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Dynamics of phosphate in soils. An isotopic outlook*

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Abstract

The quantities of phosphorus leached or carried away by erosion are always low in comparison with the quantity of P taken by plants. Therefore, without P application, dynamics of P in soil-plant systems depends mainly on plant P uptake from available soil P. This paper concerns mainly the description and the analysis of available soil phosphate. Available soil P is generally determined using extraction methods. It was shown, using isotopic exchange, method developed in soil-solution mixtures in steady-state, that available soil P could be described as a system with many pools. For agronomic purposes, available soil P was described with five pools of phosphate ions which have increasing rates of transfer from soil particles to soil solution. The most important is a pool which contains only directly available phosphate ions. These phosphate ions leave the solid phase of the soil to enter in the soil solution in a time shorter than 15 seconds: this time is the minimum time required to realize its determination. The intensity, quantity and capacity factors recommended to describe the available soil P are derived from experimental data characterizing this pool. The four other pools all are directly branched on this central pool. They are characterized by the quantities of P they contain and by the time required for the phosphate ions they contain to enter into the soil-solution. Effects of continuous P uptakes and of various P applications on these compartments were described. It was shown that: (i) continuous cropping without P return decreases ineluctably the intensity and quantity factors, and consequently soil P fertility (ii) applications of P quantities higher than P outputs with crops do not always increase the intensity and quantity factors, and consequently available soil P and its availability. The absolute values of the increase depends on: the type of P fertilizer or crop residues applied on the soil, on the level of soil P fertility before P application and on the fixing capacity of the soil for phosphate ions.

Introduction

In "natural" ecosystems, as forests, wetlands or permanent grasslands, plant nutrients return to soils at, or near, the place where they were previously taken as bioavailable soil P by plants. In such ecosystems the P cycle can be considered as closed and the rate of P cycling depends on biogeochemical soil properties and on climatic conditions. Sun, through the photosynthesis, is the alone source of energy supplied to the "motor" of this cycle.

In agrosystems, two or three sources of energy must be supplied to feed the motor for the P cycle and other nutrient cycles: they are solar energy, human or animal energy and fossil energy applied as fuel, fertilizers and pesticides. In such ecosystems, a part of the phosphorus taken from soils as bioavailable soil P is exported out of fields with harvest and is transferred as foods to towns (Frissel, 1978). Usually this P does not return to the soils where it has been previously extracted by plant roots as bioavailable soil P. In some countries, generally called developed countries, P extracted from mines of other countries, generally developing countries, is applied on soils and crops as P ferlilizers. So, in agrosystems, the global and local

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cycles of P depend not only on soil properties but also on agricultural practices of farmers (Frossard et al., 1992a). Many P cycles have been published (Blair et al., 1977; Stevenson, 1985). Whatever the cycle, the bioavailable soil P, or the soil solution P which is a part of this soil P, is given as the main, and the weakest, link of the P cycle. The aims of this paper were to present a functional model of the bioavailable soil P deduced from the utilization of the isotopic methods and to analyze, using parameters obtained by these methods, the effects of P outputs with harvests and P inputs with different kinds of phosphate fertilizers on bioavailable soil P.

Phosphorus status in soils

Total P in soils is included between 200 mg P kg^{-1} and 3000 mg P kg^{-1}. Orthophosphate is the main form of P in soils. Minus than 0.1% of the total soil P is found in the soil solution as free orthophosphate ion. There is no correlation between the quantity of total soil P and the quantity of P in the soil solution. In soils cropped since a very long time, for example more than 50 years, about 2/3 of the total phosphorus is inorganic and linked to Al, Fe or Ca and 1/3 of the total P is linked to organic matter.

Phosphate behavior in soil-solution systems

All soils release phosphate ions

1. When a soil is shaken with distilled water, or with a solution containing various chemical reactants, the phosphate ion concentration in the solution increases during 4-6 hours up to an equilibrium value. In agricultural soils, the concentration of P, as phosphate ions, in soil soution can be included between 0.002 mg P^{-1} and 2 mg P^{-1}.
2. Plants take the phosphorus they need in soils as phosphate ions.

All soil particles adsorb phosphate ions

When phosphate ions are applied to soils in a quantity greater than the quantity which can be dissolved in the soil solution, a fraction of the added phosphate ions disappeared from the soil solution. This fraction is adsorbed by soil particles and is sometimes said "fixed". This transfer from soil solution towards soil particles occurs with most of the soil components (Frossard et al., 1995). Just after a P application, phosphate ions are adsorbed on the surface of soil particles, during a time always shorter than time required to harvest a crop; further, phosphate ions are slowly included into soil minerals (Barrow, 1980; Syers & Lu Ru-kun, 1990). The fraction of the phosphate applied which is transferred on soil components varies with soils. But, whatever the soil, this fraction increases: (i) when the time of contact between phosphate and soil increases (Barrow, 1991); (ii) when the temperature increases (Barrow, 1980). For an infinite time of reaction between P applied and soil components, the equilibrium phosphate ion concentration in the soil solution could be near the concentration found without P application. In fact, for each soil, there is an equilibrium value for phosphate ion concentration in the soil solution as far as chemical properties, pH for example, are not modified by fertilizers applications and agricultural practices. Whatever the soil, this soil property, which decreases the phosphate ion concentration in the soil solution after an application of water-soluble P fertilizer, decreases the chemical potential of phosphate ions (Aslyng, 1964). As P uptake is proportional to P concentration (Barber, 1984), the nutritive potential of P applied as fertilizer always decreases when time of contact between soil and P applied increases.

Phosphorus dynamics in agrosystems

The general aim of dynamics is to explain a movement in relation with driving forces. Two main driving forces act on phosphate ions in soil-solution-plant systems. One is the gravitation which controls movements of water, solutes and particles in and on soils. The other is the diffusion process which controls movements under concentration gradients. In the case of phosphate ions in soil-solution-plant systems two situations create concentration gradients. When roots take phosphate in soil solution to satisfy the P needs of plants a positive gradient is created between soil particles and roots through the soil solution and when water soluble P fertilizers are applied a positive gradient is created between P fertilizers and soil particles or/and plant roots through soil solution.

Gravitation as driving force: leaching and losses of P from the upper layer of soils

The quantities of phosphate leached under the ploughed layer of soil is proportional to the quantity of drained water and to the P concentration in the soil solution; they are always smaller than 3 kg P ha^{-1} $year^{-1}$. The quantities of P which leave the soil surface as dissolved P or particulate P by run-off or erosion depend on the type of particles carried by water and on the volume of water; they are generally lower than 5 kg P ha^{-1} year^{-1} but they can reached 20 kg P ha^{-1} year^{-1} in special cases (Sharpley & Whiters, 1994). But in such a situation the main problem, in an agronomic point of view, becomes the loss of soil more than the loss of phosphorus.

Diffusion as driving force: uptake of phosphate by crops without and with a P application

Plants, even when they are associated with mycorrhizae (Gianinazzi et al., 1981), take the P they need only as orthophosphate ions (Barber, 1984). As ions can exist only in solution, a water layer between soil particles containing available P and active roots is absolutely necessary continuously to authorize the transfer of soil P from soil particles towards the roots.

Conditions of P uptake without recent P application. When 1 g of dry matter is produced, a plant evaporates, in average, 300 ml of water from the soil solution which contains, in average, 0.2 mg Pl^{-1} in Western Europe soils. Thus, when 300 ml of soil solution enter in plant roots and are evaporated, $0.2 \times 0.3 = 0.06$ mg P are absorbed by mass flow. The mean content of P in dry matter about 3 mg P g^{-1} even if very large variations of P contents can be observed in plant dry matter (Walworth and Sumner, 1987). These facts show that mass-flow explains, in average, only $100(0.06/3) = 2\%$ of the total P uptake by crop. This fact also means that an average of 98% of the P taken by roots is released from soil particles during the growth period. Consequently, the greater part of the bioavailable P of a soil must be researched in the solid phase of the soil.

Conditions of P uptake after a recent application of an efficient P fertilizer. When an efficient P fertilizer is applied in fields, or in pot experiments, plants satisfy their nutrient needs from two nutritive sources: the fertilizer and the available soil P. The percentage of utilization of the P of the fertilizer is never higher than 15% (Dean et al., 1947; Morel, 1988; Morel & Fardeau, 1990), and sometimes is near 0% (Morel & Fardeau 1988). So whatever the soil, 85%, or more, of the P applied one year remains in the soil and continues to react with soil components or becomes, for no more than 2% of the P applied, microbial P. These facts summarize the hard and continuous competition for phosphate ions between plants and soil components. Finally, the fate of phosphate ions applied as fertilizer depends more on reactions with soil components than on the P uptake by plants during the year following their applications on, and further in, soils. Consequently, researching the maximal utilization by plants during the year of the application will not significantly decrease the constitution, or the maintenance, of a pool of available P in soil.

In field experiments, or in pot experiments when P applications are lower than 50 mg P kg^{-1} in order to be of the same order of magnitude than the quantities of P applied in field experiments, the P in plants derived from fertilizer (Pdff %) is always lower than 25%: 75%, or more, of the P taken by plants is derived from the bioavailable soil P. Nevertheless, when the rates of P applications are as high as 100 or 200 mg P kg^{-1} in pot experiments (Khasawneh & Doll, 1978) the Pdff % can be greater. But such applications correspond to field applications as high as 300 or 600 kg P ha^{-1} which cannot be considered as realistic for farmer use. Therefore it can be concluded that, whatever the rate of P application, the main source of P for plants in field conditions is the pool of bioavailable soil P. The P nutrition of plants depends mainly on the ability of phosphate ions to be released by desorption, or dissolution, from the solid phase of the soil. The rate of release is controlled by the type of bindings between phosphate ions and soil components, the soil conditions, and mainly its water content at the root-particle interface, the spatial organization of the root system which is specific to each plant species and which varies with period of growth and the rates of N and P applications. *The pool of bioavailable soil P is really the main link of the P cycling in agrosystems and, consequently, one of the keys of the life on our earth.*

Bioavailable soil phosphorus: a system made of many compartments

Bioavailable soil P could be defined as all the soil phosphorus which can contribute to the P nutrition of plants. It was recommended, there is a long time ago, that the bioavailable soil phosphorus should be characterized using three factors deduced from three soil data: a quantity factor, an intensity factor and a capacity factor which describes the variations of the quantity factor when the intensity factor is modified by P uptake or P applications (White & Beckett, 1964). More, as P uptake by plants is a time depending process, parameters describing the ability of available soil P to be released in soil solution with time could be added to the three previous factors.

Bioavailable soil P using an extraction method: a simple model

When using an extraction method, available soil phosphate is described only by a quantity factor: the P quantity extracted by the reactant. It is assumed that the availability of all this quantity is homogeneous. Any time depending parameter has been deduced from such an approach. It was shown that with extraction methods: (i) a fraction of the unavailable soil phosphate is generally extracted: (ii) only a fraction of the available soil P is extracted (Fardeau et al. 1988; Morel & Fardeau, 1987). The ratio between the fraction of available soil phosphate extracted and the fraction of unavailable soil P extracted varies with soils and, for a given soil, with its fertilization history. This explains why these methods are considered as rough methods (Bolland & Gilkes, 1992), and why they will remain rough methods, to predict P uptakes by plants or effects of P fertilizers on crops (Bolland & Gilkes, 1992). The use of successive sequential methods of extraction does not greatly increase the interest of such an approach (Nirel & Morel, 1990), even if they contributed to put forward the idea ihat available soil P was not an homogeneous entirety.

Nevertheless, routine analysis methods using extractants to determine "available soil P" can be applied to follow, in a given soil which receive different P treatments, the direction of the modifications of soil P fertility (Boniface & Trocmé, 1988).

Bioavailable soil P determined using an isotopic exchange method. a functional model

Relation between bioavailable soil P and isotopically exchangeable phosphate ions. It was assumed that isotopically exchangeable P was the bioavailable soil P (Larsen, 1952). The assumption was verified, and can continue to be verified. Two complementary experimental procedures, using isotopes of phosphorus, are required. In one of them, an isotopic exchange is carried out in soil solution mixture in steady-state, using phosphate ions labeled with ^{32}P, between phosphate ions in soil solution and phosphate ions of the soil particles. The isotopic composition, IC = 32P/31P, of the phosphate ions in the soil solution is determined at various times (Morel & Plenchette 1994; Wiklander, 1950). It was shown that IC decreases with time. Let R be the radioactivity applied, IC_t the isotopic composition of phosphate ions in the soil solution at the time t, IC_1 the isotopic composition at time t=1, n an empirical parameter which depends on soil and P_T the quantity of total P in the soil. The mathematical relation between IC_t and the time t of exchange is the following:

$$IC_t = IC_1[t + (IC_1\ P_S)1/n] - n + 1/P_T \qquad (1)$$

In the other procedure (Larsen, 1952), Iabeled phosphate ions are applied to a soil. An isotopic exchange takes place between added labeled phosphate ions and exchangeable phosphate ions of the soil. Further a plant is sown and harvested after different period of growth. The IC_{pl} of P in harvested dry matter are determined. Then IC_t and IC_{pl} are compared for the IC_t of the phosphate ions in the soil solution obtained after a time of isotopic exchange equal to the time of plant growth (Morel & Plenchette, 1994).

It was shown that, when experiments are realized taking into account all the theoretical constraints to be followed, the IC_t of P in the soil solution is equal to the IC_{pl} of P in harvest (Fardeau & Jappé, 1976; Frossard et al., 1994; Morel & Plenchette, 1994). It was also shown that only one compartment of P in soil contains phosphate ions with such IC_{pl}. In the other P compartments the IC is lower than IC_{pl}.

It was concluded that the available soil phosphate ions are the isotopically exchangeable phosphate ions. Therefore, available soil P can be studied analyzing isotopically exchangeable P and characterized uising the parameters describing the status phosphate ions isotopically exchangeable in a soil-solution system in steadystate. These parameters can be derived from analysis, either by stochastic analysis or by compartmental analysis, of isotopic exchange kinetics performed in soil solution mixtures (Sheppard, 1972).

Isotopic exchange: stochastic analysis. The isotopic exchange kinetic Equation [1] was analyzed using the stochastic method (Sheppard, 1972). According to stochastic analysis, the function [1] is to be considered as the Laplace transform of a density function $g(k_i)$ where the k_i are the rates of exchange of phosphate ions between soil solution and soil particles containing isotopically exchangeable phosphate ions. This $g(k_i)$ function was found by studying tables of functions and their Laplace transforms (Feller, 1966). Among the known function, only a gamma density function

$$g(k_i) = [1/\Gamma n][r_1/R]g_i^{n-i}(\exp) - g_i(r_1/R)^{1/n} \qquad (2)$$

can have a transform Laplace as [1]. The parameter $r_1/R = P_S IC_1$ is the ratio of the radioactivity r_1 remaining in soil solution after 1 minute of isotopic exchange and the radioactivity R applied in the soil solution system. This gamma density function indicates that there are many k_i and that these different k_i are continuously distributed from 0 to ∞ these two values being excluded.

Finally, this result is similar to data previously published when studying the rate of slow reactions between phosphate ions and soil components (Barrow & Shaw, 1975) which concluded that the surfaces that react with ions are heterogeneous.

A mathematical mean rate of exchange, K_m, can be calculated, from the experimental parameters, n, P_S and r_1/R, for the k_i of this $g(k_i)$ function (Feller, 1966). Thus, three kinetic parameters characterizing the ability of phosphate ions to enter into the soil solution can be determined:

- the mean rate of exchange, $K_m = n/[r_1/R]^{1/n}$, between soil phosphate ions in soil and phosphate ions in solution with a variance $n/[r_1/R]^{2/n}$;
- the mean sojourn time, $T_m = 1/K_m$, of phosphate ions in the soil solution;
- the mean flux of exchange, $F_m = P_S K_m$, of phosphate ions between the solid phase of the soil and its solution (Fardeau et al., 1991).

Isotopic exchange: compartmental analysis and functional model with many compartments. Another complementary way to analyze isotopic exchange kinetic is the compartmental analysis. When an isotopic exchange kinetic takes place in a complex system, it can be concluded that the isotopically exchangeable elements are distributed in a system with more than one compartment. This property was scarcely taken into account earlier for the analysis of isotopically exchangeable P. Each compartment can be defined by its size and by its rate of exchange with the compartment that had received the tracer (Sheppard, 1972). Thus, a compartment is defined as a part of the system where all the rates of exchange are equal.

It was shown, using stochastic analysis, that there is an infinity of rate of exchange k_i. Consequently, strictly and mathematically speaking, each exchangeable phosphate ion could be considered as a compartment with its individual rate of exchange with the other phosphate ions. Such approach was considered as mechanistic (Barrow, 1991), even though it looks like a probabilistic model. Such a mechanistic model is difficult to transfer in term of agronomic application where the problem is to satisfy continuously the phosphorus needs of plants. Therefore the functioning of roots and root system was considered to adapt to the agronomic situation, the mathematical results and a practical model was developed.

Firstly it was shown that all the P compartments included in solid phase of the soil are organized as a mamellary system (Sheppard, 1962) whose the soil solution is the central pool (Fardeau, 1993). Finally available soil P has been subdivided in 5 pools in relation with the functioning of roots and root systems (Fardeau, 1993). The central pool, and the first able to satisfy the P needs of plants, is the pool, P_L, of free phosphate ions. This pool contains ions which can be transferred into the soil-solution in a time smaller than 15 seconds, this time being the shorter time necessary to apply ^{32}P, to shake the mixture and to sample the soil solution to determine the IC of phosphate ions (Fardeau & Frossard, 1992; Fardeau, 1993; Salcedo et al., 1991). Therefore they are considered as directly and immediately available for crops, if, and only if, a thin layer of soil solution takes place between roots and soil particles that contain P-ions. The four other pools, A, B, C, and D are organized as a mamellary system (Sheppard, 1962). They are branched directly on the central pool. The pool A contains ions which can leave the solid phase to enter into the solution in a time included between 1 minute and 1 day which is the mean time of active uptake of phosphate ions by a given part of a root (Barber, 1984); the pool B corresponds to the ions exchangeable between 1 day and 3 months which is the mean time of uptake by a root system, the pool C corresponds to the ions exchangeable between 3 months and 1 year and the last pool C corresponds to ions exchangeable in more than 1 year.

A schematic model (Figure 1) has been developed to illustrate the factors characterizing the bioavailable soil P (Fardeau, 1993). The different pools are schematize with rectangles. The height of the pool P_L is be proportional to the concentration, C_P, of phosphate ions in the soil solution which is always taken as intensity factor (Barber, 1984; White & Beckett, 1964). The surface of the pool is proportional to the quantity P_L which is taken as quantity factor. The length of this pool is, by definition, P_L/C_P. This fraction is the ratio of the quantity factor P_L to the intensity factor, C_P. Consequently the length of this pool schematize the capacity factor which is also proportional to the fixing capacity of the soil for phosphate ions (Frossard et al., 1992b). The capacity factor is expressed in units of volume per unit of weight; its value represents the volume of solution which can be released from the soil without variation of the C_P concentration. The other

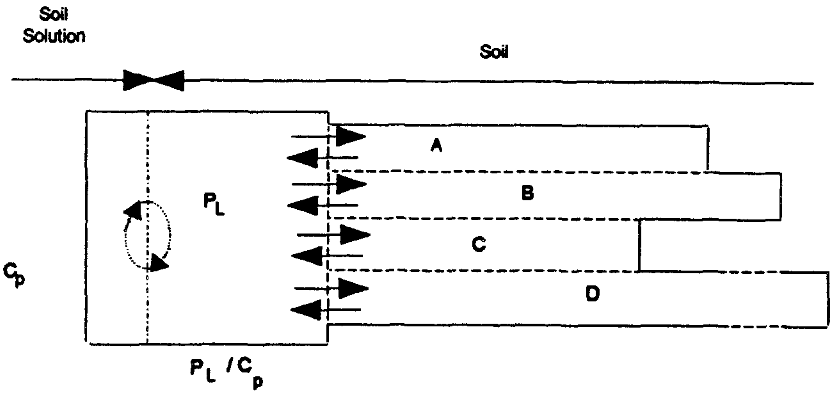

Figure 1. Pluricompartimental model of bioavailable soil P. Pool P_L : phosphate ions instantaneously exchangeable and directly available. Pool A: ions leaving the solid phase of soil towards the soil solution between 1 minute and 1 day. Pool B: ions leaving the solid phase between 1 day and 3 months. Pool C: ions leaving the solid phase between 3 months and 1 year. Pool D: ions leaving the solid phase in more than 1 year.

pools A, B, C and D are represented using a unique height for all; therefore their lengths are proportional to their P contents. The scale applied to the pool P_L can be different to the scale used for the other pools to schematize the greater importance to the P_L pool, the first to be taken by the plants.

This model concerns only inorganic P, organic P following other rules of transformation, such as microbial mineralization and organization. One of the most new information given by this mamellary model is that ions present in solution at a given time, and mainly those derived from water soluble P fertilizers recently applied, can enter directly in the less mobile pools. This functional model, which gives kinetic parameters describing the ability of available soil P to leave the solid phase of the soil, as also described for another major nutrient: the potassium (Fardeau et al., 1992; Poss et al., 1991).

Modifications of bioavailable soil phosphorus with agricultural practices

For large lots of soils, the factors intensity, quantity and capacity are statistically independent. But for a given soil which received different P treatments, or for a given soil type, they become statistically interdependent (Dalal & Hallworth, 1977).

Modifications of bioavailable soil P characteristics with P uptakes by plants and no P application or P applications significantly lower than P uptakes

When soil P is taken by a plant the intensity and quantity factors decrease and the capacity factor increases (Fardeau, 1993). Therefore with continuous cropping without P returns the soil P fertility always decreases and in such a situation there is no known "natural" biological mechanisms which can increases bioavailable soil P from unavailable soil P at a sufficient rate to sustain a continuous food production at a level sufficient to nourish the increasing world population. This fact is of a major importance in developing countries to recommend P fertilization.

Modifications of bioavailable soil P characteristics with simultaneous P uptakes by plants and P applications

Applications of water soluble P fertilizers

When, in a soil, the level of bioavailable soil phosphate is near its equilibrium value, this level is maintained by P applications of the same order of magnitude than the outputs with the harvests as far as the organic matter content of soil does not decrease under cropping. When the organic matter content decreases with continuous cropping without significant returns of organic matter, the capacity factor of soil for phosphate ions increases and the soil P fertility decreases (Fardeau et al., 1977).

When P applications are significantly greater than P outputs, the intensity and quantity factors increase and the capacity factor decreases. So the availability of the soil P increases. The absolute increase of the quantity and intensity factors depends on soil properties, and firstly on the fixing capacity for phosphate ions. P applications significantly greater than P outputs with harvests are sometimes recommended in soils low to very low in available soil P as in most of the countries under tropical climates. But such a policy is not often justify an agronomic point of view, because P applied in excess, and which is not taken by crops during the first year following the application, continues to react with soil components (Barrow, 1980, 1991) and its bioavailability decreases.

In most of the fields of the Western Europe, very large quantities were applied during the last 40 years. Then, at the present day, the level of bioavailable soil is sometimes higher than its equilibrium level. In such a situation, to maintain this level higher than its equilibrium level, quantities to be applied must be significantly higher than that taken up by crops (Oberson et al., 1993). But generally, any economical reason can justify such application policy; the right policy consists in no P application during some years.

Finally, one of the most important result derived from the mamellary model is that ions present in solution at a given time, and mainly those derived from P fertilizers very recently applied, can enter directly in the less mobile compartments without transfer through the most labile compartments (Fardeau, 1993).

Applications of water insoluble P fertilizers

The effects observed on bioavailable soil P vuith water-insoluble P fertilizers as aluminium-calcium phosphate, CCCIP or phosphate rocks, applied at a rate near the quantity of P taken by plants, are almost always lower, but sometimes equal, than the results observed with water-soluble fertilizers (Fardeau & Frossard, 1992; Khasawneh & Doll, 1978). When this type of P fertilizers are applied at a rate significantly higher than the P taken by crops, the increase of soil P availability observed of P fertilizers is always lower than that observed with water-soluble P fertilizers applied in the same rate.

Applications of crop residues and manure

P in crop residues, as straw or sugar beet leaves, is as available as water-soluble P fertilizers (Thibaud et al., 1988). Therefore, the quantities of P, and K, contained in crop residues returned to the soil must taken into account to determine P fertilizer applications required to satisfy the needs of the crop following the application of crop residues. P contained in the different available farmyard manure is generally also as efficient as water-soluble P fertilizers (Oberson et al., 1993).

Applications of residual wastes

Wastes are derived from the agricultural food production with transformations through the human, or animal, life and the sewage treatments. The P they contain is sometimes returned to soils: P mining is reduced and P cycle is closed as in "natural" ecosystems. Wastes are often applied at high rates and the P quantities returned to fields can reach 450 kg P ha^{-1} once. The contribution of P contained in wastes to plant nutrition or to bioavailable soil P depends on the chemical ar physical treatments of wastes. The P contained in biological wastes is as available as P of farmyard manure, *i.e.* as P of water-soluble P fertilizers. But all chemical treatments with components containing AI, Fe or Ca, or thermal treatments applied to reduce their biotoxicity and their water contents, decrease the bioavailability of P in wastes (Fardeau et al, 1993).

P uptakes and P returns without P output and net P application: fallow

In developed countries as far as about 1920, and at the present in developing countries, mainly in countries under tropical climates where the soil P fertility is generally very low (Fardeau & Frossard, 1992), fallow was sometimes recommended to restore soil fertility. The weak increase of bioavailable soil P sometimes observed between the beginning and the end of the fallow period, is explained either by a root effect on soil minerals, or, in some sites, by a concentration effect due to faeces of animals (Fardeau and Frossard, 1992). But in all the circumstances, the soils remain, in average, low in available phosphate.

In developed countries, and mainly in western Europe, fallow becomes now a policy to decrease the total food production. When, at the beginning of the fallow period, the level of available soil phosphate, due to continuous P applications greater than the P outputs with harvests, is higher than its equilibrium level, the soil P fertility decreases up to its equilibrium level, even though there is no P uptake during the fallow period.

Isotope techniques used to characterize the ability of extraction methods to extract really bioavailable soil P

"Available" soil phosphate continues to be estimated by extraction methods. The isotopic exchange method is not used for soil routine analysis, but it could be in the future. The ability of chemical methods to extract the "available" soil P can be tested, whatever the method, using an isotopic procedure. The determination of this ability is based on the fact that isotopically exchangeable soil phosphate is the available soil P.

A quantity R of radioactivity is applied, as ^{32}P-labeled phosphate ions, in a soil-solution mixture where a steady-state has been previously reached by shaking over a night. An isotopic exchange takes place between phosphate ions, labeled or not, of the soil solution and isotopically exchangeable phosphate ions of the solid phase of the soil. In a soil solution system in steady-state, bioavailable soil phosphate, and only bioavailable soil phosphate, becomes labeled by isotopic exchange and, whatever the time of isotopic exchange, its isotopic composition, IC = $32_P/31_P$, is the IC of the phosphate ions of the soil solution. After a time of isotopic exchange significantly longer than the time required for the extraction method, the soil solution is discarded using centrifugation. The quantity of radioactivity, r_w, and in the soil solution, and the isotopic composition, IC_w, of phosphate ions in the soil solution are determined. Then, extractant is added and the mixture, labeled soil and extractant, is shaken. P is extracted as usual. The quantity of radioactivity, r_e, in the extractant, and the isotopic composition, IC_e, of phosphate ions in the extractant are determined.

Three data, r_e, $r_e/R\text{-}r_w$ and IC_e/IC_w are taken into account to discuss the efficiency of the chemical method to extract available soil P. The quantity r_e increases when time of extraction increases, but sometimes decreases further (Fardeau et al., 1988), showing the pitfalls of extraction methods (Nirel & Morel, 1990). The quantity, $R\text{-}r_w$, which is the quantity of radioactivity entered in the solid phase of the soil, is compared to the quantity r_e. The ratio $r_e/R\text{-}r_w$ gives the fraction of the isotopically exchangeable soil phosphate, that is to say the fraction of the available soil phosphate, which is extracted by the chemical method tested. As unavailable soil phosphate is unlabelled by isotopic exchange and as IC_w is the isotopic composition of the available soil P, the ratio IC_e/IC_w shows the ability of the extractant to extract unlabelled phosphate that is unavailable (Morel & Fardeau 1987; Fardeau et al., 1988). For a perfect extractant which could extract all the available soil P, and only available soil P, the values of $r_e/R\text{-}r_w$ and IC_e/IC_w should be 1.

Using such procedures, the main general conclusions are the following: (i) the $r_e/R\text{-}r_w$ values depend on the method: some extractants are more efficient at extracting available soil P than other.; but whatever the method, $r_e/R\text{-}r_w$ is always lower than 1; (ii) whatever the extraction method, the IC_e/IC_w value decreases with time of extraction: the most labeled P, that is to say the most available soil P, is extracted during the first stages of extraction procedure. These results are in accordance with the idea that available soil P could be made of many compartments with decreasing rates of transfer from the solid phase towards the soil solution and conversely.

Conclusion

Sustainability of the Human Life (Lubchenco et al., 1991) on our earth depends on sustainable agriculture (Fardeau, 1992). Phosphorus, essential to ensure sustainable agriculture, and will remain, one of the main keys of this sustainability. In many countries, agricultural production and/or agricultural yields must greatly increase to satisfy the continuous increase of human needs of foods. When plant yield increases, P uptake increases. Increase of P uptake can be achieved by increasing either P fertilization or soil P exploration by the root system. In this last case the P uptake can increases but, without P return, the soil P fertility decreases ineluctably. Therefore, P applications appear strictly necessary to maintain agriculture sustainable. As P is not a renewable resource, the recycling of P could become absolutely necessary. The rate of P cycling in ecosystems, and mainly in agrosystems, depends on soil properties, types of cropped plants and on their yields.

Dynamics of P in soil-solution-plant systems depend on two driving forces: they are the gravitation acting on losses by run-off and leaching and the diffusion. This last process occurs during P uptake by plants and after P applications and can influence the dynamics of bioavailable soil P. It has shown, using two different isotopic exchange method, that available soil P is the same entity that the isotopically exchangeable soil P. Isotopically exchangeable P, and consequently bioavailable soil P, can be described as a system made of many compartments of phosphate ions. Each compartment can be characterized by its size and by its mean rate to leave the solid phase of the soil in order to enter into the soil solution. Using this approach, bioavailable soil P is described, not only by a quantity factor, as using routine analysis with extraction procedures, but also by kinetic factors describing its ability to leave, with time, the solid phase of the soil. All plants have not the same P needs: some have low P requirements and some have high P requirennents (Bolland, 1992). The further step of researches must be the comparison of the kinetic of P release from soil to the kinetic of P needs for plant growth.

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