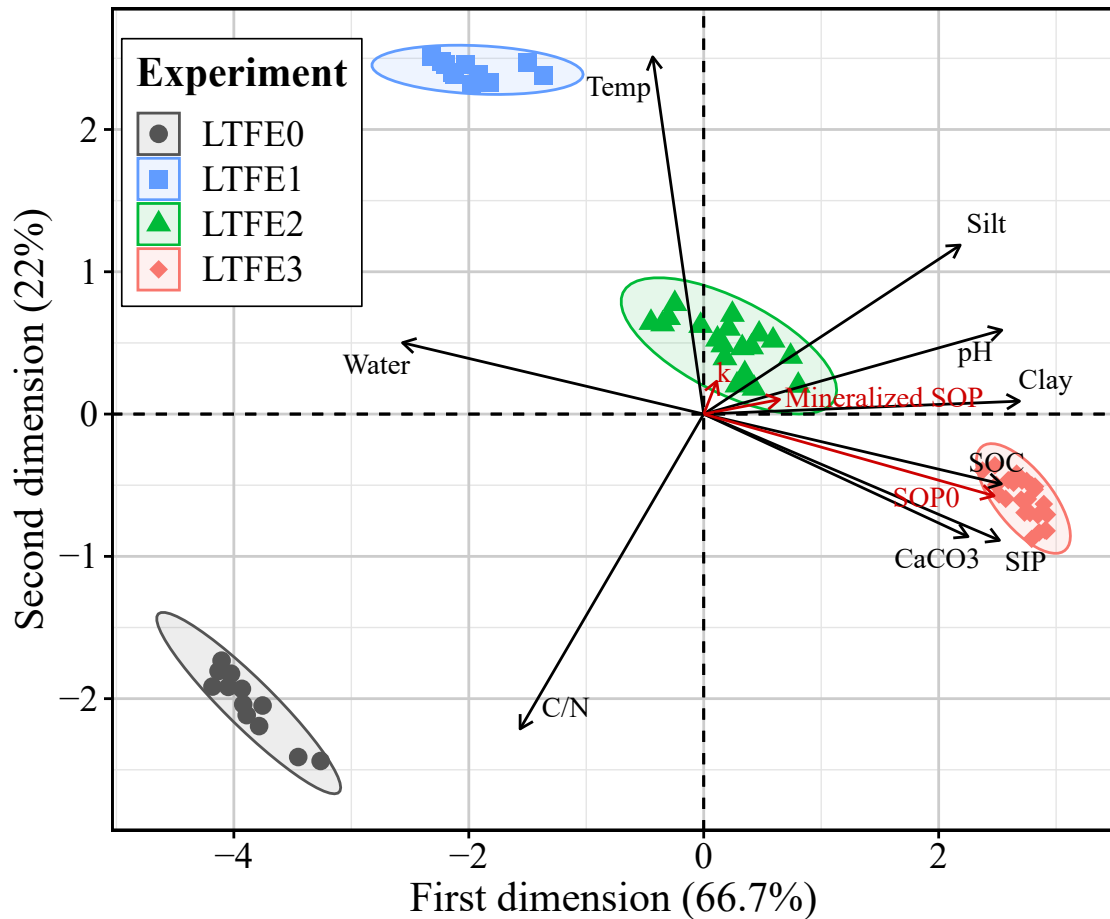


Figure SI-2.4 Principal component analysis describing relations among selected explanatory variables with initial SOP stock, coefficient k , and SOP mineralization flux as response variable. Ellipses and colors are the three LTFE, discriminated by the selected variables. Data were average over year for each bloc and treatments within LTFE.

Multiple step-wise model selection

Following the Pearson tests and the ACP, a multiple step-wise model selection was performed on the initial SOP stock (kg P ha^{-1}), coefficient k (yr^{-1}), and SOP mineralization flux ($\text{kg P ha}^{-1} \text{ yr}^{-1}$). Models were tested by adding and/or removing variables from Table SI-2.6. The best model was selected based on AIC (Akaike information criterion). This approach provides an exploratory result on linear relations between the tested response variables and a set of selected explanatory variables. Here are the resulting equations:

$$\begin{aligned} \text{Initial SOP} &= 19 \times \text{SOC} - 2.0 \times \text{Silt} + 311 \times \text{Temp} - 2.5 \times \text{Water input} \\ &+ 271; \\ (AIC &= 625.3) \end{aligned}$$

$$\begin{aligned} \text{Coefficient } k &= -9.17 \times \text{CaCO}_3 + 4.1610^{-5} \times \text{Silt} \\ &+ 0.003 \times \text{C/N} - 0.05; \\ (AIC &= -625.1) \end{aligned}$$

$$\begin{aligned} \text{SOP mineralization} &= 0.04 \times \text{Initial SOP} + 0.02 \times \text{Water input} - 7.58 \times \text{pH} \\ &- 1.5 \times \text{SOC} + 0.05 \times \text{Silt} - 0.16 \times \text{Clay} - 5.04; \\ (AIC &= 225.9) \end{aligned}$$

(SI-Eq. 2.1)

Soil and environmental factors affecting the SOP initial stock, the coefficient k, and SOP mineralization rate

The SOP initial stock was highly correlated to all the tested variables. According to the ACP, the most collinear and positively correlated variables were SOC, CaCO₃, SIP, and clay concentration. Conversely, the water input is anticorrelated to this stock. This was confirmed in the equation where climate indicators tend to be the drivers of the initial SOP stock. This result was in accordance with general knowledge on SOC, where climate was the key driver of SOC stocks at the global and regional space scale (Amundson 2001).

The coefficient of mineralization k seems more related to soil texture, carbonate concentration, organic matter C/N, and average temperature. The main soil parameter that tends to drive k is the carbonate concentration with a negative effect. Previous studies have shown that P in soil (within molecules or as phosphate ions) is strongly sorbed to the soil surface which limits its availability to the soil solution (Carreira et al. 2006; Johnston et al. 2014).

Among the tested variables, the SOP mineralization rate is dependent on the initial SOP stock. This is coherent as the flux is the result of a product between a stock and the coefficient: the higher the stock the higher the flux. Regarding the other variables, a fine soil texture with neutral to basic pH tends to stabilize SOP and limit its mineralization. Previous studies have reported the soil clay concentration as a factor of carbon storage and stabilization (Wiesmeier et al. 2019). On the other hand, pH affects phosphatase activity in soil and therefore their mineralization capacity. However, the pH optimum depends on the enzyme studied (Nannipieri et al. 2011).

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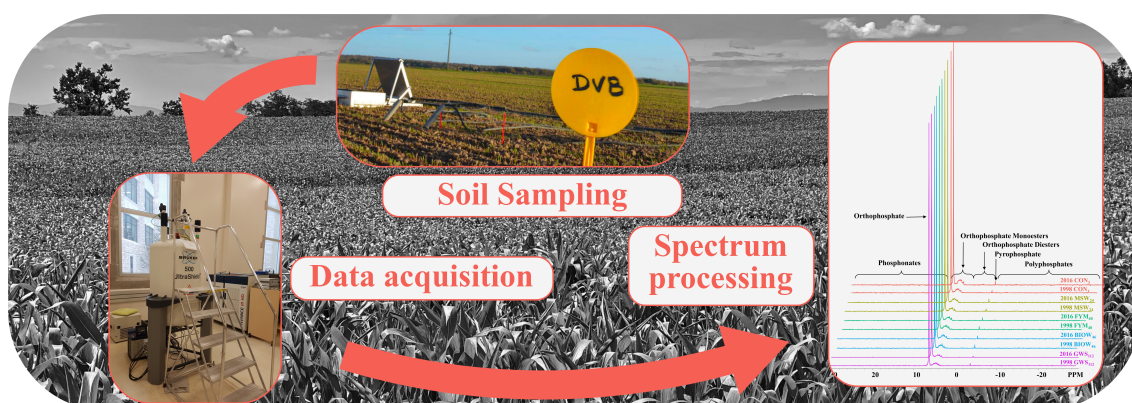
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CHAPTER 3

Phosphorus concentration, availability and speciation in soils after repeated applications of different urban composts and farmyard manure at the same carbon rate

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Abstract

Organic waste products (OWP) applied repeatedly to cropped soils make nutrient recycling possible, replacing chemical fertilizers to improve soil fertility. However, cycling of inorganic and organic phosphorus (P) forms in soils with different OWP is still poorly understood. This study assessed the effect of successive applications of four OWP on P contents of the soil plough layer and plants in a French field experiment, located on a silt loam Luvisol. The first objective was to assess relationships between cumulated budget of (P applied – P removed in crops harvests) with different P stocks in soils. The OWP included composts of green wastes and urban sewage sludge (GWS), of municipal solid waste (MSW), of biowaste compost (BIOW), and a farmyard manure (FYM). On average, OWP were applied at 2 t C ha⁻¹ yr⁻¹. Concentrations of total (TP_{HF}), inorganic (SIP), organic (SOP) and plant-available P [Olsen-P and phosphate ion concentrations in soil suspension in water: (C_P)] were determined in OWP samples, and in soils sampled in 1998 (onset of the experiment) and in 2016 after 17 years of cropping. A second objective was to determine inorganic and organic P species in NaOH-EDTA extracts of OWP and soils by nuclear magnetic resonance spectroscopy (P-NMR). Total P inputs varied from 420 to 2008 kg P ha⁻¹ among OWP, due to differences in their P concentration and C/P ratios. Phosphorus in OWP was overwhelmingly (on average about 80%) orthophosphate (P-NMR). Repeated applications of OWP for 17 years did not significantly affect grain yields (wheat, maize, barley) or grain P concentrations. Cumulated P budgets were -9, 229, 372, and 1544 kg P ha⁻¹ for MWS, FYM, BIOW, and GWS, respectively. There were strong linear regressions between cumulated P budgets and TP_{HF}, SIP, P_{NE}, P-NMR orthophosphate, Olsen-P, and C_P. By contrast, SOP stock remain constant regardless of P budget. There were no significant differences in concentrations of P species with OWP treatments; however, concentrations of some P species (orthophosphate, *myo*-inositol hexakisphosphate, glucose 6-phosphate) were significantly greater in 2016 than 1998.

Keywords:

Organic wastes recycling, P-NMR spectroscopy, P speciation dynamic, Long-term field experiment.

Highlights:

- SOP speciation were assessed on organic waste products and soils over time
- OWP speciation (P-NMR) changed very little among products
- OWP fertilization had a dose effect on total inorganic P
- No P application did not change soil speciation

Résumé

L'objectif de ce chapitre est de déterminer l'effet d'épandage répété de différents PRO (trois composts urbains, un fumier) sur la concentration du P des sols, sa spéciation et sa disponibilité, mais également d'analyser le lien entre la spéciation du P des PRO du sol. En s'appuyant sur l'essai QualiAgro (17 ans ; échantillonné en début et fin d'essai), nous avons montré que le P apporté est majoritairement sous forme d'ions phosphate, formes de P absorbées par les plantes. Par conséquent, l'effet majeur des épandages successifs est d'augmenter la quantité de P phytodisponible du sol, en proportion du bilan de P. Les autres formes inorganiques ou organiques de P du sol n'ont pas (ou peu) été affectées. Cela met en évidence le potentiel élevé des PRO à remplacer des engrais phosphatés minéraux, mais également l'écart élevé du P apporté entre PRO lorsque leur épandage est raisonné sur une base carbone.

Mots clés :

Recyclage des produits résiduels organiques, Spectroscopie RMN du P, Dynamique de la spéciation du P, Essai agronomique de longue durée.

Highlights:

- La spéciation du P a été déterminée à différentes dates sur des échantillons de PRO et de sols
- La spéciation des PRO (RMN-P) est peu différente entre les produits
- La fertilisation par les PRO a un effet dose sur le P inorganique du sol
- L'absence de fertilisation en P ne change pas la spéciation du P du sol

3.1 Introduction

The use of phosphorus (P) in agricultural systems is facing essential issues. Some studies have predicted a potential scarcity of mineral P fertilizer in the current century (Cordell and White 2011). As global food demand increases with population, the extensive use and consumption of the non-renewable phosphate rock reserve for manufacturing P fertilizers could lead to intense geopolitical and economical tensions (Tilman et al. 2002; Cordell et al. 2009; Gislev et al. 2018). This statement highlights the urgent need to enhance our use of alternative P sources, such as urban organic wastes or farm effluent (i.e. organic waste products, OWP). Indeed, recycling organic wastes by bioconversion for field fertilization is a common practice that can be used to replenish soil P pools and ultimately replace inorganic fertilizers (Diacono and Montemurro 2011).

In agriculture, OWP are often valued for their carbon (C) or nitrogen (N) supply and their role to improve either soil stability, organic matter and C storage, or soil N supply (Annabi et al. 2007; Gopinath et al. 2008; Paetsch et al. 2016). Although OWP contain both inorganic and organic P compounds, several studies have shown that P in OWP is mostly inorganic, and might directly contribute to crop P supply (Cabeza et al. 2011; Glæsner et al. 2019). Another way OWP can contribute to crop P supply is through the mineralization of their organic P concentrations by soil microorganisms (Jarosch et al. 2015). Indeed, previous studies have found that organic P in OWP is partly composed of easily degradable compounds, which might enhance biological activity and potentially organic P mineralization (Annaheim et al. 2013; Requejo and Eichler-Löbermann 2014). However, the origin, storage, and composting parameters of OWP are highly variable and can lead to different C/N/P ratios, and different amounts and forms of the P supplying crops (Fuchs et al. 2014). Therefore, there is an urgent need to improve our understanding of P speciation and concentration changes under repeated OWP applications.

Nuclear magnetic resonance (P-NMR) spectroscopy on NaOH-Ethylenediaminetetraacetic (NaOH-EDTA) extracts is one of the most efficient and commonly used methods (Cade-Menun 2017; Menezes-Blackburn et al. 2018) to characterize organic P compounds and general inorganic P compounds in environmental samples such as soils and composts. The inorganic P forms that can be identified with solution P-NMR include phosphate ions, [orthophosphate ions (PO_4^{3-}) only in NaOH-EDTA extracts analyzed at $\text{pH} > 12.4$], pyrophosphates, and polyphosphates. Organic P forms are molecules containing a P group bonded to C groups, such as orthophosphate monoesters [e.g. sugar phosphate, inositol hexakisphosphates (IHP)], orthophosphate diesters (e.g. DNA and phospholipids), or phosphonates, with a direct covalent bond between P and C (Condrón et al. 2005; Cade-Menun 2017).

The aim of the study was to evaluate the long-term effects of repeated applications over decades of dairy farmyard manure and urban composts, as well as multiple years with no P fertilization, on the soil P status. To do that, we used the French field experiment QualiAgro started in 1998 on a typical loess Luvisol and predominantly cropped under a maize-wheat rotation. Three different urban composts and a farmyard manure were applied at the rate of 4 t C h^{-1} every 2 years. The QualiAgro experiment also included a control, which received no P from 1998 to 2016. We investigated: i) elemental composition (C, N, K, Ca, Mg) of the successive applications of urban composts and farmyard manure, and especially their P concentration and speciation by P-NMR analysis; ii) soil P concentrations and speciation before and after 17 years of fertilization and cultivation; and iii) annual crop grain yields and their P concentration over years to calculate budget between applied P and exported P over the 1998-2016 period. We hypothesized that repeated applications of a dairy farmyard manure and different urban composts could affect soil P speciation, concentration and availability, according to the organic product characteristics. Without P fertilization, we expected an initial decrease in soil inorganic P (SIP) concentration followed by a decrease in soil organic P (SOP) concentration from SOP mineralization.

3.2 Materials and methods

3.2.1 Site description and experimental design

The field experiment, called QualiAgro was established in 1998 on a cropped soil in Feucherolles (Yvelines, France: $48^{\circ}53'47'' \text{ N}$, $1^{\circ}58'21'' \text{ E}$, altitude = 177 m) to analyze the effects of different OWP fertilizations on soil properties and crop yield (Houot et al. 2002). The climate is oceanic (temperate subhumid, Cfb in Köppen classification) with a mean annual temperature of 11°C and mean annual rainfall of 695 mm (119 days per year on average). The parent material is quaternary loess decarbonated through more than 1 m and the soil type is a glossic luvisol (FAO 2014) with a silt loam texture (on average: 15% clay, 78% silt and 7% sand) for the soil plough layer (0-25 cm). The pH was neutral, and its calcium carbonate concentration below the detection limit ($< 1 \text{ g kg}^{-1}$).

In the QualiAgro field experiment, five treatments were studied: three urban composts, a farmyard manure and a control (CON) without any application of urban composts or farmyard manure. The four OWP were applied at the approximate rate of $4 \text{ t C ha}^{-1} \text{ 2yr}^{-1}$ from 1998 to 2013, and then 2 t C ha^{-1} in 2015, making ten applications over 1998-2016 period, which added different P to soils inputs depending on years and OWP (Figure 3.1). The different OWP were:

- i) a municipal solid waste compost (MWS) made from dry and clean cardboard packaging;
- ii) a dairy farmyard manure (FYM);
- iii) a biowaste compost (BIOW) made from the fermentable fraction of municipal wastes, green waste, and wood chips;
- iv) a green waste compost of wood chips and urban sewage sludge (GWS).

Composting processes are presented in the supplementary section Table SI-3.1 and in Annabi et al. (2011).

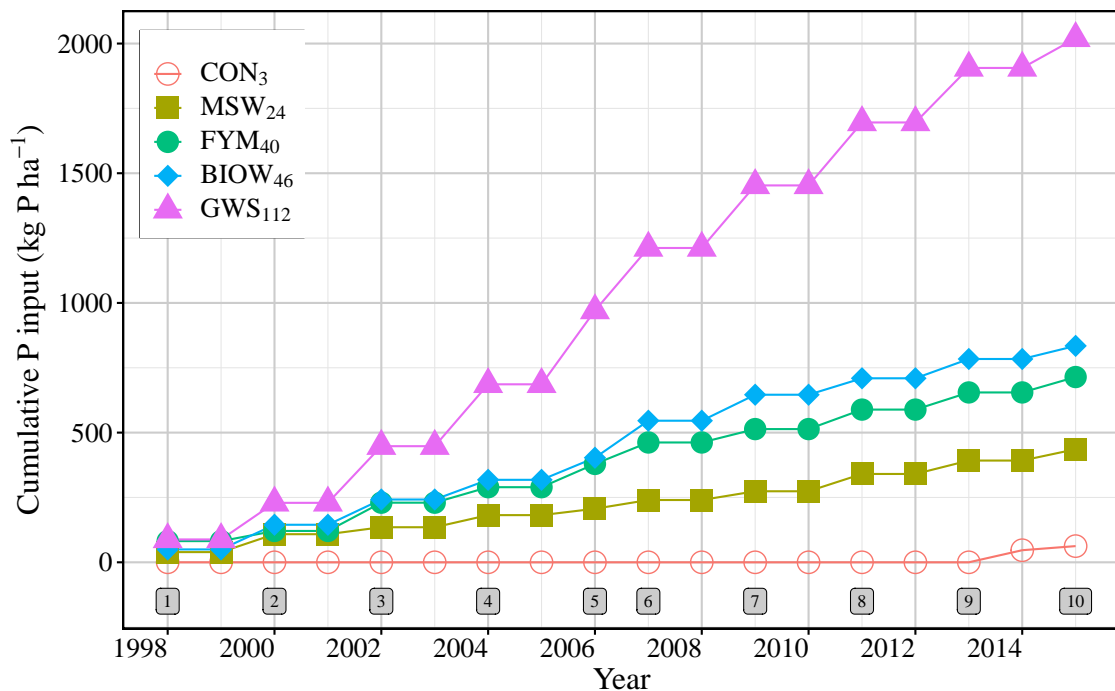


Figure 3.1 Cumulative total P input (kg P ha^{-1}) over the 1998-2016 period for the different P applications. Dots are means ($n = 4$). Grey labelled values are fertilization events. CON₃: no P applied up 2013; MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript values in treatment abbreviations are the average amount of P applied annually ($\text{kg P ha}^{-1} \text{ yr}^{-1}$).

All plots were fertilized for N at the end of winter before OWP fertilization with a (1:1) solution of urea and ammonium-nitrate (39% N) until 2013, at rates ranging from 80 to 140 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ depending on mineral N stocks measured in soils down to 90 cm depth. From 2014, the QualiAgro field experiment was managed according to organic farming practices; therefore, a mixture of meat and bone powder and blood flour (commercial name: AXE-NP-BIO[®]) replaced the synthetic N fertilization. This is a standardized product (NF U42-001), sterilized during the manufacturing process in accordance with EC regulation

1069/2009. The P applied in this product is negligible under OWP fertilization. The sum of P applied as OWP and as the above standardized organic product, gave an average P application rate of 3, 24, 40, 46, and 112 kg P ha⁻¹ yr⁻¹ for the CON₃, MSW₂₄, FYM₄₀, BOW₄₆, and GWS₁₁₂, respectively.

The experiment setup was a randomized four-block experiment with five treatments and four replicates (20 plots total). Each plot was 45 × 10 m, with 6-m cropped bands between plots and 25-m cropped bands between blocks. It was cultivated predominantly under a maize (*Zea mays* L.) / wheat (*Triticum spp.* L.) rotation and ploughed to approximately 25 cm depth. Maize residues and a third of wheat residues were returned to soil and buried. In 2007 and 2015, barley (*Hordeum vulgare* L.) was cropped instead of maize due to the presence of maize root worm (*Diabrotica virgifera* LeConte.). The OWP were applied either on wheat or barley stubble and were ploughed into the soil. Pest control was enforced until 2014, after which site management has changed to organic farming. No synthetic P or K fertilizers were applied during the 1998-2016 period of this study.

3.2.2 Characteristics of urban composts and farmyard manure

Ten samples of each OWP, collected over the 17-year study period (see Table SI-2.1), were analyzed by the *Laboratoire d'Analyses des Sols (Institut National de Recherche pour l'Agriculture, l'Alimentation et l'Environnement (INRAE), LAS, Arras, France)* using standard analytical techniques. Dry matter concentration (DM) was measured after oven-drying at 105°C. The pH in water was measured in a 1:5 (v:v) soil:water suspension (NF ISO 10390). Soil organic C (SOC) and total N concentrations were determined by catalytic combustion (NF ISO 10694 and NF ISO 13878, respectively), and CaCO₃ was determined by measuring CO₂ from HCl sample digestion, according to NF ISO 10693. Total concentrations of P, K, Ca, Mg, K, Na, Fe, Al and Mn were determined after wet digestion by concentrated hydrofluoric (HF) and perchloric (HClO₄) acids followed by ICP-OES (NF X 31-147).

In addition, the OWP samples applied in 1998, 2004, and 2011 were extracted by NaOH-EDTA solution using the modified Cade-Menun and Preston (1996) procedure and analyzed by P-NMR spectroscopy to identify and quantify P forms. Details are provided in Section SI-3.1.1. Spectra were acquired on a Bruker Avance 500-MHz spectrometer (202.5 MHz for P) equipped with a 10-mm broadband probe at the Saskatchewan Structural Sciences Centre (University of Saskatchewan, Saskatoon, Canada). The P-NMR experimental parameters were: pulse width, 13 μs (45°); acquisition 0.677 s; no proton decoupling. Delay times were 4 × T₁, with T₁ estimated from concentrations of P/(iron + manganese) in extracts using the equations in McDowell et al. (2006), and ranged from 3.3 to 18.8 s; 1660 to 2730 scans were collected (2-12 h). Chemical shifts were assigned to P compounds

based on Cade-Menun (2015) and by spiking with reference compounds. Spectra were processed with 7 and 2 Hz line broadening, using NUTS software (2000 edition; Acorn NMR, Livermore, CA), peak areas were calculated by integration and manual calculation.

Chemical shifts of identified and unidentified compounds and spectra are shown in Figure 3.2, Figure SI-3.1 and Table SI-3.2. Some orthophosphate diesters (e.g. phospholipids, RNA) are degraded in α - and β -glycerophosphate, and mononucleotides during NaOH-EDTA extraction and P-NMR analysis into peaks that appear in the orthophosphate monoester region (Liu et al. 2015; Schneider et al. 2016; Recena et al. 2018). Therefore, orthophosphate monoesters and diesters were corrected by subtracting area of degradation compounds from the total orthophosphate monoester area, and adding them to the total orthophosphate diester area (Schneider et al. 2016).

3.2.3 Plant analyses

Crop grains and aboveground residues were sampled each year in eight subplots within each plot, avoiding edge effects. Subplots areas were 1 m² for maize and 0.5 m² for wheat and barley. Grain and aboveground biomass samples were weighed before and after shredding and oven-drying at 40°C, and then were ground to < 0.5 mm in a Retsch rotor mill. Residual humidity was evaluated at 103°C. The P concentration in grain and aboveground residues were determined by the central plant testing laboratory of INRAE (USRAVE, Bordeaux, France). Plant samples were calcinated (480°C for 5 h), ashes were dissolved in concentrated nitric and hydrofluoric acids, and P concentrations were determined by radial ICP-AES (Masson et al. 2010).

The exported P concentrations in harvested grains and exported stubbles (for wheat and barley) were calculated by multiplying grain (or stubble) yield by P concentration in grains (or stubble). The annual P budget was calculated as the difference between P applied and P exported in grain (plus P exported in stubble residues for wheat and barley). The cumulative P budget was calculated by summing the annual P budget over years of cropping.

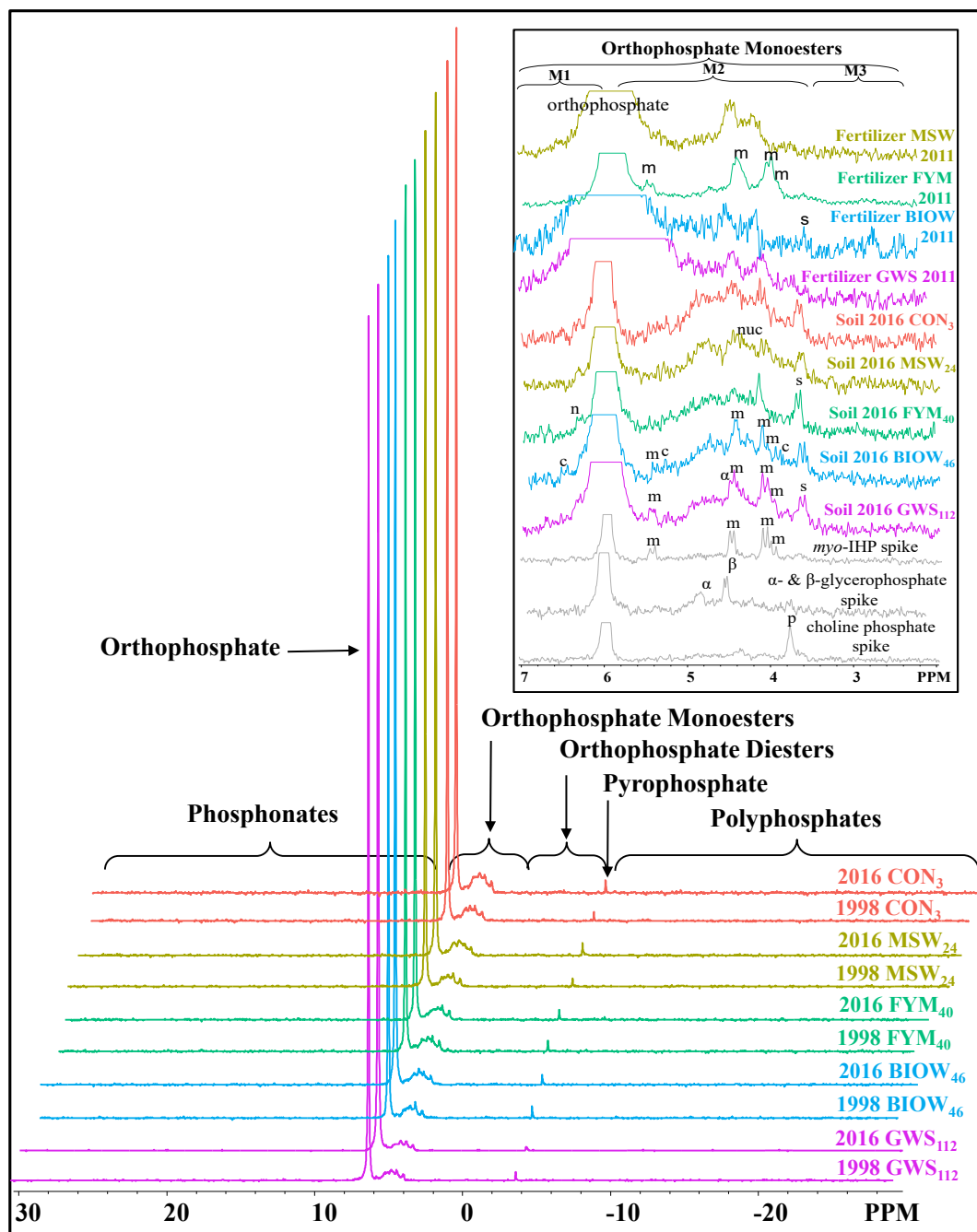


Figure 3.2 Examples of solution P-NMR spectra of NaOH-EDTA extracts of soils sampled in experimental plots of different treatments in 1998 and 2016. The main spectra show all soils, scaled to the height of the orthophosphate peak (7 Hz line-broadening). The insert shows the orthophosphate monoester region for a selection of soils and OWP treatments (2 Hz line broadening). M1, M2, and M3: other orthophosphate monoester 1, 2 and 3 respectively. m: *myo*-inositol hexakisphosphate (*myo*-IHP); s: *scyllo*-IHP; n: *neo*-IHP; c: *chiro*-IHP; α and β : α - and β - glycerophosphates; p: choline phosphate. CON₃: no P applied up 2014; MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript values in treatment abbreviation are the average amount of P applied annually (kg P ha⁻¹ yr⁻¹).

3.2.4 Soil sampling and soil properties

The soil plough layer (25-cm depth) of each experimental plot was sampled in autumn 1998 before the first application of OWP and early in 2016 (after 17 years of cropping). Each sample was obtained by mixing ten randomly-collected cores near the center of each plot, to avoid effects from adjacent plots. The cores were pooled and manually mixed, dried at 40°C, and sieved < 2 mm before analysis. Soil samples were analyzed at the LAS (INRAE, Arras, France) according to French standards (AFNOR 1999). The C and N concentrations were measured by catalytic combustion (ISO 10694 and 13878). The pH was measured in a 1:5 (v:v ratio) soil:water suspension (ISO 10390). The cation exchange capacity and exchangeable Ca, Na, Mg, and K were determined using the cobaltihexamine method (NF X 31-130), by stirring the soil sample in a solution of cobaltihexamine chloride. After filtration, cations concentration in solution were determined by ICP-OES.

The bulk density of the plough layer (0–25 cm) was 1.32 g cm⁻³ (3300 t of soil ha⁻¹) in 2013 by the soil core method (ISO 11272:1998), and was assumed to be unchanged for the duration of the study.

Total P concentration (TP_{HF}) in soils was determined by the standard NF X 31-147 procedure as describe for fertilizers. The soil organic P concentration (SOP) was determined using the Saunders and Williams (1955) procedure; the P concentration in solution was determined by the green malachite colorimetric method (Van Veldhoven and Mannaerts 1987) with a spectrophotometer at 610 nm. The SOP value was calculated as the difference between the P concentration in ignited soils and the P concentration in the non-ignited samples. The soil inorganic P concentration (SIP) was calculated as the difference between TP_{HF} and SOP. In addition, soils were also analyzed for the concentration (C_P) of phosphate ions in solution of soil suspensions (volume-to-mass ratio of 10; Morel et al. 2021), and by the Olsen-P bicarbonate extraction (Olsen et al. (1954); NF ISO 11263) followed by colorimetric analysis.

All soils, sampled in 1998 and 2016, were extracted by NaOH-EDTA solution and analyzed by P-NMR spectroscopy as described in SI Section SI-3.1.2. The NMR parameters for soils were similar to those used for OWP; delay times ranged from 5 to 10 s and 2237 to 3420 scans were collected 3 to 7.5 h. Example spectra for soils are shown in Figure 3.2 and Figure SI-3.1.

3.2.5 Statistical analysis

All statistics were carried out using R software, version 4.2.1 (R Core Team 2021). Chemical analysis data were tested for residuals normality (Schapiro test) and homoscedasticity

(Bartlett test), and log-transformed when needed. Also, prior to statistical analyses, P-NMR data for each sample (OWP and soils) were transformed using centered log-ratio (clr) to compare compositional samples (Abdi et al. 2015). One-way ANOVA were performed on chemical properties, P status and P-NMR data for testing years of sampling (Y) effect on CON₃, and no OWP applied effect on OWP. By using the same procedure, annual grain yield, P in grains, and P exported were analyzed for fertilization effect. Fertilized soils properties, P status, and compositional data of P-NMR were tested for Y, OWP, and Y×OWP interaction using a two-way ANOVA performed on a Linear Mixed Model. The model was fitted by a restrictive maximum likelihood method using the *lme* function from the *nlme* R package (Pinheiro et al. 2022). Blocks were included as a random effect to consider the pseudoreplication induced by the repeated measurements across space. The year factor was used to fit a first-order autoregressive variance structure to consider the pseudoreplication across time. ANOVA results were investigated with a post-hoc Tukey test when significant effect were detected. The two-way ANOVA results are shown in Table 3.1. Correlations among P concentrations of different inorganic soil P tests have been tested by a Pearson correlation test. Statistical tests were performed with a significance of $\alpha = 0.05$.

Table 3.1 Results (P values) for two-way ANOVA to analyze effects of OWP treatments (OWP: MSW₂₄, FYM₄₀, BOW₄₆, or GWS₁₁₂) and of soil sampling year (Y: 1998 or 2015 (main soil properties), or 2016, i.e. soil P analysis and inorganic and organic P forms analyzed by P-NMR in extracting NaOH-EDTA solution).

Soil properties	Two-way analysis of variance		
	OWP	Y	OWP×Y
Main soil properties			
pH	<0.0001	<0.0001	<0.0001
SOC (g C kg⁻¹)	<0.0001	<0.0001	<0.0001
Total N (g N kg⁻¹)	<0.0001	<0.0001	<0.0001
CEC (cmol+ kg⁻¹)	<0.0001	<0.0001	0.015
Ca (cmol+ kg⁻¹)	<0.0001	<0.0001	<0.0001
Mg (cmol+ kg⁻¹)	<0.0001	<0.0001	<0.0001
K (cmol+ kg⁻¹)	<0.0001	<0.0001	<0.0001
Soil P analysis			
TP_{HF} (mg P kg⁻¹)	<0.0001	<0.0001	<0.0001
SIP (mg P kg⁻¹)	<0.0001	0.002	<0.0001
SOP (mg P kg⁻¹)	0.84	0.025	0.57
P_{NE} (mg P kg⁻¹)	<0.0001	<0.0001	<0.0001
P_{NE}/TP_{HF} (%)	<0.0001	0.88	<0.0001

Continued on next page

Table 3.1 – Continued from previous page

Soil properties	Two-way analysis of variance		
	OWP	Y	OWP×Y
C_P (mg P L ⁻¹)	<0.0001	0.003	<0.0001
Olsen-P (mg P kg ⁻¹)	<0.0001	<0.0001	<0.0001
Soil P forms determined by P-NMR in NaOH-EDTA extract (mg P kg⁻¹)			
Orthophosphate	0.83	0.009	0.45
Pyrophosphate	0.65	0.13	0.70
Polyphosphates	0.33	0.29	0.16
All inorganic P forms	0.003	0.008	0.029
Phosphonates	0.91	0.32	0.78
Orthophosphate monoesters forms			
myo-IHP ^x	0.87	0.004	0.63
scyl-IHP	0.63	0.07	0.56
neo-IHP	0.40	0.26	0.11
chiro-IHP	0.72	0.79	0.06
Glucose 6-phosphate	0.52	0.028	0.32
Choline phosphate	0.56	0.53	0.79
Other monoesters 1 ^y	0.98	0.006	0.84
Other monoesters 2	0.46	0.08	0.53
Other monoesters 3	0.77	0.12	0.45
All monoesters	0.43	0.06	0.41
Orthophosphate diesters forms			
DNA	0.73	0.43	0.27
α-glycerophosphate	0.57	0.95	0.99
β-glycerophosphate	0.80	0.06	0.92
Nucleotides	0.26	0.20	0.38
Other diesters 1 ^z	0.67	0.07	0.08
Other diesters 2	0.99	0.51	0.77
All diesters	0.23	0.26	0.80
All organic P forms	0.0012	0.025	0.007

^x Inositol hexakisphosphates (IHP): sum of *myo*-, *scyllo*-, *neo*-, D-*chiro*-IHP stereoisomers;

^y Other orthophosphate monoesters are peaks in the monoester region not specifically identified;

^z Other diesters include phospholipids, α and β glycerophosphates (products of phospholipid degradation), nucleotides and unidentified orthophosphate diester.

3.3 Results

3.3.1 Composition of OWP applications and cumulative inputs

Concentrations (mean of 10 applications) of SOC, total N, P_{HF} , organic and inorganic P, $CaCO_3$, total Ca, total K, total Mg, total Na, total Al, total Fe, and total Mn varied significantly across OWP (Table 3.2). Among significant points to emphasize, all OWP had pH values greater than 7, with highest pH in FYM and the lowest pH in MSW and GWS. In comparison to other OWP, FYM had the highest K concentration, MSW and BIOW the highest Ca concentration, and GWS the highest Al and Fe concentrations.

Mean concentrations of P_{HF} ranged from 3.6 g P kg⁻¹ to 12.8 g P kg⁻¹, decreasing in the order: GWS > FYM > BIOW > MSW. The C/P ratios were 86, 56, 47, and 21 in MSW₂₄, FYM₄₀, BIOW₄₆, and GWS₁₁₂, respectively. The P was mostly inorganic (average 83%) in OWP. The organic P concentration represented only 7%, 9%, and 16% of P_{HF} for BIOW₄₆, MSW₂₄, and GWS₁₁₂ respectively, with a higher value in FYM₄₀ (35%).

Table 3.2 Composition of municipal solid waste compost (MSW₂₄), biowaste compost (BIOW₄₆), compost of urban sewage sludge and green waste wood chips (GWS₁₁₂), and farmyard manure (FYM₄₀) of organic C, total N, total P (TP_{HF}), organic and inorganic P, $CaCO_3$, total Ca, total K, total Mg, total Na, total Al, total Fe, and total Mn. Values are mean \pm std. err. ($n = 10$). All one-way ANOVA P -values were ≤ 0.01 ; different letters (a, b, c) indicate significant differences among treatment ($\alpha = 0.05$). Subscript values in treatment abbreviations are the average annual rate of P application, in kg P ha⁻¹ yr⁻¹.

	MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂
Dry matter (%)	87 \pm 4	78 \pm 8	90 \pm 3	86 \pm 4
pH	7.6 \pm 0.2b	9.1 \pm 0.1a	8.1 \pm 0.2b	7.5 \pm 0.2b
Organic C (g kg⁻¹)	311 \pm 13a	324 \pm 20a	219 \pm 17b	267 \pm 13ab
Total N (g kg⁻¹)	17 \pm 1c	22 \pm 1ab	18 \pm 1bc	23 \pm 1a
TP_{HF} (mg kg⁻¹)	3597 \pm 234c	5779 \pm 357b	4683 \pm 511bc	12838 \pm 1017a
Organic P (mg kg⁻¹)	320 \pm 27b	2004 \pm 152a	353 \pm 46b	2097 \pm 172a
Inorganic P (mg kg⁻¹)	3277 \pm 214b	3775 \pm 213b	4330 \pm 482b	10741 \pm 857a
CaCO₃ (g kg⁻¹)	69 \pm 7a	47 \pm 5ab	82 \pm 20a	30 \pm 4b
Total K (g kg⁻¹)	11 \pm 1d	35 \pm 1a	21 \pm 1b	15 \pm 1c
Total Ca (g kg⁻¹)	58 \pm 3a	29 \pm 3c	56 \pm 7ab	41 \pm 4bc
Total Mg (g kg⁻¹)	8.3 \pm 1.3a	5.8 \pm 0.3ab	4.4 \pm 0.3b	4.9 \pm 0.2ab
Total Na (g kg⁻¹)	12.0 \pm 2.1a	7.6 \pm 0.8ab	6.1 \pm 0.6bc	4.4 \pm 0.4c
Total Al (g kg⁻¹)	16 \pm 1b	8 \pm 2c	25 \pm 2a	25 \pm 2a
Total Fe (g kg⁻¹)	9 \pm 1bc	7 \pm 1c	16 \pm 2ab	19 \pm 3a
Total Mn (g kg⁻¹)	0.25 \pm 0.02b	0.32 \pm 0.03ab	0.43 \pm 0.07a	0.42 \pm 0.04a

As a result of different OWP compositions, applied at about 2 t C ha⁻¹ yr⁻¹ on average

over the experimental period, cumulated inputs of organic C, total N, TP_{HF}, organic and inorganic P, CaCO₃, total Ca, total K, total Mg, total Na, total Al, total Fe, and total Mn differed across OWP treatments (Table 3.3). As an example, the repeated applications of BLOW₄₆ added more total Fe, total Al, total Ca and CaCO₃ to soil than other treatments. Total P inputs to 2016 ranged from 420 to 2008 kg P ha⁻¹, in MSW₂₄ and GWS₁₁₂, respectively, varying widely among OWP treatments due to the combining effects of different TP_{HF} concentrations and C/P ratios (Table 3.3). Among OWP treatments, the greatest cumulated inputs of organic C and total N were applied with GWS₁₁₂.

Table 3.3 Cumulative inputs of organic C, total N, total P (TP_{HF}), CaCO₃, total Ca, total K, total Mg, total Na, total Fe, total Al, and total Mn over 17 years of cultivation under fertilization of municipal solid waste compost (MSW₂₄), biowaste compost (BLOW₄₆), compost of urban sewage sludge and green waste wood chips (GWS₁₁₂), and farmyard manure (FYM₄₀). Values are mean ± std. err. (*n* = 10). Subscript values in treatment abbreviations are the average annual rate of P application, in kg P ha⁻¹ yr⁻¹.

	MSW ₂₄	FYM ₄₀	BLOW ₄₆	GWS ₁₁₂
Organic C (kg ha⁻¹)	35793	38640	37496	41432
Total N (kg ha⁻¹)	2029	2646	3052	3599
TP_{HF} (kg ha⁻¹)	420	699	819	2008
Organic P (kg ha⁻¹)	37	241	64	325
Inorganic P (kg ha⁻¹)	383	458	755	1683
CaCO₃ (kg ha⁻¹)	7996	5969	16764	4506
Total K (kg ha⁻¹)	1227	4315	3829	2323
Total Ca (kg ha⁻¹)	6823	3622	10480	6218
Total Mg (kg ha⁻¹)	1010	712	823	769
Total Na (kg ha⁻¹)	1409	931	1042	701
Total Fe (kg ha⁻¹)	1886	1053	4709	4039
Total Al (kg ha⁻¹)	1042	948	3066	2854
Total Mn (kg ha⁻¹)	29	40	84	65

3.3.2 Inorganic and organic P forms in organic waste product

Total P concentrations in NaOH-EDTA extract (P_{NE}; mean of 3 samples per OWP treatments) ranged from 2.3 to 9.7 g P kg⁻¹ and differed significantly among OWP, as did total concentrations of inorganic and organic P forms 3.4. However, there were no significant differences in concentrations of individual P forms among the OWP samples. The P recovery by NaOH-EDTA extraction was 66% of TP_{HF} on average for all OWP, with no significant differences among the type of OWP (Table 3.4). The P-NMR analysis detected inorganic P forms (orthophosphate, pyrophosphate, and polyphosphate), and organic P forms (Figure SI-3.1; Table 3.4). For the latter, identified orthophosphate monoester compounds included *myo*-, *scyllo*-, *neo*-, and *D-chiro* inositol hexakisphosphate (IHP), phosphatidylcholine, and

glucose 6-phosphate (Table SI-3.2). Other peaks in the orthophosphate monoester region that could not be assigned to specific P compounds were divided into three categories (Other monoesters 1, 2, and 3). Orthophosphate diesters were divided into DNA and two regions of the spectra for peaks that could not be assigned to specific P compounds. Also identified were α - and β -glycerophosphates and mononucleotides, which are degradation compounds of orthophosphate diesters. These represented 2.3% of P_{NE} .

Table 3.4 Concentration of P (P_{NE}) in NaOH-extracts and concentration of main classes of inorganic and organic P forms determined by P-NMR of municipal solid waste compost (MSW₂₄), biowaste compost (BIOW₄₆), compost of urban sewage sludge and green waste wood chips (GWS₁₁₂), and farmyard manure (FYM₄₀). Values are mean \pm std. err. of samples applied in 1998, 2004 and 2011 ($n = 3$). Different letters (a, b) indicate significant differences among treatments ($\alpha = 0.05$). Subscript values in treatment abbreviations are the average annual P application rate, in kg P ha⁻¹ yr⁻¹. mono: monoesters; glycer: glycerophosphate

	MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	<i>P</i> -value
P_{NE} (kg P kg⁻¹)	2.4 \pm 0.2b	3.8 \pm 0.5b	2.3 \pm 0.3b	9.7 \pm 2.0a	0.0006
P_{NE}/TP_{HF} (%)	59 \pm 6	71 \pm 5	59 \pm 14	75 \pm 13	0.18
P-NMR results on inorganic P forms (mg P kg⁻¹)					
Orthophosphate	1944 \pm 213	3124 \pm 474	2041 \pm 256	8817 \pm 1759	0.09
Pyrophosphates	20 \pm 4	36 \pm 11	3 \pm 2	43 \pm 34	0.49
Polyphosphates	22 \pm 5	42 \pm 2	21 \pm 4	45 \pm 2	0.55
All inorganic P	1986 \pm 222b	3202 \pm 485b	2065 \pm 258ab	9805 \pm 1779a	0.011
P-NMR results on organic P forms (mg P kg⁻¹)					
Phosphonates	47 \pm 17	41 \pm 11	40 \pm 21	85 \pm 27	0.62
Orthophosphate monoesters					
<i>myo</i> -IHP ^w	78 \pm 31	97 \pm 29	26 \pm 8	110 \pm 29	0.08
<i>scyl</i> -IHP	3 \pm 3	6 \pm 3	2 \pm 2	7 \pm 7	0.92
<i>neo</i> -IHP	nd ^x	nd	3 \pm 3	nd	nd
<i>chiro</i> -IHP	2 \pm 2	8 \pm 8	3 \pm 3	nd	0.79
Glucose 6-P	5 \pm 1	6 \pm 3	4 \pm 2	27 \pm 3	0.25
Choline phosphate	3 \pm 3	2 \pm 2	1 \pm 1	16 \pm 8	0.69
Other mono 1^y	41 \pm 6	49 \pm 5	45 \pm 18	131 \pm 31	0.23
Other mono 2	114 \pm 9	135 \pm 23	72 \pm 6	300 \pm 75	0.05
Other mono 3	4 \pm 2	15 \pm 3	10 \pm 2	8 \pm 8	0.34
All monoesters	251 \pm 24	317 \pm 59	165 \pm 21	598 \pm 123	0.72
Orthophosphate diesters					
DNA	4 \pm 2	13 \pm 8	6 \pm 2	4 \pm 4	0.57

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Table 3.4 – Continued from previous page

	MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	P-value
α-glycero	5±1	30± 4	6± 1	16±8	0.57
β-glycero	20±5	62±15	10±3	28±5	0.53
Nucleotides	34±14	55±3	20±2	62±20	0.68
Other diesters 1^z	8±3	20±7	10±5	13±5	0.99
Other diesters 2	4±3	9±3	6±2	25±11	0.42
All diesters	76±19	190±27	58±7	147±44	0.09
All organic P	373±4b	548±39ab	263±16b	830±190a	0.004

^w Inositol hexakisphosphates (IHP): sum of *myo*-, *scyllo*-, *neo*-, *D-chiro*-IHP stereoisomers;

^x nd: not detected;

^y Other orthophosphate monoesters are peaks in the monoester region not specifically identified;

^z Other diesters include phospholipids, α and β glycerophosphates (products of phospholipid degradation), nucleotides and unidentified orthophosphate diester.

The P_{NE} was predominantly inorganic P forms (range of 85–91%, 87% on average, of which orthophosphate average 98%). Organic P forms represented only 13% on average (9-15%), as orthophosphate monoesters (58–72%, 65% on average), diesters P (18-35%, 24% on average) and phosphonates (8-15%, 11% on average). Within the orthophosphate monoester region spectra, 69% of the peak area belong to peaks that could not be assigned to specific compounds. The IHP stereoisomers accounted for 26% of all orthophosphate monoesters, i.e., 2.4% of P_{NE} on average of OWP, with *myo*-IHP the dominant form (90%).

3.3.3 Physicochemical properties of soils

The (OWP×Y) interaction of OWP treatments and years of soil sampling (Y) was significant for pH in water, SOC, total N, CEC and exchangeable cations concentrations (Ca, K, Mg; Table 3.1). For a given soil property, values did not differ significantly in 1998 (before any OWP applications; Table 3.5). For example, in 1998 soil pH was not different among plots, ranging from 7.0 ±0.1 to 7.2 ±m0.1. In 2015, the pH had significantly increases for the MSW₂₄ (7.8 ±0.0), FYM₄₀ (7.4 ±0.0) and BIOW₄₆ (7.8 ±0.0) treatments, but was unchanged for the GWS₁₁₂ treatment (Table 3.5). Both SOC and total N increased in GWS₁₁₂, of +60% and +25% respectively. Another significant change was observed for exchangeable K concentration in the FYM₄₀ plots, which increased from 0.46 to 1.02 cmol_c kg⁻¹ between 1998 and 2016. In CON₃, all soil properties values lowered significantly in 2016 in comparison to those observed in 1998, except for Mg concentration which remain stable.

Table 3.5 General properties, P status and P-NMR results of the soil plough layer showing significant Y×F interactions of sampling years (Y: 1998, 2015 (general soil properties) or 2016 (soil P status and P-NMR results)) and OWP treatments (OWP: MSW₂₄, FYM₄₀, BIOW₄₆, GWS₁₁₂) with two-way ANOVA. Values are means ± std. err. (*n* = 4). Different lower case letters (a, b, etc.) indicate significant differences among treatments and year (α = 0.05). No letter indicates no significant difference. MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript values in treatment abbreviations are the average rates of annual P application, in kg P ha⁻¹ yr⁻¹.

Soil properties	Y	OWP			
		MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂
Main soil properties					
pH in water	1998	7.0±0.1c	7.0±0.1c	7.2±0.1bc	7.0±0.1c
	2015	7.8±0.0a	7.4±0.0b	7.8±0.0a	7.0±0.0c
Organic C (g C kg⁻¹)	1998	10.4±0.3d	10.6±0.1d	10.8±0.3d	10.6±0.5d
	2015	13.2±0.1c	14.8±0.2b	16.5±0.1a	16.9±0.4a
Total N (g N kg⁻¹)	1998	1.09±0.02d	1.14±0.02d	1.13±0.03d	1.09±0.03d
	2015	1.25±0.02c	1.37±0.01b	1.62±0.01a	1.66±0.04a
CEC (cmol+ kg⁻¹)	1998	9.3±0.4c	9.8±0.4bc	9.8±0.4bc	9.4±0.3c
	2015	10.5±0.2b	10.5±0.2b	12.0±0.2a	10.7±0.2b
Ca (cmol+ kg⁻¹)	1998	7.9±0.2d	8.4±0.3d	8.4±0.3cd	8.1±0.2d
	2015	10.3±0.3b	9.2±0.2c	11.4±0.2a	10.1±0.3b
Mg (cmol+ kg⁻¹)	1998	0.48±0.02d	0.52±0.02d	0.50±0.03d	0.48±0.06d
	2015	0.52±0.02d	0.98±0.04a	0.68±0.02c	0.76±0.03b
K (cmol+ kg⁻¹)	1998	0.42±0.01cd	0.46±0.02cd	0.47±0.03cd	0.43±0.04cd
	2015	0.38±0.01d	1.02±0.03a	0.66±0.02b	0.48±0.03c
Soil P status					
TP_{HF} (mg P kg⁻¹)	1998	669±25b	676±19b	652±19b	658±32b
	2016	679±21b	723±22b	750±24b	1133±27a
SIP (mg P kg⁻¹)	1998	520±35b	509±12b	483±44b	494±29b
	2016	440±51b	493±50b	566±38b	938±58a
P_{NE} (mg P kg⁻¹)	1998	323±10bc	338±17b	344±10b	312±17bc
	2016	298±12bc	336±16b	343±16b	717±20a
P_{NE}/TP_{HF} (%)	1998	48±2bc	50±3bc	53±1b	47±1bc
	2016	44±2c	47±2bc	46±2c	63±1a
CP (mg P L⁻¹)	1998	0.9±0.1cd	1.2±0.2bc	1.0±0.1bcd	1.1±0.1bcd
	2016	0.6±0.1d	1.5±0.2b	0.9±0.1cd	2.4±0.1a
Olsen-P (mg P kg⁻¹)	1998	38±2bc	43±3bc	43±3bc	38±4bc
	2016	30±1c	50±2b	45±2b	87±4a
Soil P-NMR analysis in NaOH-EDTA extract (mg P kg⁻¹)					
All inorganic P	1998	245±8b	267±19b	270±10b	241±15b
	2016	224±12b	272±19ab	277±15ab	617±20a
All organic P	1998	78±5b	71±5b	75±2b	71±6b
	2016	74±4b	65±3b	66±3b	100±2a

3.3.4 Crop yields, P concentration in grains and P exported

The means of annual grain yields, grain P concentrations and annual amounts of P exported are shown in Figure 3.3a, 3.3b, 3.3c, respectively, for all treatments over the 17 years of cropping.

The overall average of grain yield was $8.2 \pm 1.3 \text{ t ha}^{-1} \text{ yr}^{-1}$. There were no significant differences (P -value = 0.65) in annual grain yields for all crops among urban composts and farmyard manure (Figure 3.3a). However, without P fertilization the annual grain yield was significantly lower (P -value = 0.002), $7.5 \pm 1.6 \text{ t ha}^{-1} \text{ yr}^{-1}$. This decrease compared to OWP treatments started to differentiate in 2005 and tended to accelerate thereafter. As a result, the sum over years of cropping of annual grain yields was significantly lower (P -value < 0.001) in the CON₃ treatment rather than in the four other treatments.

The average grain P concentration was $3.1 \pm 0.6 \text{ g P kg}^{-1}$ for all years and crops, and varied across years and crops (Figure 3.3b). Grain P concentrations were higher in barley ($4.1 \pm 0.3 \text{ g P kg}^{-1}$) than wheat ($3.2 \pm 0.5 \text{ g P kg}^{-1}$) and maize ($2.7 \pm 0.3 \text{ g P kg}^{-1}$). There was a significant year effect on grain P concentration in grains (P -value < 0.0001) which slightly increased by $0.046 \pm 0.006 \text{ g P kg}^{-1} \text{ yr}^{-1}$ irrespective of OWP treatment.

The overall average of P exported annually in harvest was $26.6 \pm 5.9 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. It was comparable among crops (P -value = 0.35) with $24 \pm 4 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ for P exported in maize grain, and 28 ± 6 , and $30 \pm 8 \text{ kg P ha}^{-1} \text{ yr}^{-1}$, for P exported in wheat and barley yield plus 2/3 of stubble, respectively (Figure 3.3c).

The values of cumulative budgets between P applied and P exported for the 17 years of cropping were -329 ± 15 , -9 ± 14 , 229 ± 13 , 372 ± 18 and $1544 \pm 26 \text{ kg ha}^{-1}$ for the CON₃, MSW₂₄, FYM₄₀, BIOW₄₆, and GWS₁₁₂ treatments, respectively.

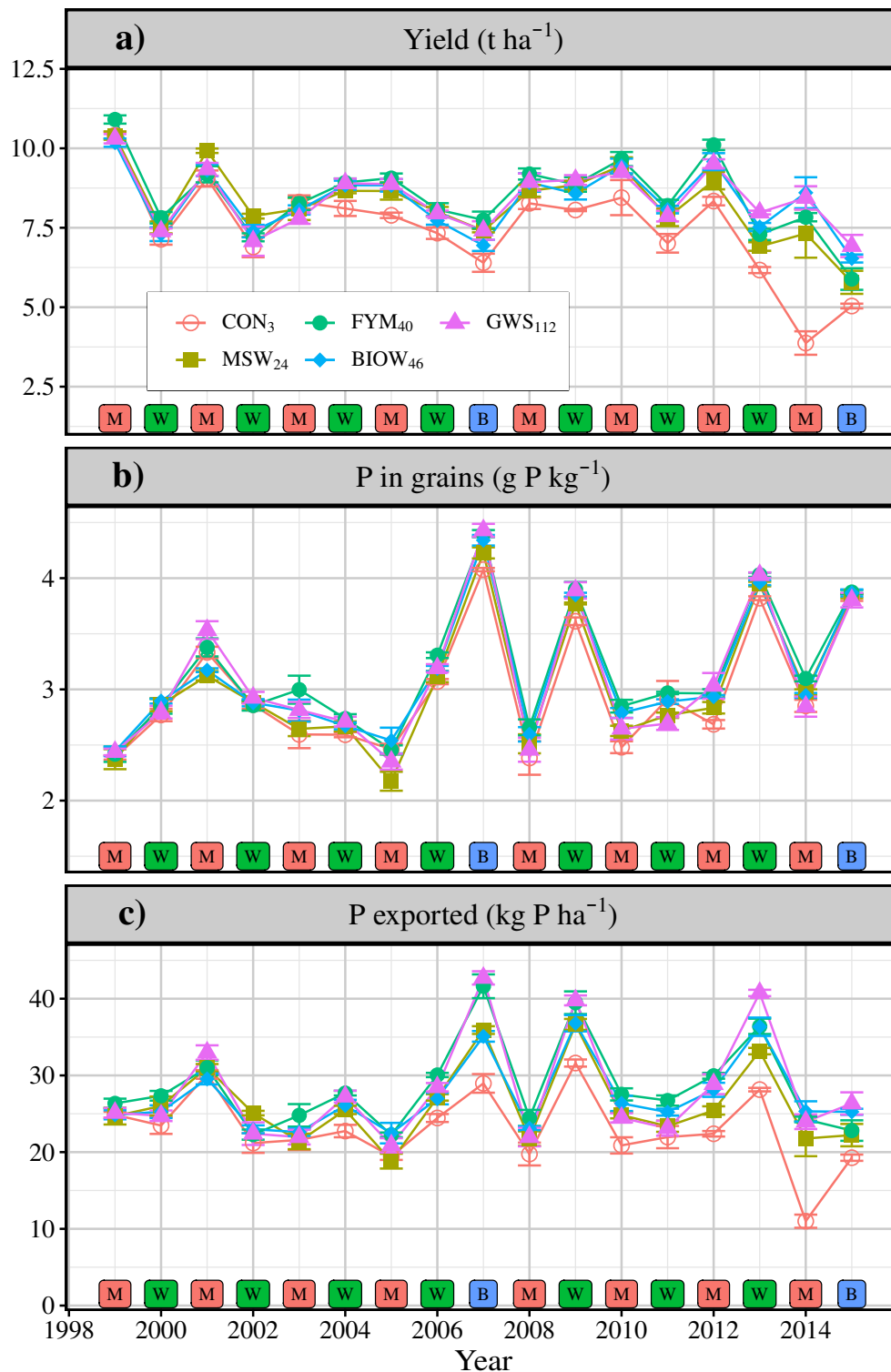


Figure 3.3 (a) Annual grain yield (t ha⁻¹), (b) grain phosphorus (P) concentration (g P kg⁻¹), and (c) amount of P exported in grain and aboveground biomass (kg P ha⁻¹) over 17 years of cultivation and OWP treatments. Dots are means ($n = 4$) with error bars are standard error. CON₃: control; MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript values in treatment abbreviations are the average amount of P applied annually (kg P ha⁻¹ yr⁻¹). M: maize; W: wheat; B: barley.

3.3.5 Soil P status

The OWP×Y interaction was significant for the TP_{HF}, SIP, P_{NE}, C_P, and Olsen-P concentrations but was not significant for SOP concentration (Tables 3.1, 3.5). In 1998, TP_{HF} concentrations ranged from 652 ±19 to 676 ±10 mg P kg⁻¹ and did not differ significantly among plots prior to OWP fertilization treatments (Table 3.5). In 2016, TP_{HF} concentrations were significantly increased compared with 1998 concentrations only for the GWS₁₁₂ treatments, which increased by (+72%). The same trend was observed for concentrations of SIP, and P_{NE} (Table 3.5). The initial mean of C_P was 1.0 mg L⁻¹ and then ranged from 0.6 to 2.4 mg L⁻¹ in 2016. Also, the initial Olsen-P concentration was 40 mg kg⁻¹ and ranged between 30 and 87 mg kg⁻¹ in 2016. Without fertilizer application (the CON₃ treatment), the concentrations of all analyzed P pools except SIP significantly decreased between 1998 and 2016 (Table 3.6).

Table 3.6 Effects of sampling year (Y) of soil plough layer on main soil properties (Y: 1998 and 2015) and on P status and P-NMR results (Y: 1998 and 2016) for the control treatment without P fertilization. Values are means ± std. err. (*n* = 4). Different upper case letters (A, B) indicate significant differences among treatments and year (α = 0.05). No letter indicates no significant difference.

	1998	2015 or 2016	ANOVA
Main soil properties			
pH in water	7.1±0.0A	6.8±0.1B	0.039
SOC (g C kg⁻¹)	10.7±0.1A	10.0±0.1B	0.003
Total N (g N kg⁻¹)	1.14±0.02A	0.98±0.02B	0.001
CEC (cmol+ kg⁻¹)	10.1±0.5A	8.6±0.3B	0.005
Ca (cmol+ kg⁻¹)	8.7±0.3A	8.2±0.4B	0.034
Mg (cmol+ kg⁻¹)		0.47±0.02	0.14
K (cmol+ kg⁻¹)	0.45±0.01A	0.28±0.01B	<0.0001
Soil P status			
TP_{HF} (mg P kg⁻¹)	646±15A	609±12B	0.015
SIP (mg P kg⁻¹)		458±23	0.25
SOP (mg P kg⁻¹)		169±15	0.45
P_{NE} (mg P kg⁻¹)	323±13A	263±8B	0.005
P_{NE}/TP_{HF} (%)	50±2A	43±1B	0.013
C_P (mg P L⁻¹)	0.95±0.08A	0.52±0.04B	0.011
Olsen-P (mg P kg⁻¹)	38±2A	25±2B	0.002
P-NMR results of inorganic P forms (mg P kg⁻¹)			
Orthophosphate		213±13	0.62

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Table 3.6 – Continued from previous page

	1998	2015 or 2016	ANOVA
Pyrophosphate		2.8±0.3	0.53
Polyphosphates		4.5±0.2	0.28
All inorganic P forms	248±13A	191±9B	0.030
P-NMR results of organic P forms (mg P kg⁻¹)			
Phosphonates		5.6±0.8	0.46
Orthophosphate monoesters			
<i>myo</i> -IHP ^x		13±1	0.89
<i>scyllo</i> -IHP		3.6±0.5	0.14
<i>neo</i> -IHP		1.6±0.4	0.99
<i>chiro</i> -IHP		1.4±0.6	0.97
Glucose 6-phosphate		0.93±0.13	0.14
Choline phosphate		1.1±0.1	0.10
Other monoesters 1 ^y		3.4±0.4	0.05
Other monoesters 2		26±2	0.20
Other monoesters 3		1.6±0.2	0.49
All monoester		52±4	0.09
Orthophosphate diesters			
DNA		0.64±0.17	0.54
α-glycerophosphate		2.1±0.3	0.57
β-glycerophosphate		3.5±0.3	0.50
Nucleotides		6.8±0.6	0.55
Other diesters 1 ^z		1.3±0.4	0.08
Other diesters 2		0.75±0.09	0.35
All diesters		15±1	0.69
All organic P forms	75±8A	72±7B	0.028

^x Inositol hexakisphosphates (IHP): sum of *myo*-, *scyllo*-, *neo*-, D-*chiro*-IHP stereoisomers;

^y Other orthophosphate monoesters are peaks in the monoester region not specifically identified;

^z Other diesters include phospholipids, α and β glycerophosphates (products of phospholipid degradation), nucleotides and unidentified orthophosphate diester.

The OWP × Y interaction was not significant for SOP concentration (Table 2.1, 3.7). The average SOP concentration was significantly lower (*P*-value = 0.012) in 1998 (161 ± 8 mg P kg⁻¹) than in 2016 (206 ± 15 mg P kg⁻¹), and did not differ significantly among fertilization treatments.

3.3.6 Soil P speciation by P-NMR analysis of NaOH-EDTA extracts

Extraction with NaOH-EDTA recovered about 50% in average of the TP_{HF} concentration of soils sampled in 1998, with no significant differences among plots (P_{NE}/TP_{HF} ; Table 3.5). This ratio was not significantly different in 2016 compared to 1998 for the MSW_{24} and FYM_{40} treatments, but was significantly lower in 2016 than 1998 for the $BIOW_{46}$ treatment and was significantly higher in 2016 than 1998 for the GWS_{112} treatment. There was a significant difference in P_{NE} concentration only for the GWS_{112} treatment in 2016, which was significantly higher than in 1998 and compared to all other treatments for both dates. Without P fertilization, both the P_{NE} concentration and the P_{NE}/TP_{HF} ratio decreased in 2016 compared to 1998 (Table 3.6).

The soil P speciation by P-NMR analysis in NaOH-EDTA solution showed similar peaks among all years of soil sampling and OWP treatments (Table SI-3.2). In all spectra, the dominant peak was for orthophosphate. Calculation of relative species composition indicated that 77% of P_{NE} was inorganic (97% as orthophosphate ions); 23% of P_{NE} was organic, divided into orthophosphate monoesters (70%), orthophosphate diesters (22%), and phosphonates (8%). An important proportion (62%) of orthophosphate monoesters and 14% of the orthophosphate diesters were not identified. Degradation of orthophosphate diesters to orthophosphate monoesters accounts for 3.9% of P_{NE} .

The OWP and Y factors had generally no significant interactive effect on soil inorganic and organic P forms concentrations, except summing all inorganic and organic P forms (Table 3.1). The summed concentration of all inorganic P forms followed the same trend as concentration of TP_{HF} , SIP, P_{NE} , C_P , and Olsen-P (Table 3.5). The summed concentration of all organic P forms did not differ significantly among years of soil sampling and OWP treatments except for GWS_{112} , for which there is a significant increase from 1998 to 2016 (Table 3.5).

Table 3.7 Soil organic P concentration (SOP) and inorganic and organic P forms in soil NaOH-EDTA extracts analyzed by P-NMR for which there were no significant interactions of sampling year (Y: 1998 or 2016) and OWP treatments (OWP: MSW₂₄, FYM₄₃, BIOW₄₆, or GWS₁₁₂) with two-way ANOVA. Values are means \pm std. err. (mean by treatments: $n = 8$; mean over all: $n = 32$). Different lower case letters (a, b) indicate significant differences among treatments within a year, while different upper case letters (A, B) indicate significant differences among years within a treatment ($\alpha = 0.05$). No letter indicates no significant difference. MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript values in treatment abbreviations are the average rate of annual P application, in kg P ha⁻¹ yr⁻¹.

P forms (mg P kg ⁻¹)	Y			OWP		
	1998	2016		MSW ₂₄	FYM ₄₀	BIOW ₄₆ GWS ₁₁₂
SOP	161 \pm 8B	206 \pm 15A				187 \pm 11
Orthophosphate	P-NMR results of inorganic P forms					
Pyrophosphate	246 \pm 7B	338 \pm 41A				292 \pm 22
Polyphosphates			4.1 \pm 0.3			
			5.4 \pm 0.3			
Phosphonates	P-NMR results of organic P forms					
			5.4 \pm 0.3			
	Orthophosphate monoesters forms					
<i>myo</i> -IHP ^x	11.4 \pm 0.5B	14.4 \pm 1.2A				12.9 \pm 0.7
<i>scyllo</i> -IHP			3.3 \pm 0.2			
<i>neo</i> -IHP			1.1 \pm 0.2			
<i>chiro</i> -IHP			0.8 \pm 0.2			
Glucose 6-phosphate	0.82 \pm 0.06B	0.99 \pm 0.1A				0.9 \pm 0.1

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P forms (mg P kg ⁻¹)	Y			OWP			
	1998	2016		MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂
Choline phosphate				0.9±0.1			
Other monoesters 1 ^γ	3.0±0.4B	4.4±0.5A				3.7±0.3	
Other monoesters 2			28±1				
Other monoesters 3			1.5±0.2				
All monoesters			53±2				
				Orthophosphate diester forms			
DNA				0.3±0.1			
α-glycerophosphate				1.8±0.1			
β-glycerophosphate				3.5±0.2			
Nucleotides				8.0±0.3			
Other diesters 1 ^z				1.4±0.1			
Other diesters 2				0.9±0.1			
All diesters				16±1			

^x Inositol hexakisphosphates (IHP): sum of *myo*-, *scyllo*-, *neo*-, *D-chiro*-IHP stereoisomers;

^γ Other orthophosphate monoesters are peaks in the monoester region not specifically identified;

^z Other diesters include phospholipids, α and β glycerophosphates (products of phospholipid degradation), nucleotides and unidentified orthophosphate diester.

There were no significant $Y \times \text{OWP}$ interactions for any soil P forms or pools determined by P-NMR, except total inorganic P and total organic P (Table 3.1). Concentrations of total inorganic P were greater for the GWS_{112} treatment in 2016 than 1998, and were greater than the MSW_{24} treatment only in 2016 (Table 3.5). This is consistent with the results in Table SI-3.6 (reported as % of P_{NE}). Concentrations of total organic P were greater for the GWS_{112} treatment in 2016 than 1998, and were greater for the GWS_{112} treatment than all other OWP treatments in 2016 (Table 3.5). This differences from the results in Table SI-3.6 (reported as % of P_{NE}), showing GWS_{112} to be lower than all other treatments and dates. In the control plots without P fertilization (CON_3), both the concentration and percentage of total inorganic P decreased in 2016 (248 mg P kg^{-1} , 77%) compared to 1998 (191 mg P kg^{-1} , 73%; Tables 3.6, SI-3.6). However, while the concentration of total organic P decreased from 2016 compared to 1998 (from 75 to 72 mg P kg^{-1} ; Table 3.6), the relative percentage increased, from 23 to 27% (Table SI-3.6).

For the OWP treatments and the untreated control, the concentrations of most P species and/or compound classes were not affected by either years or fertilization treatment. For OWP treatments, concentrations of orthophosphate, *myo*-IHP, and the general Other monoesters 1 region were significantly greater in 2016 compared to 1998, as were the percentages of P_{NE} , while the concentration of glucose 6-phosphate was greater but not the percentage (Tables 3.7, SI-3.6). The orthophosphate concentration increased significantly from 246 mg P kg^{-1} in 1998 to 338 mg P kg^{-1} in 2016 (Table 3.7). The total concentration of IHP stereoisomers content was $18 \pm 5 \text{ mg P kg}^{-1}$, accounting for 34% of all orthophosphate monoesters (23% of all organic P forms in P_{NE}); the *myo*-IHP stereoisomer accounted for 71% of total IHP. The concentrations or percentages of P species were not affected by OWP fertilizer treatment, or by no fertilization in the control treatment (Tables 3.6, 3.7, SI-3.6).

3.4 Discussion

This study examined cumulated effects of ten applications of three urban composts, a farmyard manure on soil P concentration, availability and speciation from 1998 to 2016. In the control treatment, we analyzed the effects of not applying any of these OWP over the same cropping period Few studies have analyzed P speciation in OWP and its effect soil P speciation, and none after multiple years of cropping. Given differences in OWP composition and application rates (on average about $2 \text{ t C ha}^{-1} \text{ yr}^{-1}$), the average of annual P inputs for 17 years of cropping were of 3, 24, 40, 46, and $112 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ for CON_3 , MSW_{24} , FUM_{40} , BIOW_{46} , and GWS_{112} , respectively.

3.4.1 Considerable input of P applied as GWS

It is worth noting that GWS has a high P concentration with a low C/P, which lead to a huge P input of $112 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ when applying $2 \text{ t C ha}^{-1} \text{ yr}^{-1}$. This high P concentration is explained by the presence of the urban sewage sludge, which was obtained by the most common methods of P removal from municipal waste water, enhanced biological P removal, i.e. activated sludge (Staal et al. 2019), and precipitation by aluminum (Al) and/or iron (Fe) salts (Atees 2016). This is shown by the high total Al and Fe concentrations (Table 3.2) and high Fe and Al concentrations in NaOH-EDTA extracts of GWS (Table 3.4) and GWS-fertilized soils (Table SI-3.6). The P inputs from other OWP were comparable to those of many European long-term field experiments where different OWP were applied at C rates. For example, in the Annaheim et al. (2015) study, cattle manure and compost were applied at $2.5 \text{ t C ha}^{-1} \text{ yr}^{-1}$, which added 23 and $41 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ respectively. Likewise, in (Pizzeghello et al. 2014), farmyard manure was applied at $40 \text{ t DM ha}^{-1} \text{ yr}^{-1}$, adding $43 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. In Vanden Nest et al. (2014), three compost types (vegetable, fruit and garden waste compost; farm composts with high or low C/N), dairy cattle slurry, and farmyard manure, all applied at almost $3 \text{ t C ha}^{-1} \text{ yr}^{-1}$, added between 49 and $69 \text{ kg P ha}^{-1} \text{ yr}^{-1}$. When different OWP (urban composts, urban sewage sludge, farmyard manure) were applied at $170 \text{ kg organic N ha}^{-1} \text{ 2yrs}^{-1}$, annual P inputs, were smaller, from 17 to $45 \text{ kg P ha}^{-1} \text{ yr}^{-1}$ (Chen et al. 2022).

3.4.2 Phosphorus speciation in organic waste products

The TP_{HF} concentration (Table 3.2) differed strongly among the studied OWP (Table 3.3) but were predominantly inorganic P (83% of TP_{HF}) and only 17% was organic P, with values ranging from 9% in MSW_{24} to 35% in FYM_{40} . This distribution is in accordance with previous published results (Hansen et al. 2004; Requejo and Eichler-Löbermann 2014). Similar distributions were also observed in P_{NE} after P-NMR analysis with 87% as inorganic P forms (98% as orthophosphate) and 13% as organic P forms; organic P compounds were on average 65% orthophosphate monoesters, 24% orthophosphate diesters, and 11% phosphonates. This general distribution among the main classes of P compounds agreed well with previous studies where compost of green waste and dairy manure were analyzed similarly, i.e., P-NMR analysis after extraction with NaOH-EDTA (Hansen et al. 2004; He et al. 2007; Annaheim et al. 2015). Various factors can affect OWP composition such as raw materials, animal diet, dry or wet form, composting duration, heat treatment, etc. (Benoît et al. 2014). For example, McDowell et al. (2008) reported a parallel in animal feed and P in produced manure: a grain based diet over forage increased the *myo*-IHP concentration. In addition, the composting process tends to reduce the

proportion of polyphosphate and pyrophosphate (Ajiboye et al. 2007; Galvez-Sola et al. 2010).

3.4.3 Modifications of soil properties

Associated C, N, K, Ca, and Mg inputs from OWP applications (Table 3.3) increased SOC, total N, K, Ca, and Mg and CEC in the soil plough layer (Table 3.5). As an example, SOC concentration soils treated with OWP were linearly related to cumulated C input. These results are consistent with those of previous studies, showing that soils fertilized with different manure types had higher concentrations of SOC, P, K, Ca and Mg in topsoils (Edmeades 2003; Herencia et al. 2007; Möller 2018; Chen et al. 2022). Zavattaro et al. (2017), reviewing effects of repeated applications of cattle manure in 80 long-term European field experiments, reported marked increases in SOC and soil N. A consequence of the increase of soil organic matter is that some soil biological (microbial biomass; earthworms) and physical (soil water retention; air permeability) properties are also improved (Edmeades 2003; Eden et al. 2017; Paradelo et al. 2019). The MSW, FYM and BIOW applications increased soil pH compared to soils without alkaline OWP due to their high amounts of basic cations and CaCO₃, as has been reported for other alkaline organic amendments (Rusli et al. 2022).

3.4.4 Effects of OWP treatments on time series crop data

Grain yields (overall average: 8.2 t ha⁻¹ yr⁻¹) were of the same order of magnitude to those recorded in general for France (Agreste 2022), which were 9.3, 7.0, 6.2 t DM ha⁻¹ for non-irrigated maize, wheat and barley cropped in average of 2020 and 2021. Similar yields were also observed in other countries with comparable climate conditions (Eghball et al. 2004; Cadot et al. 2018). No significant effect was found on annual grain yields after applying OWP regardless of crop species (Figure 3.3a). This result is in accordance with that of Herencia et al. (2007) in which different vegetal compost and green residue of previous crops, applied repeatedly in a Spanish calcareous loamy soil, did not significantly impact crop yield. By contrast, grain yield, but not grain P content, decreased slightly but systematically in control-plots from 2003 for all crop species (Figure 3.3b). Given the high grain P concentration even for the control plot (see the following paragraph), it is unlikely that P was the factor limiting grains yields in CON₃. It is more likely that the application rate of mineral N fertilizer was insufficient to ensure optimal yield in the control plots. The decline in grain yields in CON₃ over years led to a lower dilution of P (Lemaire et al. 2019; Morel et al. 2021), which explains the absence of a grain P concentration decrease.

The overall means of grain P concentrations were 2.7, 3.2, and 4.1 g kg⁻¹ DM for maize, wheat, and barley, respectively (Figure 3.3b), which were not significantly affected by OWP treatments. These values are similar to those found in other experiments located on different soils types. Cadot et al. (2018) using a long-term Swiss field experiment located on a Gleyic Cambisol that P concentrations in grain, ranged from 1.9 to 2.4 g kg⁻¹ DM for maize and 3.8 to 4.5 g kg⁻¹ DM for winter wheat depending on P fertilization rate. In addition, Tang et al. (2008) reported grain P concentrations of 2.8-3.5 for wheat and 2.0-2.8 g P kg⁻¹ for maize for various combinations of N, P and K fertilizer in five Chinese field experiments. Evaluating the 17-year effects of OWP applied to a French silty loam Calcosol, Chen et al. (2022) found that grain P concentration for maize, and wheat were 2.7 and 3.9 g kg⁻¹ DM, respectively. All these P concentrations were generally higher than reference values in the French fertilization guidelines to manage P applications (COMIFER 2009), which are 2.6 g kg⁻¹ DM for maize and 2.8 g kg⁻¹ DM for wheat and barley.

3.4.5 Changes in topsoil P status and relationship with P budget

Phosphorus extracted in different soil P pools, i.e. TP_{HF}, SIP, P_{NE}, P-NMR orthophosphate, C_P, and Olsen-P (Table 3.5), are all closely correlated two-by-two by Pearson's correlation (Figure SI-3.2) with variables values in relation to cumulated P inputs in OWP. We calculated the P budget at the plot scale to evidence eventual decrease or increase in soil P concentration in relation to OWP applications. This field-scale mass balance approach provides a quantitative analysis of the effects of fertilizers applications on soil P, which is of special interest to understand changes in soil P concentration and to evaluate the sustainability of cropping systems (Öborn et al. 2003).

Using the plough layer depth of 25 cm, and bulk density determined in 2013 (1.32 g cm⁻³) to calculate P stocks, we found strong linear relationships between cumulated P budget and stocks of TP_{HF}, SIP, P_{NE}, and P-NMR orthophosphate (Figure 3.4). For a given pool, stocks from different OWP treatments fell on the same regression line, suggesting that they are all equally effective as P sources, their efficiency depending only on applied P rates. The slope of the linear regression did not differ significantly from 1:1 line (bissectrice), meaning that 100% of the P removed by crops or applied in excess was recovered in pools of TP_{HF}, SIP, P_{NE}, and P-NMR orthophosphate. It means that one kg P ha⁻¹ of P budget would affect these different soil P stocks by 1 kg ha⁻¹. So, there is a strict correspondence between stock and budget for all these pools, which differed only by the intercepts (i.e. soil P stock when P budget is nil) for each regression.

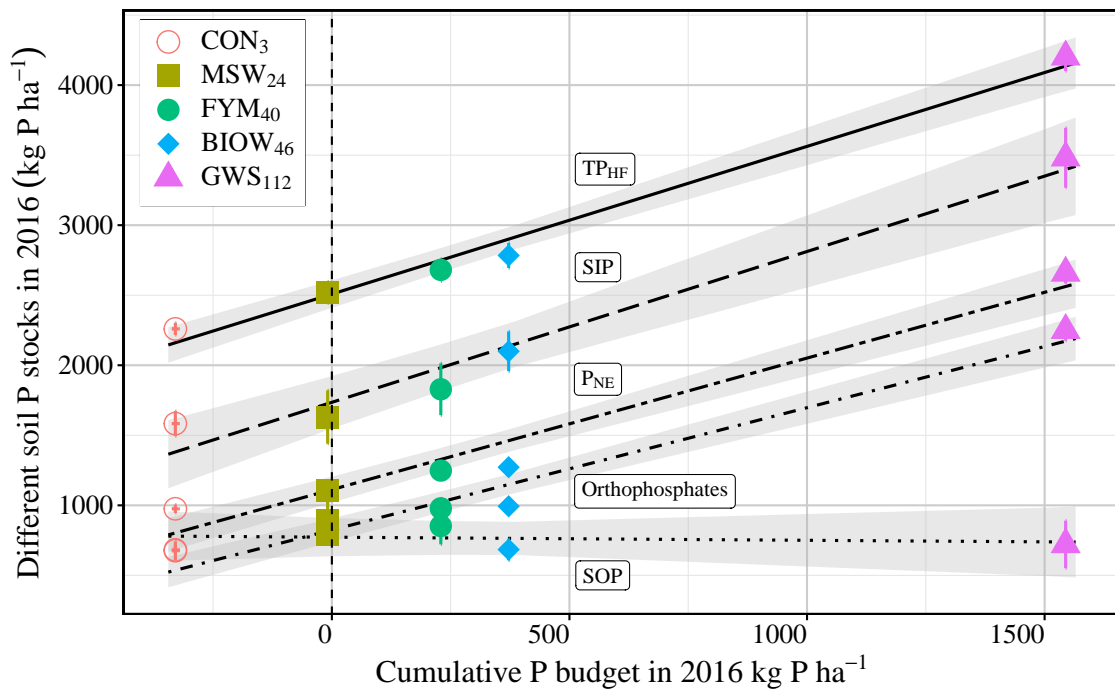


Figure 3.4 Total soil P (TP_{HF}), soil inorganic P (SIP), P in NaOH-EDTA extraction (P_{NE}), and orthophosphate (P-NMR results) stocks ($kg P ha^{-1}$) in the soil plough layer (0 – 25 cm) in relation to the cumulative P budget (B_{cum}) in 2016 for the different treatments. Dots are means ($n = 4$) with standard error (error bar). CON_3 : control (no P applied); MSW_{24} : municipal solid waste compost; FYM_{40} : farmyard manure; $BIOW_{46}$: biowaste compost; GWS_{112} : green waste wood chips and sewage. Subscript values in treatment abbreviations are the average amount of P applied annually ($kg P ha^{-1} yr^{-1}$).

Significant linear relationships were also observed in 2016 between the cumulated P budget and plant-available soil P assessed by water-soluble P ($C_P: 0.0010 \pm 0.0001 \times B_{cum} + 0.82$; $R^2 = 0.78$) and Olsen-P ($0.124 \pm 0.008 \times B_{cum} + 130$; $R^2 = 0.93$; Figure SI-3.3). Those linear regressions were comparable to previously reported results in other cropped soils receiving either zero or increasing application rates of superphosphate (Boniface and Trocmé 1988; Blake et al. 2003; Messiga et al. 2010), or poultry litter applications (Shepherd and Withers 1999). Relationships depended on the method to determine soil test P (C_P , Olsen-P, Mehlich III) but, for a given test, linear regression was irrespective of increasingly cropping periods (Messiga et al. 2010). However, differences in experimental variability were found with lower R^2 values in our study. This difference may be because repeated OWP applications modified soil properties; this in turn would alter the transfer of phosphate ions at the solid-to-solution interface (sorption-desorption), which would affect C_P values and extraction in soil test such as bicarbonate for Olsen-P (Barrow and Shaw 1976; Fardeau et al. 1988).

3.4.6 Modifications in soil P speciation from 1998 to 2016

The TP_{HF} recovery in soil NaOH-EDTA extracts (TP_{NE}/TP_{HF}), 49% on average, was in the same magnitude as similar soils reported by Doolette et al. (2011). However, the TP_{NE}/TP_{HF} differed among OWP treatments in 2016, with the GWS₁₁₂ greater than other OWP treatments. Those discrepancies should not affect our results, as the majority of unextracted P was probably sparingly water-soluble phosphate minerals, with substantial amounts of Fe, Al, Ca, and Mn (Nriagu and Moore 1984). Additionally, the degradation of orthophosphate diesters to monoesters (3.9% of P_{NE}) was in the lower range of previous results from studies which also account for compounds degradation during P-NMR processing, and represented 2 – 11% of P_{NE} (Doolette et al. 2011; Liu et al. 2014; Cade-Menun et al. 2015; Schneider et al. 2016).

In general, soil P speciation was barely affected by the different OWP treatments and was comparable to previous studies (Annaheim et al. 2015; Glæsner et al. 2019). The sum of all inorganic P forms increased under GWS₁₁₂ fertilization (i.e. the OWP in this study with the highest P rate of P application and the SIP concentration). However, this distinction among OWP treatments was not observed with concentration of individual inorganic P species, which were not significantly different among OWP treatments. On average, about 57 kg ha⁻¹ of orthophosphate was applied at each fertilization event, considering an initial stock of 1013 kg ha⁻¹. Therefore, its concentration increased with P fertilization regardless of the product applied. Similar increases were also often reported under both mineral and organic fertilization (Schneider et al. 2016; Weyers et al. 2016; Cade-Menun 2017; Liu et al. 2017; Menezes-Blackburn et al. 2018; Glæsner et al. 2019). Nevertheless, the inorganic P proportion remain higher than in previous studies on OWP fertilization (Requejo and Eichler-Löbermann 2014; Glæsner et al. 2019).

Within organic P species concentration, orthophosphates monoesters were the main group and the unidentified monoesters were the predominant form, followed by *myo*-IHP, as previously reported (Liu et al. 2019; Perillo et al. 2021). The sum of all organic P forms follows the same trend as the sum of all inorganic P forms. The sum of all organic P species in GWS₁₁₂ represents about 12 kg ha⁻¹ applied at each fertilization event on an initial stock of 280 kg ha⁻¹. For most organic P species and groups, the different OWP treatments did not affect speciation. Only *myo*-IHP, glucose 6-phosphate and the unidentified monoester from region 1 increased in concentration from 1998 to 2016. Small changes in organic P speciation under long-term OWP applications have already been reported in previous studies (Annaheim et al. 2015; Glæsner et al. 2019). The small observed increase can be related to the amount of these compounds applied with OWP. The IHP stereoisomers concentration were not different among OWP (90% as *myo*-IHP) and are likely stabilized by sorption on soil solid surface, and thus tends to accumulate in soils. Thus, considering

the high OWP inputs (i.e. about 1 kg *myo*-IHP applied at each fertilization event on 45 kg ha⁻¹), it is consistent to observe a slight increase in *myo*-IHP concentration in soil over 17 years of experimentation. Additionally, the *myo*-IHP can also come from plant residues (Raboy 2003; Noack et al. 2012, 2014). Although without significant changes, the other IHP stereoisomers are likely to follow the same trend as they were previously reported as a degradation compounds from *myo*-IHP by epimerization (L'Annunziata 1975), microbial transformation (Giles et al. 2011) or low pH (Abdi et al. 2019).

For CON₃, the only major changes observed were a decreased in concentration in total inorganic and organic P forms determined by P-NMR without any effect on individual P species or group of unidentified species. Comparable results were reported in literature (Liu et al. 2019). Such changes can be associated with plant P uptake (as phosphate ions) in the inorganic P pools and (Frossard et al. 2000; Condon et al. 2005; Dodd and Sharpley 2015).

3.5 Conclusion

In this study, four OWP were applied to soils at rates based reasoned on C inputs. Thus, depending on the C/P ratios within each OWP, huge amounts of P were applied, especially in GWS₁₁₂ with the greatest the TP_{HF} concentration. In addition, the P in all OWP was mainly inorganic as orthophosphate. Due to highly variable P inputs and relatively constant P exported in harvest, the P budgets were highly different among treatments, from excessive P applied, in BLOW₄₆ and GWS₁₁₂, to P depletion in CON₃. The cumulative P budget explained all the observed variations, in soil TP_{HF}, SIP, and orthophosphate stocks and concentrations. Within organic P compounds, small changes were observed on orthophosphate *myo*-IHP and some other orthophosphate monoesters due to the amount of P applied within OWP. The high inorganic P inputs caused the high SIP stocks in soils with an already high initial SIP. Therefore, in order to use organic products from urban and farm waste in a sustainable way without nutrients imbalance, fertilization should reasoning be based on N or P.

SI-3.1 Supplementary information

SI-3.1.1 Parameters of composting organic waste products

Table SI-3.1 Organic waste products (OWP) origin, composition and composting parameters.

OWP	Year	Origin: City (French department)	Product input	Refining	Fermentation		Maturation	
				mm	Process	Duration	Process	Duration
GWS	1998	Nantes (44)	Green wastes of wood chips + sewage sludge	20	Sheltered swath	3 months	Sheltered	2 months
	2000				Outside	1 month	Outside	1 month
	2002	Cernay (68)	Green wastes of wood chips + sewage sludge (Colmar) + grounded pallets	40	Forced ventilation under shelter	6 weeks	Outside	3 months
	2004					4 weeks		4 months
	2006							3 months
	2007					2011		
BIOW	1998	Cergy (95)	Fermentable fraction of municipal waste + Green wastes	20	SILODA Sheltered	1 month	Sheltered	2 months
	2000	Sim le Noble (59)			Forced ventilation under tarpaulin	26 days	Outside swath	4 months
	2002	Marbache (54)		25	Slowly composted (turning)	3 months	Outside swath	3 months
	2004			Caudan (56)	15	Accelerated fermentation in compost tunnel	5 weeks	Sheltered (with 2 weeks with forced ventilation)
	2006	Sheltered (with 2 weeks with forced ventilation)						3 months
	2007							
MSW	1998	Murianette (38)	Residual municipal wastes ²	10-12	SILODA Sheltered	22 days	Sheltered	5 days
	2000							
	2002	Lantic (22)	Mixed	12,5	Forced ventilation (no turning)	1 month	Outside	5 days
	2004							
	2006	2007	2009	2011	2013	2015		
2006	2007	Ecorpain (72)	Residual municipal wastes ²	6	Forced ventilation + 1 turning	3 weeks	Sheltered	3 weeks
FYM	1998	Grignon (78)	Dairy cattle manure from the Grignon experimental farm					
	2000							
	2002							
	2004							
	2006							
	2007							
	2009							
	2011							
	2013							
	2015							

² Residual municipal wastes: the waste remaining after sorting the recyclable waste (used paper, plastic packaging, metal packaging, beverage containers, biodegradable waste, glass and textiles)

SI-3.1.2 Supplemental information on P-NMR analysis

Methodology

The soil samples (1998 and 2016) and the organic amendments samples (1998, 2004 and 2011) were analyzed by solution P-NMR according to the modified (Cade-Menun and Preston 1996) procedure. Soils (3 g) and organic amendment samples (1.2 g) were shaken in 30 mL 0.25 mol L⁻¹ NaOH and 0.05 mol L⁻¹ Na₂EDTA for 4 h in the dark at 20°C and then centrifuged (20 min, 10000 × g). An aliquot (1 mL) was removed and diluted to 10 mL with deionized water for P, Al, Fe, Ca, and Mn determination by ICP-OES (Thermo Scientific ICAP 6300 Duo). These analyses were used to determine NMR delay times based on the ratio of P/(Fe + Mn) in the extracts (McDowell et al. 2006; Cade-Menun and Liu 2014). The remaining supernatants were frozen and freeze-dried. Freeze-dried extracts of soils were redissolved in 0.7 mL D₂O, 0.7 mL of deionized water, 0.7 mL of the NaOH-EDTA extracting solution and 0.5 mL of 10 mol L⁻¹ NaOH. The majority of the organic amendment samples were redissolved the same way as for soils. However, several were very viscous after initial preparation (FYM 1998, FYM 2004, GWS 1998), so reagent volumes were doubled. The samples extractions were centrifuged (1500 × g, 20 min) to remove particles > 0.1 μm and transferred to 10-mm NMR tubes.

Chemical shifts

Table SI-3.2 Chemical shifts of peaks detected in the P-NMR spectra of NaOH-EDTA extracts for both fertilizer and soil samples.

Category	P form	Chemical shift (ppm)
Inorganic P forms		
	Orthophosphate	6.00±0.00
	Pyrophosphate	-3.99±0.08
	Polyphosphates	-4.19±0.07; -4.85±0.28; -7.51±0.45; -14.14±0.65; -14.77±0.28; -21.06±0.52
Organic P compounds		
	Phosphonates	29.31±0.24; 28.44±0.45; 24.86±0.53; 16.28±0.37; 13.65±0.66; 8.65±0.60
Orthophosphate monoesters		
	<i>myo</i> -IHP ^y	5.43±0.03; 4.49±0.01; 4.10±0.01; 4.00±0.02
	<i>scyllo</i> -IHP	3.64±0.01
	<i>chiro</i> -IHP 2e/4a ^z	6.48±0.02; 5.23±0.02; 3.92±0.02
	<i>neo</i> -IHP 4e/2a ^z	6.21±0.02; 4.32±0.02
	Glucose 6-phosphate	5.20±0.02
	Choline phosphate	3.79±0.02
	Other monoesters 1	7.93±0.05; 7.31±0.19; 6.33±0.02
	Other monoesters 2	5.77±0.02; 5.68±0.02; 5.46±0.04; 5.27±0.03; 4.71±0.05
	Other monoesters 3	3.56±0.01; 3.40±0.05; 3.24±0.02
Degradation compounds		
	α-glycerophosphate	4.81±0.02
	β-glycerophosphate	4.45±0.01
	Mononucleotides	4.41±0.01; 4.37±0.02; 4.32±0.02; 4.28±0.01; 4.23±0.01; 4.20±0.01; 4.14±0.05
Orthophosphate diesters		
	DNA	-0.62±0.25; -0.86±0.21
	Other diesters 1	1.73±0.26; -0.18±0.11
	Other diesters 2	-1.66±0.12; -2.64±0.32

^y IHP: inositol hexakisphosphate;

^z 2e/4a: 2 equatorial/4 axial conformation; 4e/2a: 4 equatorial/2 axial conformation.

Additional spectra

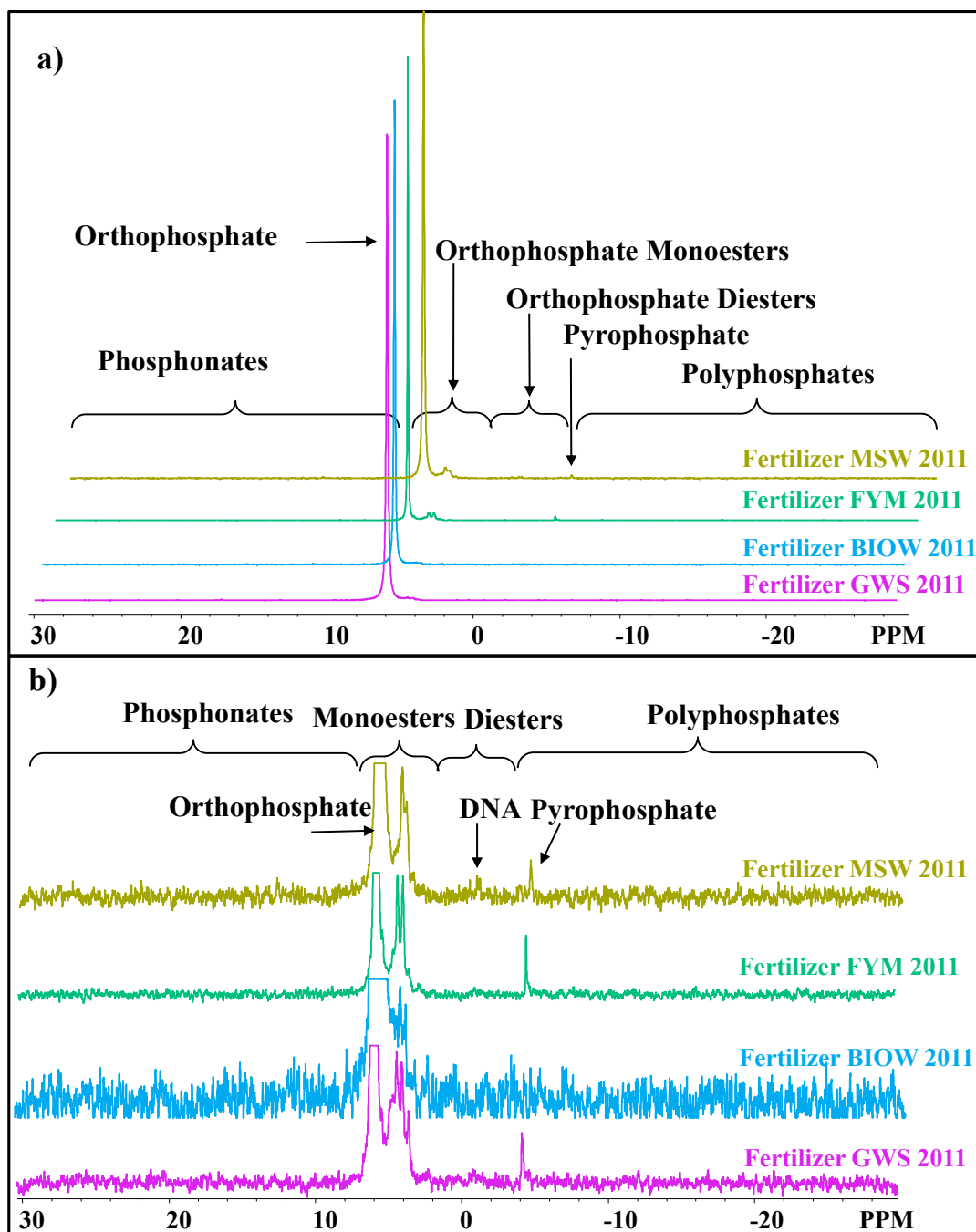


Figure SI-3.1 P-NMR spectra from NaOH-EDTA-extracts of organic waste products, applied in 2011, plotted with 7 Hz line broadening. (a): the full spectra with the main regions highlights. (b): the same samples, expanded to show details and scaled to the tallest peak in the orthophosphate monoester region. See Figure 3.2 (inset) for details of the orthophosphate monoesters region. MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BLOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript value in treatment abbreviation is the annual P applied in average in kg P ha⁻¹ yr⁻¹.

OWP speciation

Table SI-3.3 Concentrations of Al, Ca, Fe, Mg and Mn in NaOH-EDTA extracts of organic waste products determined by ICP-OES. Mean \pm std. error ($n = 3$). MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript value in treatment abbreviation is the annual P applied in average in kg P ha⁻¹ yr⁻¹. Different lowercase letters (a, b, c) indicate significant differences among organic amendments ($\alpha = 0.05$) according to the one-way ANOVA.

Concentration (mg kg ⁻¹)	MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	ANOVA <i>P</i> -value
Al	1128 \pm 458	62 \pm 46	364 \pm 236	4936 \pm 3570	0.27
Ca	39206 \pm 3086 a	19012 \pm 1246 b	34685 \pm 4469 ab	31724 \pm 6548 ab	0.05
Fe	707 \pm 144 b	231 \pm 65 b	932 \pm 278 b	1838 \pm 178 a	0.002
Mg	735 \pm 227	2126 \pm 259	1002 \pm 252	1117 \pm 518	0.08
Mn	75 \pm 8	139 \pm 14	165 \pm 8	155 \pm 65	0.31

Table SI-3.4 Percentage of P species in NaOH-EDTA extract, determined by P-NMR, of organic waste products. MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript value in treatment abbreviation is the annual P applied in average in kg P ha⁻¹ yr⁻¹. Samples analyzed were collected in 1998, 2004, and 2011. Values are means ± std. err.; *n* = 3. Different lowercase letters (a, b) indicate significant difference among treatments ($\alpha = 0.05$). Letters were determined with a one-way ANOVA.

	MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	ANOVA <i>P</i> -value
Inorganic P forms in NaOH extracting solution					
Orthophosphate	82±1	83±2	88±1	91±1	0.08
Pyrophosphate	0.8±0.1	0.9±0.2	0.1±0.1	0.4±0.3	0.34
Polyphosphates	0.9±0.2	1.2±0.2	0.9±0.1	0.5±0.1	0.99
Sum of inorganic P	84±1 b	85±2 b	89±1 ab	92±1 a	0.011
Organic P forms in NaOH extracting solution					
Phosponates	2.1±0.8	1.1±0.2	1.8±0.9	0.8±0.1	0.71
Orthophosphates monoesters					
Inositol hexakisphosphates (IHP)					
<i>myo</i> -IHP	3.5±1.6	2.7±0.8	1.2±0.5	1.1±0.1	0.12
<i>scyllo</i> -IHP	0.1±0.1	0.2±0.1	0.1±0.1	0.1±0.1	0.92
<i>neo</i> -IHP	n.d	n.d	0.1±0.1	n.d	-
<i>chiro</i> -IHP	0.1±0.1	0.2±0.2	0.1±0.1	n.d	0.93
Sum of IHP	3.7±1.7	3.0±1.0	1.5±0.6	1.2±0.1	0.19
Glucose 6-phosphates	0.2±0.1	0.2±0.1	0.2±0.1	0.3±0.1	0.25
Choline phosphate	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.66
Other monoesters 1 ^y	1.7±0.2	1.4±0.3	1.8±1.6	1.4±0.2	0.36
Other monoester 2	4.9±0.1	3.8±0.9	3.2±0.5	3.0±0.2	0.05
Other monoesters 3	0.2±0.1	0.4±0.1	0.4±0.1	0.1±0.1	0.37
Sum of monoesters ^z	10.8±1.5	8.9±2.1	7.2±0.9	6.1±0.1	0.82
Orthophosphates diesters					
DNA	0.2±0.1	0.3±0.2	0.2±0.1	0.1±0.1	0.61
α-glycerophosphates	0.2±0.1	0.9±0.2	0.3±0.1	0.1±0.1	0.39
β-glycerophosphates	0.8±0.1	1.7±0.3	0.4±0.1	0.3±0.1	0.38
Nucleotides	1.4±0.5	1.5±0.2	0.9±0.2	0.6±0.1	0.97
Other diesters 1 ^y	0.3±0.1	0.5±0.2	0.4±0.2	0.1±0.1	0.98
Other diesters 2	0.2±0.1	0.2±0.1	0.3±0.1	0.2±0.1	0.50
Sum of diesters ^z	3.1±0.6	5.1±0.6	2.5±0.3	1.4±0.2	0.09
Sum of organic P	16±1 a	15±2 a	11±1 ab	8±1 b	0.004

^y Total orthophosphate monoesters and diesters corrected for degradation of diesters to monoesters during sample analysis;

^z Other orthophosphate monoesters and diesters are peaks in the monoester and diesters region not specifically identified.

Soil speciation

Table SI-3.5 Concentration of Al, Ca, Fe, Mg, and Mn in NaOH-EDTA extracts of soils sampled in 1998 and 2016 determined by ICP-OES. Mean \pm std. err. ($n = 4$). Different lowercase letters (a, b, etc.) indicate significant differences among years of soil sampling and fertilization treatments ($\alpha = 0.05$). The unfertilized and fertilized treatments are analyzed separately. CON₃: control (no P applied as OWP); MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript value in treatment abbreviation is the annual P applied in average in kg P ha⁻¹ yr⁻¹. ANOVA factors: OWP = OWP treatments, Y = years of soil sampling.

Concentration (mg kg ⁻¹)	Year	CON ₃	ANOVA		MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	ANOVA P-values		
			Y	Y					OWP	Y	OWP × Y
Al	1998	410±27a	0.043	0.002	422±42ab	393±25bc	395±17bc	351±29bc	0.003	0.59	<0.0001
	2016	340±17b			359±39bc	287±24c	307±8bc	549±18a			
Ca	1998	1988±75a	0.002	0.002	1834±73c	1995±78bc	2106±200abc	1775±75c	0.012	<0.0001	0.017
	2016	1600±70b			2369±108ab	1947±103bc	2538±97a	2333±68ab			
Fe	1998	47±5	0.09	0.08	48±5b	44±4b	40±1b	39±3b	0.002	<0.0001	<0.0001
	2016	38±2			47±4b	43±4b	68±3a	70±2a			
Mg	1998	29±2	0.08	0.08	29±2d	33±2d	29±2d	28±2d	<0.0001	<0.0001	<0.0001
	2016	26±3			34±2d	63±2a	44±2c	53±2b			
Mn	1998	38±2	0.45	0.45	42±3a	41±1a	38±2ab	42±2a	0.024	<0.0001	0.046
	2016	36±1			19±1d	24±2cd	23±1cd	30±1bc			

Table SI-3.6 Percentage of P species in NaOH-EDTA solution determined by P-NMR in soils, sampled in 1998 and 2016 from the different fertilization treatments. CON₃: control (no P applied); MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: compost of urban sewage sludge and green waste wood chips. Subscript value in treatment abbreviation is the annual P applied in average in kg P ha⁻¹ yr⁻¹. Values are means ± std. err. (mean by treatments: *n* = 8; mean by years: *n* = 20; mean over all: *n* = 40). Different lowercase letters (a, b, c) indicate significant differences among treatments means within a year, while different uppercase letters (A, B) indicate significant differences among years means within a treatment ($\alpha = 0.05$). The unfertilized and fertilized treatments are analyzed separately. Letters were determined with an ANOVA, factors are OWP = OWP treatments and Y = years.

P species (% of PNE)	Sampling year	CON ₃	ANOVA		MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	ANOVA P-values		
			Y	Y					OWP	Y	OWP × Y
Inorganic P forms in NaOH extracting solution											
Orthophosphate	1998										
	2016	72±2	0.62			76±1			0.83	0.009	0.45
Pyrophosphate	1998										
	2016	1.0±0.1	0.53			1.1±0.1			0.65	0.13	0.70
Polyphosphates	1998										
	2016	1.5±0.1	0.28			1.5±0.1			0.33	0.29	0.16
Sum of inorganic P	1998	77±2A			76±1b	79±2b	78±1b	77±2b			
	2016	73±2B	0.030		75±1b	80±2ab	81±1ab	86±1a	0.003	0.008	0.029
Organic P forms in NaOH extracting solution											
Phosphonates	1998										
	2016	1.9±0.2	0.46			1.5±0.1			0.91	0.32	0.78

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Table SI-3.6 – Continued from previous page

P species (% of P _{NE})	Sampling year	CON ₃	ANOVA		MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	ANOVA P-values			
			Y	Y					OWP	Y	OWP × Y	
Orthophosphate monoesters												
Inositol hexakisphosphates (IHP)												
<i>myo</i> -IHP	1998	4.5±0.3	0.89		3.4±0.1B				0.87	0.004	0.63	
	2016				3.5±0.1A							
<i>scyl</i> -IHP	1998	1.23±0.16	0.14			0.92±0.05			0.63	0.07	0.56	
	2016											
<i>neo</i> -IHP	1998	0.51±0.14	0.99			0.32±0.05			0.40	0.26	0.11	
	2016											
<i>chiro</i> -IHP	1998	0.48±0.20	0.97			0.20±0.05			0.72	0.79	0.06	
	2016											
Sum of IHP	1998	6.7±0.5	0.57			4.9±0.2			0.48	0.72	0.94	
	2016											
Orthophosphate diesters												
Glucose 6-phosphate	1998	0.31±0.04	0.14		0.25±0.02A				0.52	0.028	0.32	
	2016				0.24±0.02B							
Choline phosphate	1998	0.39±0.05	0.10			0.23±0.02			0.56	0.53	0.79	
	2016											
Other monoesters I ^y	1998	1.2±0.1	0.05		0.89±0.11B				0.98	0.006	0.84	
	2016				1.06±0.08A							

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Table SI-3.6 – Continued from previous page

P species (% of P _{NE})	Sampling year	CON ₃	ANOVA		MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	ANOVA P-values		
			Y	Y					OWP	Y	OWP×Y
Other monoesters 2	1998	8.9±0.9	0.20			8.0±0.4			0.46	0.08	0.53
	2016										
Other monoesters 3	1998	0.55±0.06	0.94			0.44±0.07			0.77	0.12	0.45
	2016										
Sum of monoester ^z	1998	17.9±1.8	0.09			14.8±0.5			0.43	0.06	0.41
DNA	1998	0.21±0.05	0.54			0.10±0.02			0.73	0.43	0.27
	2016										
α-glycerophosphates	1998	0.75±0.13	0.57			0.52±0.03			0.57	0.95	0.99
	2016										
β-glycerophosphates	1998	1.23±0.14	0.50			0.98±0.05			0.80	0.06	0.92
	2016										
Nucleotides	1998	2.4±0.3	0.55			2.3±0.1			0.26	0.20	0.38
	2016										
Other diesters 1 ^y	1998	0.44±0.11	0.08			0.40±0.03			0.67	0.07	0.08
	2016										
Other diesters 2	1998	0.26±0.04	0.35			0.27±0.03			0.99	0.51	0.77
	2016										
Sum of diesters	1998	5.3±0.4	0.69			4.5±0.2			0.23	0.26	0.80
	2016										

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Table SI-3.6 – Continued from previous page

P species (% of P _{NE})	Sampling year	CON ₃	ANOVA		Y	MSW ₂₄	FYM ₄₀	BIOW ₄₆	GWS ₁₁₂	ANOVA P-values			
			Y	Y						OWP	Y	OWP×Y	
Sum of organic P	1998	23±2B			22±1	24±1a	21±2a	22±1a	23±2a				
	2016	27±2A	0.028		25±1a	20±2a	19±1a	14±1b		0.0012	0.025	0.007	

^y Other orthophosphate monoesters and diesters are peaks in the monoester and diesters region not specifically identified;

^z Total orthophosphate monoesters and diesters corrected for degradation of diesters to monoesters during sample analysis.

SI-3.1.3 Correlation matrix among soil P indicators

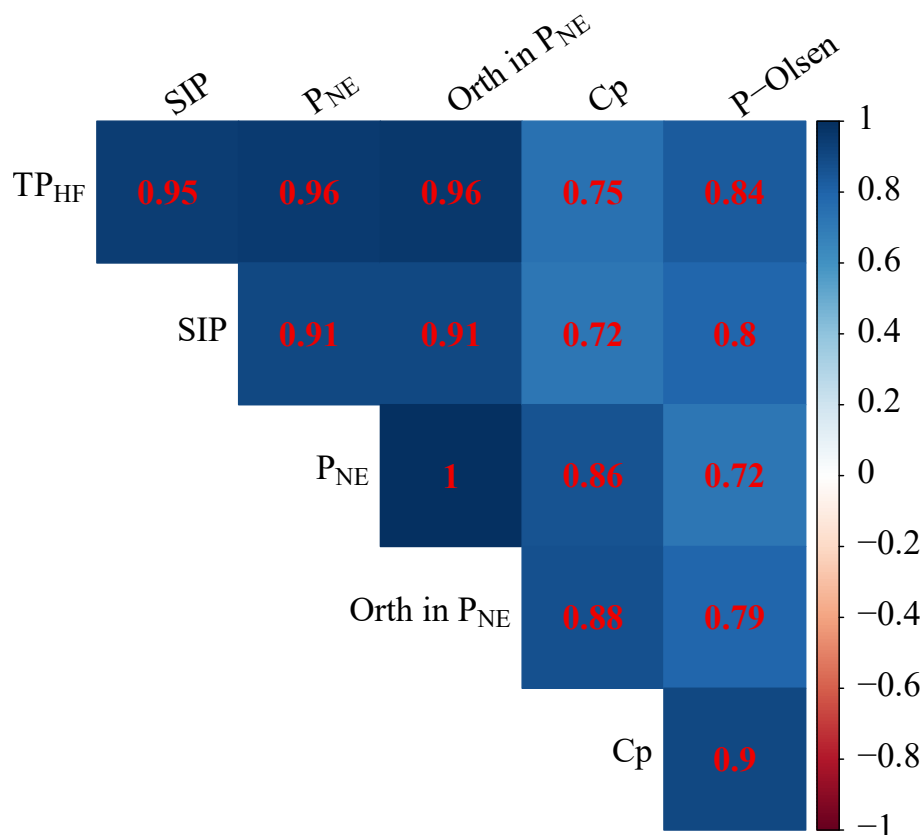


Figure SI-3.2 Matrix of correlation coefficients (R^2) among P concentrations of different soil P tests. TP_{HF}: total soil P (TP_{HF}), determined by digestion in concentrated acid fluoric and perchloric solutions. SIP: soil inorganic P (SIP=TP_{HF} - SOP, with SOP the soil organic P determined by the ignition method of Saunders and Williams (1955)). P_{NE}: NaOH-EDTA extracted P (P_{NE}). Orthophosphate in P_{NE} determined by P-NMR. Cp: phosphate ions concentration in solution of water-soil suspensions. Olsen-P: P extracted by sodium bicarbonate solution.

SI-3.1.4 Plant-available soil P concentration in relation to cumulative P budget

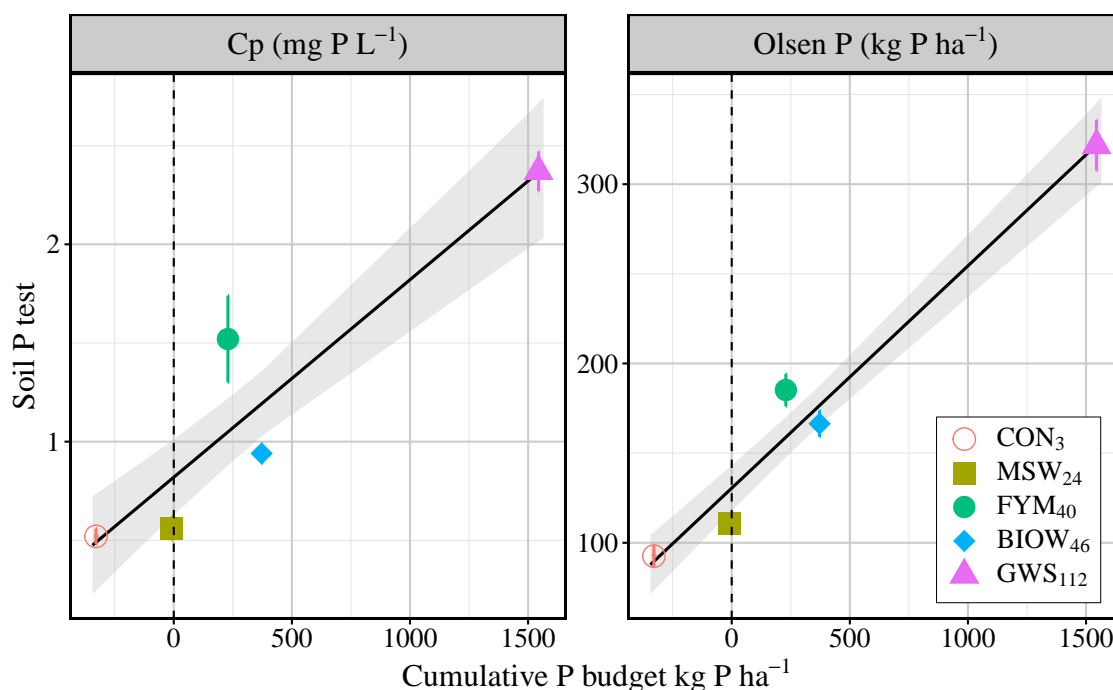


Figure SI-3.3 Concentration of phosphate ions in soil solution of water-soil suspensions (C_P) and soil P stock extracted by sodium bicarbonate solution (Olsen et al. 1954), sampled in 2016, in the soil plough layer (0 – 25 cm) in relation to the cumulated P budget (B_{cum}) for the different fertilization treatments. Values are means ($n = 4$); error bars are standard error. CON₃: control (no P applied); MSW₂₄: municipal solid waste compost; FYM₄₀: farmyard manure; BIOW₄₆: biowaste compost; GWS₁₁₂: green waste wood chips and sewage. Subscript value in treatment abbreviation is the annual P applied in average in kg P ha⁻¹ yr⁻¹.

Variable	Regression	Slope P	R^2
C_P (mg P kg ⁻¹)	$0.0010 \pm 0.0001 \times B_{cum} + 0.82$	< 0.001	0.78
Olsen-P (kg P ha ⁻¹)	$0.124 \pm 0.008 \times B_{cum} + 130$	< 0.001	0.93

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GENERAL DISCUSSION AND CONCLUSION

D General discussion

The purpose of this thesis was to determine the soil organic phosphorus (SOP) mineralization and its potential contribution to plant P nutrition. To better understand soil-plant relationships in relation to plant nutrition and P cycling in cropland, it is required to improve the assessment plant-available soil P. A functional and process-based approach has been developed by considering that soil-solution diffusion of phosphate ions was the major process that contributes to resupply phosphate ions in soil solution. However, the role of SOP compartment was assumed more or less negligible, which is questionable to fully capture long-term P dynamics in cropped soils. So, this thesis aimed at first at determining the release of phosphate ions into solution by the SOP mineralization. Then, the resulting objective was to study links between SOP mineralization rates determined in several sites and its speciation. And, finally, more generally, soil and climate properties were examined in their ability to control long-term SOP mineralization in cropland by annual crops.

Several factors can affect this mineralization such as the type of fertilization (i.e. organic products or mineral fertilizers), the SOP speciation, or the agropedoclimatic conditions. Four long-term field experiments (LTFE) under various managements, soils, and climates were studied. Two LTFE were fertilized with triple superphosphate and the two other with urban waste composts, dehydrated sewage sludge, and farm effluents. The LTFE were selected based on the time-series database and stored sampled available on soils, crops, and organic waste product (OWP). The SOP were determined by the Saunders and Williams (1955) method. Speciation were assessed in two LTFE by NMR spectroscopy (Cade-Menun 2005). The SOP mineralization were determined by transposing a model on soil organic carbon (C) dynamic (Hénin and Dupuis 1945). Conceptual diagram of the SOP dynamic model was presented in Figures 1.1 and 2.1.

This "general discussion" part, presents a synthesis of the important and new results of the thesis, their consequences on the understanding of the transfer of phosphate ions at the solid-to-solution interface of the soil and their agronomic consequences. They are

analyzed and interpreted by considering different aspects of the P cycle in agrosystems. The main points covered are:

- i) a summary of the results, obtained in the 4 studied LTFE, on the multi-year evolution of the SOP;
- ii) a performance analysis of the model describing the long-term dynamics of the SOP;
- iii) model sensitivity analysis. Hypothesis of partitioning SOP stocks between one active compartment and one stable compartment. Does the rate h of P incorporation into the SOP affect the dynamics of the SOP?
- iv) the significant results on P speciation, in particular before and after repeated applications of urban composts, urban sewage sludge, and farmyard manure for 17 years of cropping;
- v) a comparative analysis of the evolution of C/N and C/P ratios in LTFE0;
- vi) the multi-year dynamics of SOP and SIP stocks as a function of the cumulative P budget due to different cropping systems;
- vii) the replenishment of the soil solution with phosphate ions. What is the dominant process between SOP mineralization or soil-solution diffusion of phosphate ions?
- viii) What are the soil properties and/or climatic variables that influence SOP mineralization?

D.1 Long-term multi-year SOP dynamics and associated fluxes and stocks

This model was developed to monitor SOP in soil plough layer and predict its stock for long-term periods. It considers the initial SOP stock in the plough layer, which is increased by an annual P incorporation from crop residues and OWP, and decreased by the annual mineralization of the SOP stock. The P incorporation was calculated for each crop residues and OWP with the h parameter (dimensionless), based on previous results on literature (Table D.1). A fraction of OWP crop residues P was incorporated to SOP during the year following inputs. The remainder was released as phosphate ions or easily degradable organic P compounds in the soil solution. Therefore, the only unknown parameter was the gross mineralization coefficient k (yr^{-1}), which was calculated for each plot within each long-term field experiment by adjusting simulated SOP values to the observed time series SOP data (minimization of sum of square). The SOP stocks, all P fluxes, and main model parameters used to describe SOP dynamics are presented in Table D.1 for the four LTFE.

The simple model framework and averages P fluxes and SOP stock over the four long-term field experiments are presented in Table D.1 and Figure D.1, diagram presenting the synthesis of results and allowing to elaborate general findings of the thesis.

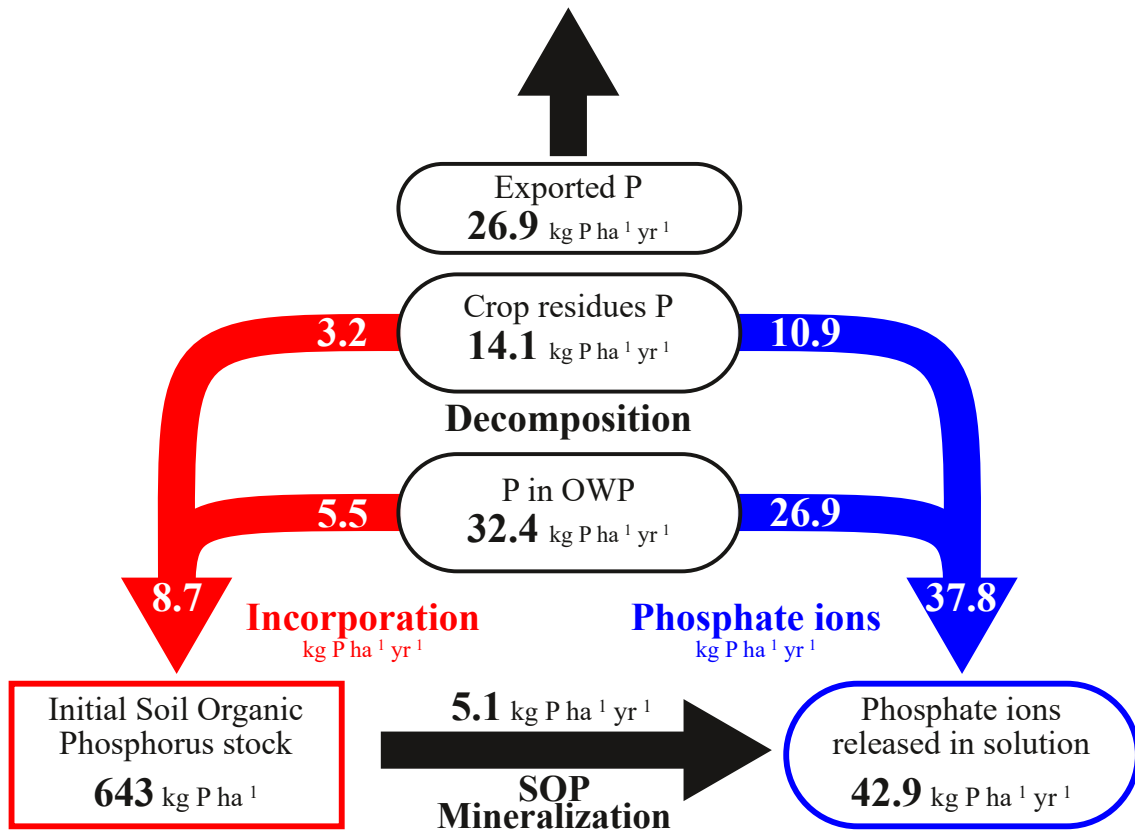


Figure D.1 Diagram of the model describing the average over the four LTFE of SOP stock, P fluxes and processes that drives its dynamics. The P inputs as crop residues and organic P in OWP (only for LTFE2 and LTFE3) are either released [P applied × (1-h)] in solution as phosphate ions or incorporated (P applied × h) into SOP. The SOP stock mineralizes according to the k mineralization constant.

The P applied within OWP and crop residues was superior to the P removed by crop, with 46.5 kg P ha⁻¹ yr⁻¹ compared to 26.9 kg P ha⁻¹ yr⁻¹, on average over the four LTFE. After harvest, the degradation of crop residues (< 1 yr) in soils leads to P incorporation into SOP stocks or P flux toward soil solution. The P fluxes that supplied to SOP stocks and the soil solution were significantly different among LTFE, with 3 to 5 folds higher in OWP-fertilized sites than the two others (Section 1.3.3; Table 2.8), with small differences observed among treatments within each LTFE and among different plant parts (e.g. aboveground residues). More than 80% of P applied within OWP and crop residues are released as phosphate ions in soil solution. In comparison, the SOP mineralization flux is 7 times smaller and only represent 0.8% of SOP stock. The cumulated P incorporated to SOP from both OWP and crop residues was within the range of SOP stock variability, with an average incorporation of 82 (LTFE0), 45 (LTFE1), 197 (LTFE2), and 118 kg P

ha⁻¹ (LTFE3) over years and treatments, against a SOP standard deviation of 92 (LTFE0), 46 (LTFE1), 123 (LTFE2), and 131 kg P ha⁻¹ (LTFE3). Therefore, the incorporation P fluxes have only a small impact on SOP stock changes. Our results also indicate that, regardless of treatment, the annual release of phosphate ions in solution through OWP and crop residue decomposition is always higher than the annual supply of SOP.

The four examined LTFE exhibited a strong difference on the initial SOP stocks in the plough layer. This may be attributed to differences in soil composition/properties (Section 1.2.2; Table 2.2) and management history. It is well known that phosphate ions have a strong affinity for soil mineral components such as Al- and Fe-oxides, clay minerals, organic matter, or CaCO₃ (Carreira et al. 2006; George et al. 2018; Menezes-Blackburn et al. 2018). Therefore, the presence of CaCO₃ in LTFE3 (as shown in Table 2.2) could account for the higher SOP value observed at that site relative to the other three LTFE, because of the high CaCO₃ specific surface area (Carreira et al. 2006; Johnston et al. 2014). In addition, some authors have reported calcium phosphate precipitation in high C_P and CaCO₃ soil content (Cole et al. 1953; Lindsay et al. 1989). Moreover, differences in management history among the LTFE, including those that were not carbonated, might also have contributed to the observed variability in initial SOP stocks. However, the management history prior to the start of the experiment was not always well known, and as such, definitive conclusions cannot be drawn.

Table D.1 Synthesis across the four LTFE of model parameters *k*, *h* and initial SOP, and P fluxes, either annually incorporated to SOP or annually mineralized from SOP. 1/*k*: residence time, Inc: P incorporation to SOP; Res. release of phosphate ions in solution, Min. mineralized.

	initial SOP	h	Inc.	Res.	k	1/k	Min.
	kg P ha ⁻¹		kg P ha ⁻¹ yr ⁻¹		yr ⁻¹	yr	kg P ha ⁻¹ yr ⁻¹
LTFE0	368±16	0.17	2.8±0.1	14±0.5	0.005±0.001	208	1.7±0.1
LTFE1	466±13	0.17	2.5±0.1	13±1	0.005±0.001	217	2.1±0.1
LTFE2	595±28	0.16	11.0±1.0	46±6	0.018±0.004	56	11.2±0.5
LTFE3	1145±22	0.18	7.9±0.7	27±3	0.004±0.001	227	5.3±0.3

Among the different LTFE, the calculations of coefficient *k* were often comparable and averaged 0.005 yr⁻¹. Only the LTFE2 presented higher values of *k*, and therefore a lower residence time. Among fertilization treatments within each LTFE, significant differences in the calculated coefficient *k* (and SOP residence time) were observed only at LTFE2

(Table 2.8). However, those differences did not result in any significant difference in the SOP mineralization rate. The coefficient k in MSW_{24} was at the lower limit allowed for calculation. Indeed, the incorporation rate to SOP in MSW_{24} ($= 5 \text{ kg P ha}^{-1} \text{ yr}^{-1}$) was insufficient to account for the observed increase in SOP (Figure D.2a), and only the smallest P flux was allowed to reduce SOP stock.

The mineralization rate of SOP was computed, and the outcomes ranged from 1.7 to 11.2 $\text{kg P ha}^{-1} \text{ yr}^{-1}$, showing noteworthy variability among LTFE (Table D.1). In all LTFE, the SOP mineralization rates were significantly different from zero. The values obtained for each LTFE were similar among the treatments and were lower than the amount of phosphorus taken up by crops (approximately $30 \text{ kg P ha}^{-1} \text{ yr}^{-1}$). The low rate of SOP mineralization can be attributed to the extended residence time of phosphorus in SOP. The average residence time of P in SOP was 177 years, which is 6 to 13 times the duration of the LTFE. Coupled with a mineralization rate within the range of SOP variability, this mineralization did not significantly alter the SOP stock over this period. The SOP coefficient of variation was 24% (LTFE0), 10% (LTFE1), 24% (LTFE2), and 11% (LTFE3), and these values were comparable to previous research findings using ignition method (Saunders and Williams 1955; Song et al. 2011; Liu et al. 2015). This variability is a common occurrence since the SOP concentration is the difference between two extractions, and the variability obtained is the sum of the two variability (Saunders and Williams 1955). Soil properties are often heterogeneous at the infra-plot scale and sampling procedure could result in abnormal measurement due to nugget effect (Cambardella et al. 1994). Furthermore, despite the relatively shorter residence time in LTFE2, the duration of this LTFE remained brief in comparison, and no evident variation could impact SOP stock due to mineralization. Soil sampling is another factor that contributes to the SOP variability, specifically through operator-dependent variables, depth, or changes in bulk density. The use of soil equivalent mass can mitigate this variance (Ehlert et al. 2003; Lee et al. 2009); however, the calculation was unavailable for most of LTFE, thereby restricting comparisons between the study situations.

By utilizing the Hénin and Dupuis (1945) simple framework model, we obtained new insights on the rate of SOP mineralization in cropped soils under both mineral and organic fertilization. However, was the model able to properly simulate the SOP stock across LTFE and treatments, and therefore was the calculation of k and SOP mineralization correct?

D.2 Model performance: precision and accuracy

The simulated SOP stock values with the model were in the range of observed SOP values (Figure D.2a). The relative root mean square error (RRMSE) of the model was 16%, which was within the same magnitude as SOP coefficient of variation of 14%, the SOP stock was appropriately predicted.

The model accuracy refers to the closeness between simulated and observed SOP values and is related to systematic bias. The model precision refers to dispersion between simulated and observed values and is related to unsystematic (or random) bias. Considering the four LTFE, the regression line coefficient approximates the 1:1 line with a R^2 of 0.90 (Figure D.2b). Additionally, the SOP dynamic model presents a root means square error (RMSE) of 118 kg P ha⁻¹ compare to 704 ±16 kg P ha⁻¹, the simulated SOP mean and standard error. Therefore, the model applied to SOP accurately calculate the observed SOP values. About 93% of the model's error is attributable to a lack of precision, while only 7% is attributable to a lack of accuracy. However, simulated SOP values are very dispersed (std. dev. = 338 kg P ha⁻¹) and the adequacy between the observed and simulated SOP stock is primarily due to differences of the initial SOP stock among LTFE.

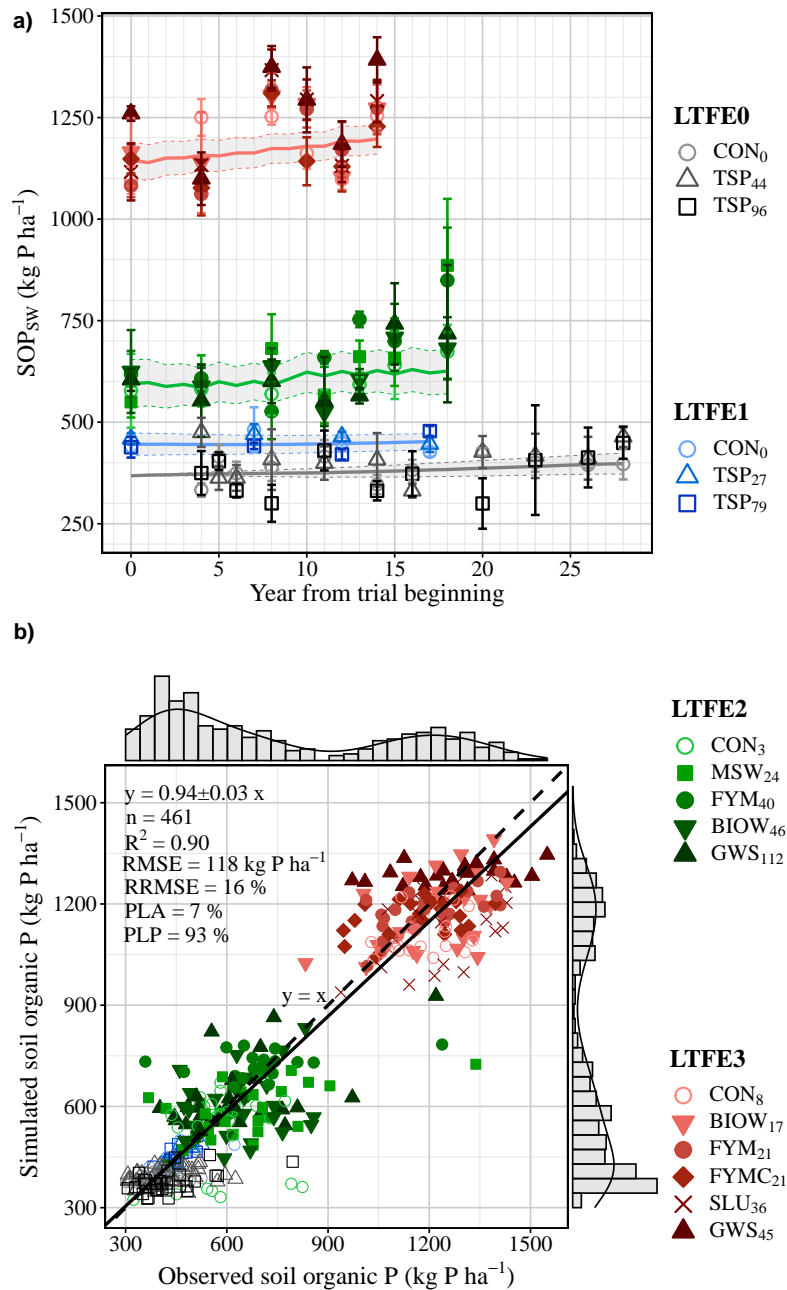


Figure D.2 Observed (symbols) vs simulated (lines) SOP stocks in the ploughed soil layer of the four LTFE. Simulation data were obtained by model described in Figure 1.1. **(a)** Means and standard error (4 replicates). Grey areas are confidence interval (95%) of simulated SOP. **(b)** Solid line is the symmetric linear model of simulated SOP vs observed SOP (Correndo et al., 2021). Dashed line is the 1:1 line of simulated vs. observed SOP. CON: no P input, MWS: municipal solid waste compost, FYM farmyard manure, FYMC: FYM compost; GWS: compost of green waste and SLU: SLU: dehydrated urban sewage sludge; BIOW: bio-waste compost; TSP: triple superphosphate. Numbers in treatments names are P annually applied on average (kg P ha⁻¹ yr⁻¹). Numbers in treatments names are P annually applied on average (kg P ha⁻¹ yr⁻¹). LTFE0: $n = 130$, LTFE1: $n = 48$, LTFE2: $n = 140$, LTFE3: $n = 144$.

Considering the variation of SOP stock (Δ SOP) from its initial value at the beginning of LTFE allow us to overcome the initial SOP stock effect. Therefore, the Figure D.3 show the model capacity to represent the SOP stock variation. With this perspective, model error remained comparable to the previous figure (RMSE = 125 kg P ha⁻¹).

By taking into account the observed SOP variability and the stability of stock across years (or cumulative P budget) and fertilization treatments, the observed Δ SOP were highly variable without clear pattern. Therefore, the model hardly simulates the observed Δ SOP. Indeed, the model error related to accuracy increased drastically to 42%. This systematic bias can be related to underlying flaw in the model's design or data used to build it.

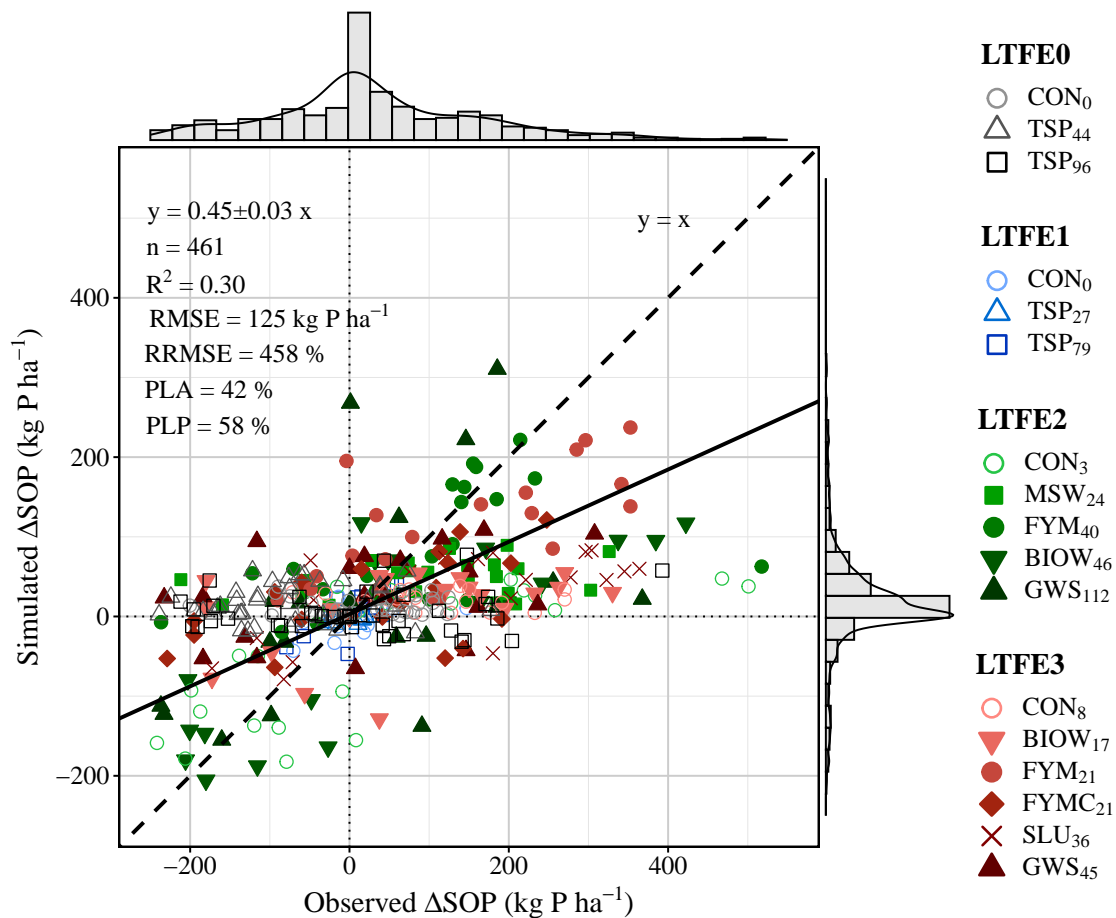


Figure D.3 Observed (symbols) vs simulated (lines) Δ SOP stocks (SOP – initial SOP) in the ploughed soil layer of the four LTFE. Solid line is the symmetric linear model of simulated Δ SOP vs observed Δ SOP. Dashed line is the 1:1 line of simulated vs. observed SOP. CON: no P input, MWS: municipal solid waste compost, FYM farmyard manure, FYMC: FYM compost; GWS: compost of green waste and SLU: SLU: dehydrated urban sewage sludge; BIOW: bio-waste compost; TSP: triple superphosphate. Numbers in treatments names are P annually applied on average (kg P ha⁻¹ yr⁻¹). Numbers in treatments names are P annually applied on average (kg P ha⁻¹ yr⁻¹). LTFE0: $n = 130$, LTFE1: $n = 48$, LTFE2: $n = 140$, LTFE3: $n = 144$.

One of the possible model flaw and source of variability is the h parameter that governs the incorporation and decomposition P fluxes from P inputs. It was based on literature on degradation. However, as few studies have specifically investigated P degradation in residues and OWP, several h parameters (Table 2.3) were derived from studies on degradation of N or C. Previous results have reported comparable dynamics between C, N, and P residues decomposition in cropped soils with infra daily rate of decomposition comprise between 0.015 and 0.030 d^{-1} on average (Singh and Shekhar 1989; Linères and Lubet 1990; Buchanan and King 1993). Therefore, similar h values for C, N, and P can be expected. The use of N- or C-based h parameters implies a non- or low-decoupling biogeochemical cycle between C, N, and P. It should be noted that this assumption may not be entirely accurate in cropped systems, as numerous disturbances can lead to decoupling of these cycles (Bertrand et al. 2019; Recous et al. 2019).

Another source of variability, is the P input in crop residues and OWP. This flux is highly variable among LTFE, treatments, and years. It ranges on average from 12.5 $\text{kg P ha}^{-1} \text{ yr}^{-1}$ in LTFE1 CON₀ to 126 $\text{kg P ha}^{-1} \text{ yr}^{-1}$ in LTFE2 GWS₁₁₂.

D.3 Brief sensitivity analysis of the model

By running the model, we used a few hypotheses to calculate k values, such as C- or N-based h values for P decomposition in exogenous inputs. Therefore, it is questionable what are the consequences of them on parameters calculation and SOP simulations, and how the model precision is affected: does considering different h values or P inputs would significantly affect the calculation of k and model error?

Ability of the soil organic C (SOC) dynamic model of Hénin and Dupuis (1945), on which we based our approach, to predict observed SOC stocks was improved by Andriulo et al. (1999) by dividing the SOC stock into an active and a slow compartment, inert at the time-scale of simulations (i.e. stable over a century). Including such slow kinetics compartment was needed in order to reduce the model systematic bias and improve SOC stocks model prediction on the long-term according to C inputs. This improved model was previously shown to accurately simulate SOC stock under various crop management and agropedoclimatic conditions (Saffih-Hdadi and Mary 2008; Autret et al. 2016; Clivot et al. 2019; Levavasseur et al. 2020).

This option of an active compartment and inactive compartment within SOP was studied by testing if a stable SOP pool would benefit the model prediction by reducing its error. Regarding SOP mineralization results in section 1.3.3 and Table 2.8, a stable SOP compartment and an active SOP compartment were considered (Figure D.3).

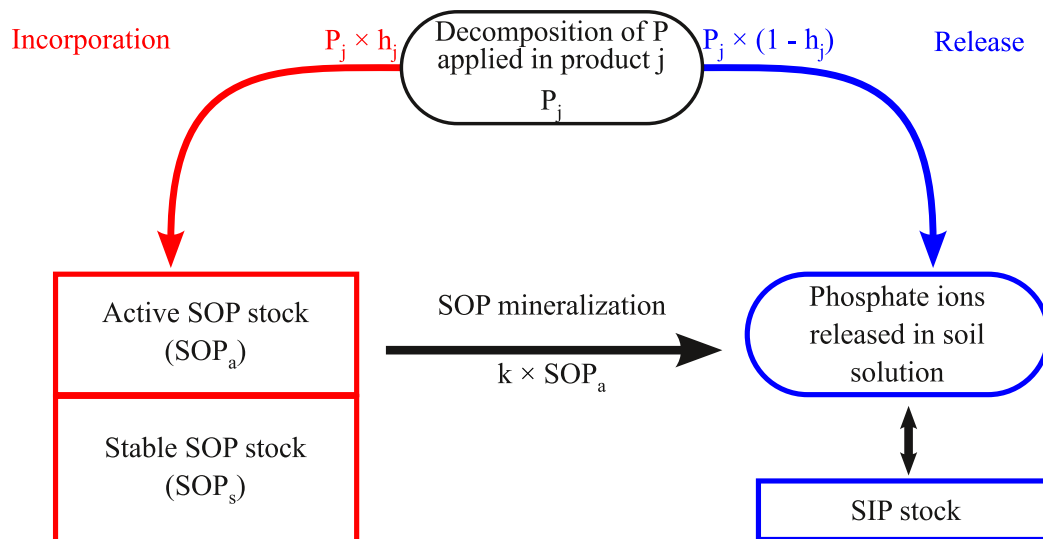


Figure D.4 Conceptual diagram of the model describing soil organic phosphorus (SOP) dynamics by considering two kinetic SOP pools. During decomposition of P applied (P_j) (<1 yr), the h fraction of P_j is incorporated into SOP_a and the remainder ($1-h$) fraction is released in solution. Phosphate ions are released from SOP_a mineralization with the coefficient (k). Rounded forms are P fluxes ($\text{kg P ha}^{-1} \text{ yr}^{-1}$); rectangular forms are P stocks (kg P ha^{-1}).

SOP_a : active soil organic P (kg P ha^{-1})

SOP_s : stable soil organic P (kg P ha^{-1})

P_j : P amount that is applied on the plough layer ($\text{kg ha}^{-1} \text{ yr}^{-1}$)

h_j (dimensionless): incorporation coefficients to SOP_a of P_j

Different levels of SOP stable fraction were tested and range from 0% to 50%, with an increment of 5%. All other parameters were set to their initial values as presented in Figure D.4. Model precision was evaluated by the RMSE.

The SOP stock is the only parameter related to a non-linear term in model equation. Therefore, the k parameter increased exponentially with the stable fraction. However, the effect on model prediction is extremely small ($-0.0014 \text{ kg P ha}^{-1}$). Although the error exponentially, the contribution this to the modeling improvement is not significant. Therefore, it was reasonable in this thesis to consider a unique SOP stock that contributes to its mineralization, unlike SOC dynamic modeling where including a stable pool have improved the results (Andriulo et al. 1999; Clivot et al. 2019).

In order to test variations on h values or stable SOP fraction, data from LTFE1 on TSP27 treatment were used. This dataset was selected because LTFE1 was the experiment where the model was the most accurate ($\text{RMSE} = 30 \text{ kg P ha}^{-1}$), and TSP₂₇ was the treatment the closer to null P budget (TSP₂₇ $\text{RMSE} = 19 \text{ kg P ha}^{-1}$). Due to high discrepancies in P inputs across LTFE and treatments, variation on P inputs were also tested. Here are the parameters values tested:

- i) 1. Incorporation parameter h: average initial value = 0.17; tested values range from -20% to +50% of initial value (increment 5%), which represents values from 0.136 to 0.255, with an increment of 0.0085;
- ii) 2. P inputs flux: average initial value = 15 kg P ha⁻¹ yr⁻¹; tested values range from -20% to +50% of the initial value (increment 5%), which represents values from 12 to 22.5, increment of 0.75 kg P ha⁻¹ yr⁻¹.

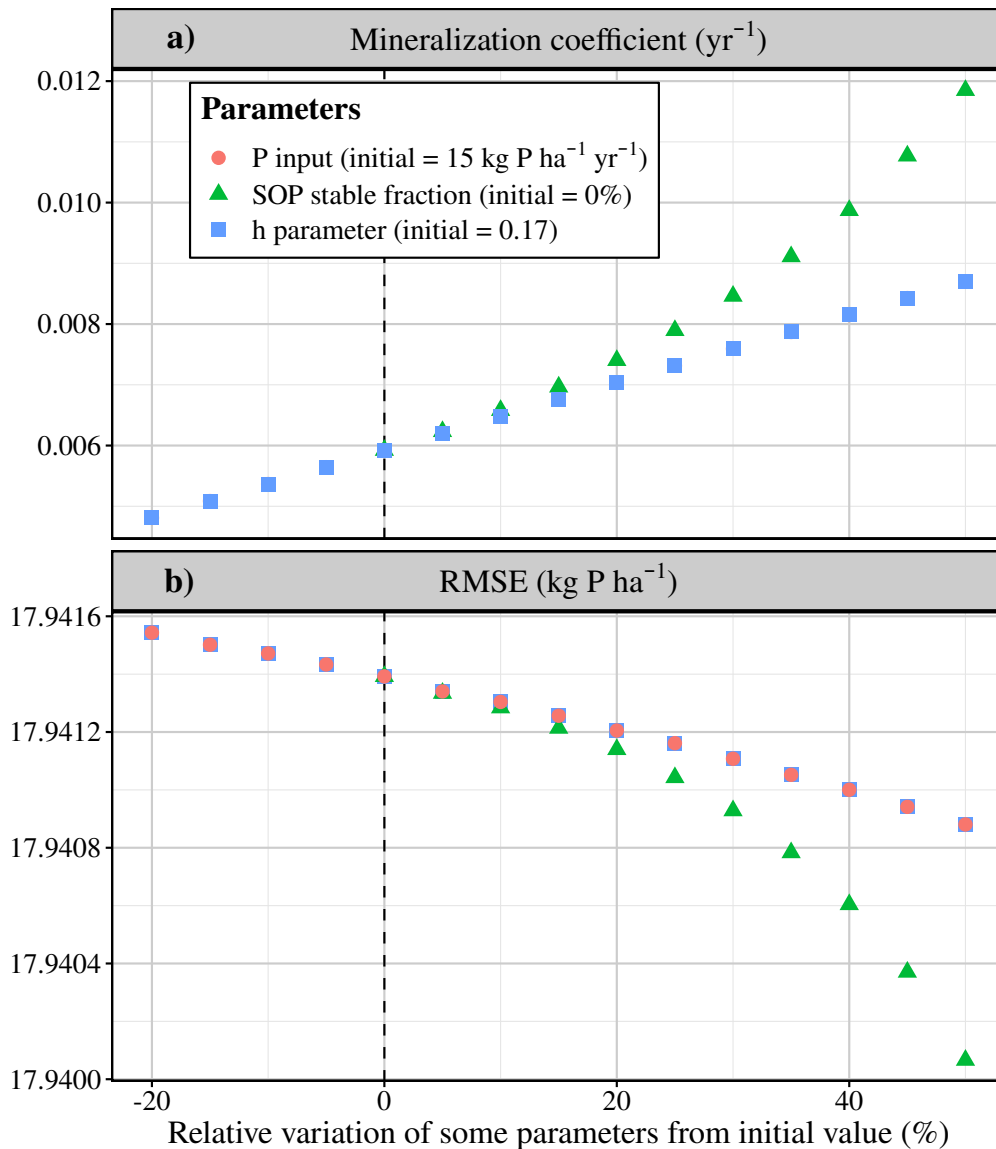


Figure D.5 Effect of changing proportion of P incorporated to SOP (h parameter), P inputs in residues (kg P ha⁻¹ yr⁻¹), and SOP stable fraction on calculated k coefficient and values of relative root mean square error of the model (RMSE). Calculations were done for TSP₂₇ of LTFE1. Calculated SOP mineralization coefficient k (a) and model RMSE (b) in LTFE1 TSP₂₇, according to variation in average h parameters (from 0.136 to 0.255, increment of 0.0085), average P inputs (from 12 to 22.5, increment of 0.75 kg P ha⁻¹ yr⁻¹), and stable SOP fraction (0% to 50%, by 5%).

Only one parameter at a time was allowed to vary. The others parameters were set to their initial values as presented in Figure D.5.

Both h and P inputs flux presented the exact same effects on k parameter and model precision for a same variation from the initial value (Figure D.5). As P incorporation to SOP is the product of h and P input, this result was expected. In the model equation, any non-linear term is related to P incorporation, therefore, the k parameter increased according to a linear relation with either h or P input flux variation ($k = 5.6 \cdot 10^{-5} \times \text{Percentage of variation} + 5.9 \cdot 10^{-3}$).

The effect of these two variables in improving the model prediction is extremely small ($-0.0008 \text{ kg P ha}^{-1}$). The error decreases linearly, but the contribution to the modeling improvement is not significant. Therefore, the use of h values presented in this thesis was reasonable.

D.4 Soil P speciation

Another key point studied in this thesis is the identification and quantification of the different forms of P involved in the constitution and composition of the inorganic and organic soil P forms. This soil P speciation analysis was carried out under the scientific, and technical, supervision of Dr. Barbara Cade-Menun ([AAFC profile](#)), research scientist of Agriculture and Agri-Food Canada at the Swift Current Research and Development Centre (Saskatchewan, Canada). Barbara is a world-renowned specialist on soil P biogeochemistry, nutrient cycling and minimizing nutrient loss from agriculture.

The analytical procedure consists of first extracting soil P with a NaOH-EDTA solution, then identifying and quantifying in the solution the different forms using ^{31}P nuclear magnetic resonance spectroscopy (P-NMR) (Cade-Menun 2017). P-NMR analysis were carried out at the Saskatchewan Structural Sciences Centre at the University of Saskatchewan (Saskatoon, Canada). The soil P speciation by P-NMR was only carried out in two of the four LTFE. P speciation was analyzed in the soil samples, taken up in 2000 in LTFE0 after 28 years of experiment on increasingly doses of annual applications of triple superphosphate. P speciation was also analyzed in LTFE2 by sampling the plough soil layer before (1998) and after (2016) regularly applying 10 applications of OPW over 17 years.

In addition, I also analyzed these LTFE2 samples by the P K-edge X-ray absorption near-edge structure spectroscopy (P-XANES) at the Canadian Light Source (CLS) in Saskatoon (Saskatchewan, Canada) to insight SIP speciation and its relationships with soil constituents. Due to time constraints, these results are still under process and are not yet available.

The main information on soil P speciation we can derive from the P-NMR results in LTFE0 and LTFE2 is that regardless of the LTFE or fertilization treatments, soil P was primarily inorganic (Table D.2). On average orthophosphate ions accounted for 77% of the extracted P in the NaOH-EDTA solution, while all organic species accounted for 21%. Among the organic P species, orthophosphate monoesters were always the most abundant group, with mainly inositols hexakisphosphates (IHP), which accounted for 23 to 50% of organic P forms (Table D.2), and unidentified forms, as previously reported (Liu et al. 2019; Perillo et al. 2021).

In LTFE0, mineral P fertilization has affected SOP speciation, with a tendency for *myo*-IHP to increase with P rates. However, the origin of this increase was uncertain and could be related to fertilization and thus the amount of P returned in crop residues (Noack et al. 2014; Perillo et al. 2021), grain losses during climatic events, field management history, or its stronger affinity to Fe- or Al-oxides compared to other organic P forms.

The approach in LTFE2 allowed us to study the temporal variation of soil P speciation under different fertilization treatments, either no P applied or different OWP, from which P speciation was determined. The only difference in P speciation between OWP was the content of all inorganic and organic P species. On average, the OWP were composed at 85% as orthophosphate, which was consistent with previous studies where comparable OWP were analyzed by P-NMR (Hansen et al. 2004; He et al. 2007; Annaheim et al. 2015). Therefore, OWP application could only play a minor role in SOP speciation changes, which is contrary to our hypothesis in (Section 3.1). The main effect of OWP fertilization was an increase in the sum of all inorganic P forms concentration depending on the fertilization P rate, and an increase in orthophosphate ions over 17 years of cropping. Such increases have been frequently reported under both mineral and organic fertilization (Schneider et al. 2016; Weyers et al. 2016; Cade-Menun 2017; Liu et al. 2017; Menezes-Blackburn et al. 2018; Gläsner et al. 2019).

In the two LTFE studied (LTFE0 and LTFE2), the control treatment, which did not receive any P application, the SOP speciation did not vary significantly and plant P uptake leads to a decrease in the concentration of all inorganic P forms. These results are consistent with previous studies (Liu et al. 2019) and contribute to our understanding of soil P dynamics under different organic waste management practices.

Table D.2 Concentrations in the extracting NaOH-EDTA solution, determined by P-NMR, of main classes of inorganic and organic P forms in LTFE0 (2000) and LTFE2 (1998 and 2016) soils samples. IHP: inositol hexakisphosphate. Values are mean \pm std. err. Values from literature are minimum – maximum (see Table A.2).

P form (mg P kg ⁻¹)	LTFE0	LTFE2		Literature (118 situations)
		1998	2016	
P_{NE}	351 \pm 45	328 \pm 28	391 \pm 172	65 – 2966
TP_{HF} recovery (%)	82 \pm 1	50 \pm 4	48 \pm 8	11 – 143
All inorganic P	274 \pm 43	254 \pm 6	316 \pm 36	34 – 2520
Orthophosphate	271 \pm 43	245 \pm 6	307 \pm 36	30 – 2520
All organic P	77 \pm 2	74 \pm 2	75 \pm 3	7.5 – 482
Phosphonates	2.1 \pm 0.2	5.8 \pm 0.4	5.0 \pm 0.3	0 – 8.5
All monoesters	59 \pm 2	52 \pm 9	55 \pm 12	1.5 – 315
IHP	39 \pm 1	17 \pm 1	19 \pm 1	0 – 427
Unidentified monoesters	17 \pm 1	32 \pm 1	33 \pm 2	0 – 315
All diesters	15 \pm 0.8	16 \pm 2	15 \pm 3	0 – 90
Unidentified diesters	2.3 \pm 0.1	2.6 \pm 0.2	2.0 \pm 0.2	0 – 79

D.5 Soil organic matter C/N/P

The model results highlighted the higher residence time of SOP (several decades to century) compare to SOC, which is about 6 to 50 years (Boiffin et al. 1986; Plénet et al. 1993; Andriulo et al. 1999). This difference is due to difference of mineralization rate which suggests a decoupling cycle on the plough soil layer. Indeed, in LTFE0, the ratio of SOC over total N (N_{tot}) slightly decrease by -0.84 over 28 years with an average of 14.4, while the SOC/SOP ratio strongly decrease from 111 in 1972 by -24 over 28 years (Figure D.6). The mineralization is driven by the appetite of microorganisms for energy or a specific resource such as C, N, and/or P in order to maintain its C/N/S ratio, which depends on ecological strategy (McGill and Cole 1981; Swift et al. 1981; Bertrand et al. 2019). Therefore, microorganisms and soil organic matter stoichiometry would tend to converge by either physiological flexibility or mineralization.

McGill and Cole (1981) proposed that SOP mineralization is independent of SOC and N_{tot} dynamics. On another hand, McConnell et al. (2020) proposed a more nuanced point of view with a SOP mineralization more or less coupled with SOC mineralization depending on SOC/SOP values: the higher the SOC/SOP the more decoupled the mineralization as

higher SOC/SOP ratio was related to limited P resource environment. In addition, the main organic molecules in plant derivate residues, such as cellulose, hemicellulose, and lignin, do not contain P (Kögel-Knabner 2002), and are mostly mineralized for C supply. Such molecules represent between 30-45%, 25-40%, and 15-20% of crop residues dry mass for cellulose, hemicellulose, and lignin respectively (Abiven et al. 2011; Harindintwali et al. 2020). Therefore, those organic compounds do not contribute to SOP cycle do not release phosphate ions in soil solution. The absence of P in most organic molecule in crop residues support the SOC and SOP decoupling dynamics as not all molecules release the same amount of C or nutrients.

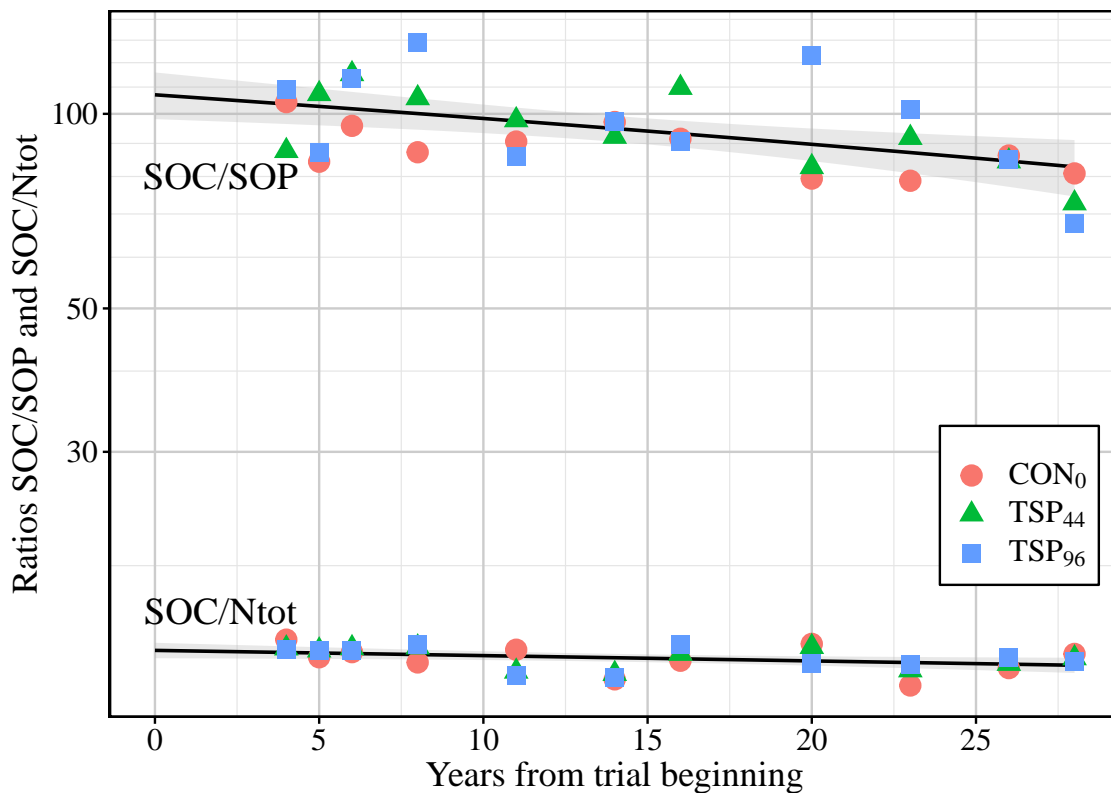


Figure D.6 Changes in SOC/SOP and SOC/Ntot ratios (log scale) in the plough soil layer of the LTFE0 long-term field experiment over 28 years of continuous cropping and fertilization at three different rates of triple superphosphate (0, 27 and 96 kg P ha⁻¹ yr⁻¹) at the LTFE0.

Regressions equations:

$$\text{SOC/SOP} = -0.86 \pm 0.26 \times \text{Year} + 107 \pm 4; P\text{-value} = 0.002; R^2 = 0.26; n = 33;$$

$$\text{SOC/Ntot} = -0.03 \pm 0.01 \times \text{Year} + 14.8 \pm 0.2; P\text{-value} = 0.03; R^2 = 0.14; n = 33$$

D.6 SIP and SOP multiyear dynamics with cumulative plot P budget

The plot cumulative P budget (Bcum), i.e. the sum over years of budget (P input in fertilization – P output in harvest) at the field-plot scale is an indicator of accumulation or depletion of SIP in the plough soil layer (Figure D.7a).

Slopes of SIP vs. Bcum took into account between 100% (LTFE2) and 61% (LTFE3) of SIP recovered in Bcum values irrespective of negative or positive values. Thus, the fertilization application rates and crop P removal mostly affected SIP stock. In LTFE3, not all SIP was recovered by Bcum due to variation in plough sole and soil mixing with the just underneath soil layer (personal communication). The observed relations between Bcum and SIP were comparable to previous results, where Bcum was the driven variable of P concentration in soil solution (C_P) in plough soil layer (Messiga et al. 2010; Morel et al. 2014).

In LTFE0 and LTFE1, the SIP relations were explained by the mineral fertilization application rates. In LTFE2 and LTFE3, they can be explained by the high content of inorganic P as orthophosphate in OWP highlight by P-NMR results as well as in the absence of any changes in concentrations of organic and other (i.e., poly- and pyrophosphates) inorganic P forms (Table 3.7). As previously reported (Oberson et al. 2001; Morel 2002; Steffens et al. 2010; Dodd and Sharpley 2015), OWP fertilization can contribute to replenish the soil solution in phosphate ions, and thus, contribute to crop nutrition.

In comparison to SIP, SOP stock was not affected by the cumulated P budget: none of the slope regression were significantly different from 0 (Figure D.7b). Either under repeated high OWP fertilizations or long-term unfertilized situation, the SOP stock remain stable. As a first conclusion, only SIP can play a significant role in crop nutrition. It is then interesting to compare the mechanisms of phosphate ions fluxes at the soil solid-to-solution interface, which are related to SIP and SOP, i.e. diffusion and mineralization, respectively.

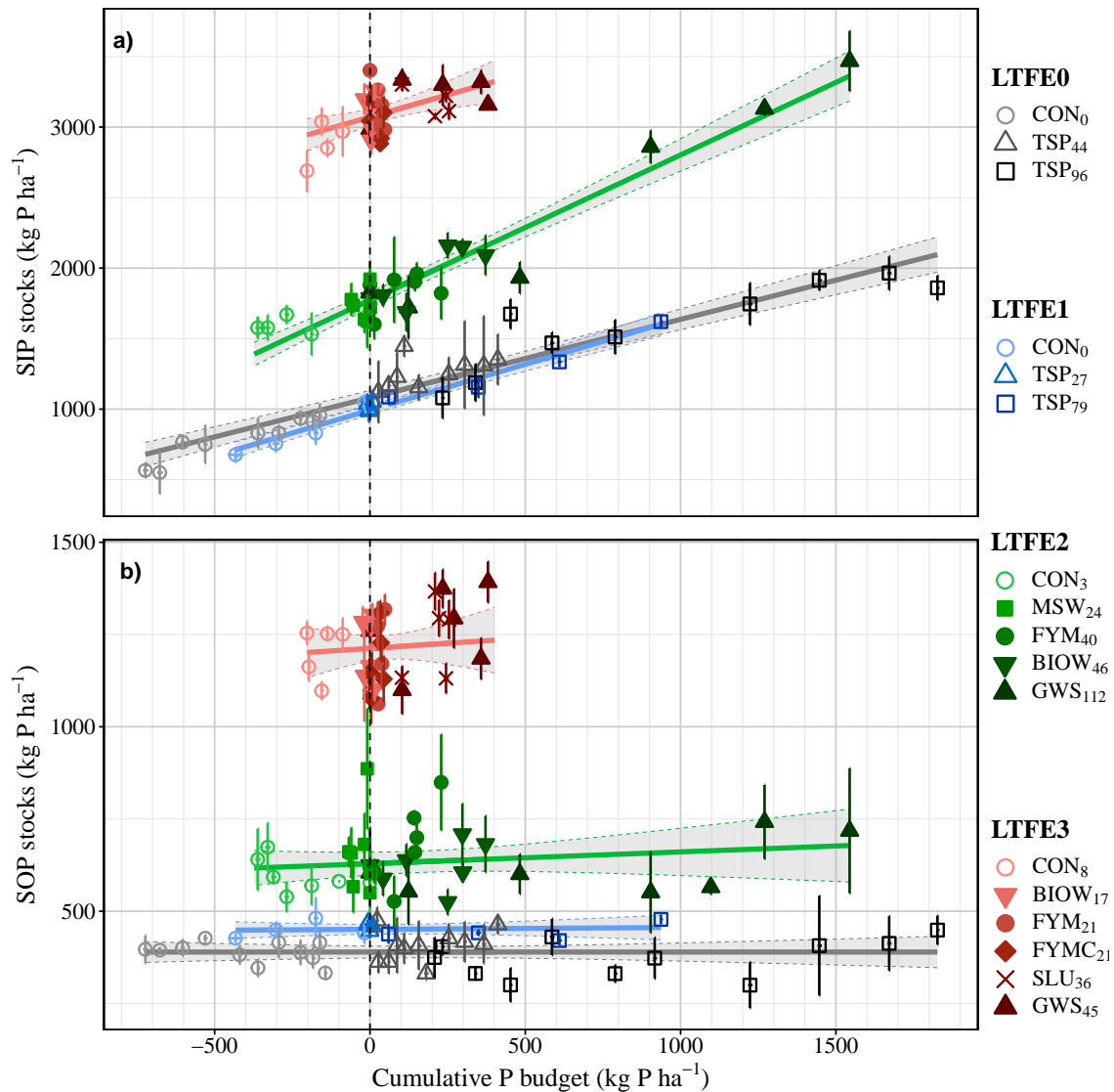


Figure D.7 SIP ($TP_{HF} - SOP$) (a) and SOP (b) stocks in the soil ploughed layer in relation to cumulated P budget of (P applied minus crop P removal) in the four studied LTFE. Values are means \pm std. err. ($n = 4$). Grey areas are confidence interval (95%) of linear regression. CON: no P input, MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; SLU: dehydrated urban sewage sludge; GWS: compost of green waste and SLU; BIOW: bio-waste compost; TSP: triple superphosphate. Numbers in treatments names are P annually applied on average ($kg P ha^{-1} yr^{-1}$).

SIP

LTFE0: $0.56 \pm 0.03 \times Bcum + 1081 \pm 28$ ($P < 0.0001$; $R^2 = 0.91$; $n = 33$)

LTFE1: $0.65 \pm 0.04 \times Bcum + 993 \pm 15$ ($P < 0.0001$; $R^2 = 0.96$; $n = 12$)

LTFE2: $1.03 \pm 0.06 \times Bcum + 1773 \pm 27$ ($P < 0.0001$; $R^2 = 0.92$; $n = 35$)

LTFE3: $0.61 \pm 0.20 \times Bcum + 3073 \pm 29$ ($P = 0.005$; $R^2 = 0.14$; $n = 36$)

SOP

LTFE0: $1.0 \cdot 10^{-5} \pm 0.01 \times Bcum + 389 \pm 8$ ($P = 0.99$; $R^2 = 0.00$; $n = 33$)

LTFE1: $0.005 \pm 0.02 \times Bcum + 451 \pm 6$ ($P = 0.76$; $R^2 = 0.01$; $n = 12$)

LTFE2: $0.03 \pm 0.03 \times Bcum + 629 \pm 15$ ($P = 0.35$; $R^2 = 0.03$; $n = 35$)

LTFE3: $0.05 \pm 0.1 \times Bcum + 1212 \pm 17$ ($P = 0.64$; $R^2 = 0.01$; $n = 36$).

D.7 Phosphate ions fluxes that replenish the soil solution

Plants absorb P as phosphate ions in the rhizosphere, which represent a volume of 1 millimeter around roots (Barber 1984; Hinsinger 1998). About 1% of the absorbed phosphate ions originate from the soil solution, therefore the 99% remaining come from solid phase and have replenished the soil solution by various mechanisms at the solid-to-solution interface (Barber 1984). Among those mechanisms, diffusion (i.e. movement of chemical compounds within or between medium phases along a concentration gradient) appear to be the most important one and can be described by a Freundlich kinetic equation (Morel 2002; Ehlert et al. 2003; Stroia et al. 2007). The equation is presented in General Introduction Section A.3.4, and its parameters for the four studied sites are presented in Table D.3.

Comparing SOP mineralization to phosphate ions diffusion at the solid-to-solution interface would provide an estimation of their respective contribution to replenish soil solution in phosphate ions balance the soil-to-solution transfer of phosphate ions in the four studied LTFE (Figure D.8).

Table D.3 Phosphate ions that replenish C_P through either diffusion at the solid-to-solution interface according to the Freundlich kinetic equation: $P_r = v \times C_P^w \times t^p$; with $P_r < SIP$.

With P_r the phosphate ions diffusible at the solid-to-solution interface (mg P kg^{-1}); C_P the phosphate ions concentration in solution (mg P L^{-1}); t the time in minute; v the P_r value for $C_P = 1 \text{ mg P L}^{-1}$ and $t = 1$ minute; w account for C_P effect; and p for time effect.

Soil P_r was calculated for $t = 1 \text{ year} = 525600 \text{ min}$. P_r values presented in the table were calculated for the following treatments, for each site, by using the corresponding C_P value: LTFE0: TSP₄₄; LTFE1: TSP₂₇; LTFE2: FYM₄₀; LTFE3: FYM₂₁; P_r stocks at 1 year were calculated by multiplying P_r by soil mass. Source: LTFE0 and LTFE1: Morel et al. 2021, LTFE2: determined according to method describe in General Introduction A.3.3, LTFE3: personal communication.

	C_P mg P L^{-1}	v	w	p	P_r 1yr $\text{kg P ha}^{-1} \text{ yr}^{-1}$
LTFE0	1.45±0.05	1.64±0.09	0.73±0.02	0.376±0.012	1187±32
LTFE1	0.74±0.06	5.9±0.2	0.68±0.02	0.236±0.007	370±20
LTFE2	1.31±0.05	9.3±0.4	0.51±0.02	0.258±0.009	1172±22
LTFE3	0.64±0.02	10.3±0.5	0.67±0.04	0.233±0.009	629±13

In the plough soil layer of conventional agrosystems, SOP mineralization represents between 0.1% and 1% of phosphate ions flux that replenish the soil solution, thus SOP mineralization remain stable when plot against C_P (Figure D.8). This result is in accordance to previous finding where phosphate ions diffusion represented about 90% ±1% of plant-

absorbed P (General Introduction Section A.3.3). Therefore, the SOP mineralization was inferior to the experimental variability observed in isotopic dilution studies, and can only play a minor role in crop nutrition. The fact that SOP mineralization represents a small portion of the phosphate ions flux at the solid-to-solution interface highlights that the plant-availability of organic phosphorus is not a predominant factor for plant growth in conventional agrosystems. Hence, incorporating the POS into the current models used for P management in agrosystems will bring only small improvements.

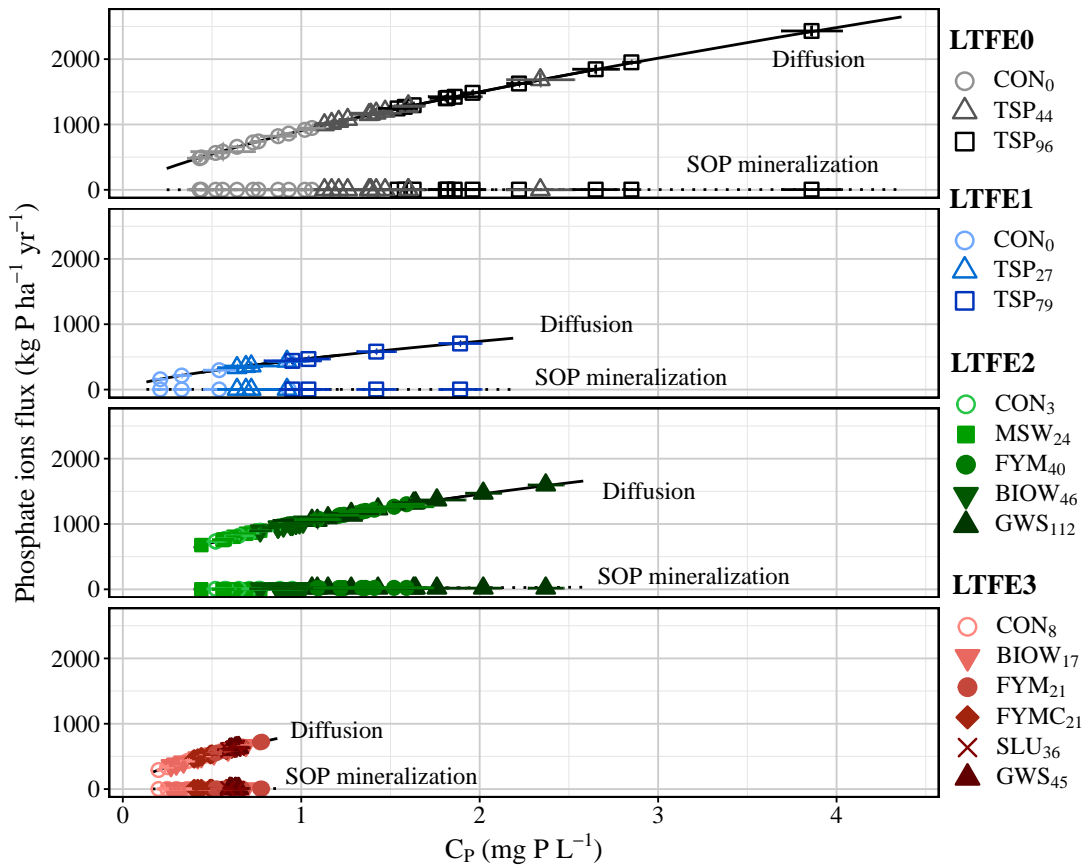


Figure D.8 Phosphate ions fluxes replenishing the soil solution through diffusion at the solid-to-solution interface and through SOP mineralization in relation to cumulated P budget in the four studied sites.

Values are means \pm std. err. ($n = 4$). Grey areas are confidence interval (95%) of linear regression. CON: no P input, MWS: municipal solid waste compost; FYM: farmyard manure; FYMC: FYM compost; SLU: dehydrated urban sewage sludge; GWS: compost of green waste and SLU; BIOW: bio-waste compost; TSP: triple superphosphate. Numbers in treatments names are P annually applied on average ($\text{kg P ha}^{-1} \text{ yr}^{-1}$).

D.8 Potential drivers of SOP mineralization

While SOP mineralization only represents less than 1% of SOP (0.3% of total P stock on average), significant differences were observed on average mineralization fluxes among the four LTFE studied (Table D.1). Therefore, effects of soil and climate properties on SOP mineralization can be investigated considering soil and climate properties relevant for describing SOC dynamics (e.g. average annual temperature, soil clay concentration). Multivariate analysis approaches are interesting exploratory methods to determine the relationship between environmental variables and the parameters studied.

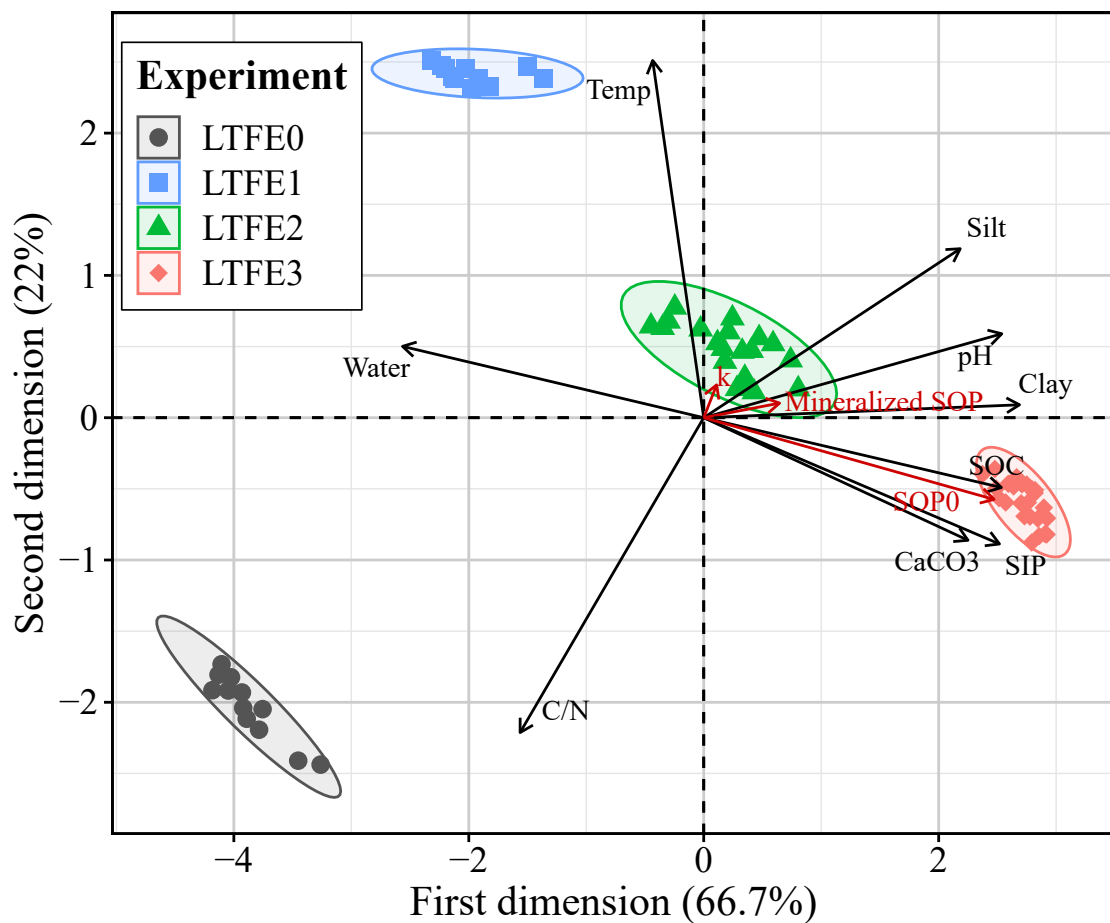


Figure D.9 Principal component analysis describing the relations among selected explanatory variables and SOP initial stock, coefficient k , and SOP mineralization as response variables (red arrows) according to the four LTFE (ellipses).

The SOP mineralization drivers are a set of agropedoclimatic variables that impact either SOP availability for microorganisms, community of microorganisms, or condition needed for mineralization. It is reasonable to consider that these variables are the same as those that are related to the SOC storage or N mineralization (Clivot et al. 2019; Wiesmeier et al. 2019; Basile-Doelsch et al. 2020). We therefore selected SOC stock, organic matter C/N, CaCO₃

concentration, soil water pH, clay and silt concentration, mean annual temperature, mean annual water inputs (rainfall + irrigation), and SIP stock as potential explanatory variable of SOP mineralization and its related variables. The following principal component analysis (PCA) provide an insight of the selected variables relations with SOP mineralization, coefficient of mineralization k , and SOP initial stock. The four LTFE are discriminated according to those variables, then explained variables are placed on the scatterplot. When an explanatory variable was unique for a specific site, the value was repeated for each treatment and bloc within site.

Another approach to explore relation of the three variables with pedoclimatic factors is the multiple step-wise model selection. Models were tested by adding and/or removing the selected, and the best model was selected based on AIC (Akaike information criterion). This approach provides a linear relation between the tested response variables and a set of selected explanatory variables. Here are the resulting equations (clay and silt content were combined as Fine texture):

$$\begin{aligned} \text{Initial SOP} = & 20.6 \times \text{SOC} - 2.9 \times \text{Fine texture} + 514 \times \text{Temp} \\ & - 3.0 \times \text{Water input} + 204; \\ & (\text{AIC} = 627) \end{aligned}$$

$$\begin{aligned} \text{Coefficient } k = & -1.2510^{-4} \times \text{CaCO}_3 + 3.6710^{-5} \times \text{Fine texture} \\ & + 0.004 \times \text{C/N} - 0.05; \quad (\text{Eq. D.1}) \\ & (\text{AIC} = -624) \end{aligned}$$

$$\begin{aligned} \text{SOP mienralization} = & 0.01 \times \text{Water input} + 0.02 \times \text{Fine texture} - 7.71 \times \text{pH} \\ & + 2.25 \times \text{SOC} + 11.01; \\ & (\text{AIC} = 231) \end{aligned}$$

Temperature can be seen as a proxy for climatic condition and its increase was often related to a SOC decrease (Amundson 2001; Koven et al. 2017). According to the ACP, the most collinear and positively correlated variables with the initial SOP stock were SOC, CaCO_3 , SIP, and clay content. Therefore, soils under dry climate and with high sorption surface would tend to have a higher SOP stock. This result was in accordance general knowledge on SOC, where climate is the key driver of SOC stocks at the global and regional space scale (Amundson 2001). The coefficient of mineralization k seems more positively related to fine soil texture and average temperature, and negatively related to organic matter C/N. Among the tested variables, the SOP mineralization tends to be related to higher pH, dry climate, and fine texture soil. A fine soil texture with neutral to basic pH tends to stabilize SOP and limits is mineralization. Previous studies have reported the soil clay content as a factor of carbon storage and stabilization (Wiesmeier et al. 2019). On another hand, pH

affects phosphatase activity in soil and therefore their mineralization capacity. However, the pH optimum depend on the enzyme studied (Nannipieri et al. 2011).

Correlations between explained variables and pedoclimatic conditions are coherent with literature, but no further conclusion can be drawn as those relations need to be validated in different situations (Burkitt et al. 2006).

E Conclusion and perspectives

The SOP mineralization and its potential contribution to plant-available P and crop nutrition was assessed in the plough soil layer of four contrasting French LTFE. With such a limited number of experiments, it is difficult to extrapolate and quantify the drivers controlling the SOP mineralization. To better understand the SOP dynamics in agrosystems, a modelling approach must be applied on a large array of LTFE, and should take into account other factors such as microbial and enzymatic activity, phosphate ions in solution (as it can inhibit phosphatases activity), soil mineralogy, water content, soil organic matter content, or pH.

Despite representing an important proportion of total soil P, the contribution of SOP to the replenishment of the soil solution in phosphate ions through mineralization is very small. This was clearly shown by the limited impact of the plot cumulated P budget on SOP, indicating that the SOP stock was hardly affected by P inputs and outputs. Instead, the dominance of SIP, mainly in the form of phosphate ions, was highlighted as the key driver of plant P nutrition in these agrosystems. The diffusion of phosphate ions at the solid-to-solution interface was previously identified as the dominant mechanism that replenishes the soil solution in phosphate ions, and thus plays a critical role in determining plant P uptake and growth. This highlights the importance of accurately measuring and managing the phosphate ions pool and fluxes, to optimize plant P nutrition and yield. Furthermore, the effect of OWP fertilization on soil P dynamics was relatively small because most of this P supply is phosphate ions, which primarily affects SIP with minimal effects on SOP. It suggests that, even with the application of OWP, phosphate ions remain the primary form of P affecting plant P nutrition in temperate agrosystems.

Further research should focus on the major processes that significantly replenish the soil solution in phosphate ions, such as diffusion at the solid-to-solution interface. Integrating diffusion mechanisms into agronomic models (e.g. STICS) would greatly benefit to agronomical management, while including SOP mineralization would only slightly improve such models. Since my thesis focuses on temperate cropped soils, the question remains for other agrosystems (e.g. grasslands, orchards, or vineyards) and other climates (e.g. tropical, arctic).

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Titre : Minéralisation à long terme du phosphore organique dans des sols cultivés : évaluation et facteurs de contrôle

Résumé : La minéralisation du phosphore organique du sol (POS) pourrait contribuer au P phytodisponible du sol. Chiffrer ce mécanisme permettrait d'ajuster au mieux la fertilisation des sols cultivés aux besoins des cultures. Dans cette thèse, la dynamique d'incorporation et de minéralisation du POS a été chiffrée dans quatre essais agronomiques de longue durée, menés sur la fertilisation minérale (superphosphate) ou organique (composts urbains, boues de STEP, fumier de vaches) dans des situations agropédoclimatiques diverses. Le stock initial de POS varie entre essais, et les flux d'incorporation et de minéralisation sont équivalents. Par conséquent, le stock de POS ne varie pas ou peu en fonction des essais, des traitements et des durées d'expérimentation. Au contraire, le stock de P inorganique du sol suit fidèlement les évolutions du bilan cumulé de P en fonction des pratiques agricoles. La minéralisation du POS est donc un mécanisme mineur du réapprovisionnement du P phytodisponible du sol, contrairement à la diffusion des ions phosphates à l'interface solide-solution.

Mots-clés : Phosphore organique du sol, Agrosystèmes, Cycle biogéochimique, Fertilisation, Phytodisponibilité, Essai agronomique de longue durée.

Title: Long-term mineralization of organic phosphorus in agricultural soils: evaluation and control factors

Abstract: The mineralization of soil organic phosphorus (SOP) may contribute to the plant-available P. Quantifying this mechanism would allow to better adjust the fertilization of cropped soils according to crop needs. In this thesis, the dynamics of incorporation and mineralization of SOP have been quantified in four long-term field experiments, carried out with mineral (superphosphate) or organic (urban composts, sewage sludge, farmyard manure) fertilization in different agropedoclimatic situations. Initial SOP stocks were different among trials, and the incorporation and mineralization fluxes were equivalent. Therefore, the SOP stock varies little or not with experiments, treatments and trial duration. Instead, the inorganic P stock in the soil closely follows changes in the cumulative P budget as a function of cropping practices. Thus, the SOP mineralization is a minor mechanism for replenishing plant-available P in soils, as opposed to phosphate ions diffusion at the solid-to-solution interface.

Keywords: Soil organic phosphorus, Agrosystems, Biogeochemical cycle, Fertilization, Plant-availability, Long-term field experiment.

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