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Determination of water-soluble phosphate content of soil using heterogeneous exchange reaction with ^{32}P radioactive tracer

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ABSTRACT

The nutrient uptake by plants is significantly influenced by the quantity of phosphate in the soil solution. Optimal fertilization rate demands the determination of water soluble phosphate quantity, the rate of desorption and phosphate exchange between the soil and soil solution at steady state. The aim of this paper was to determine the ratio of water-soluble/exchangeable to mineralized/organic phosphate after incubation of the soil with different phosphate quantities. The sorption process of phosphate on soil was studied by heterogeneous isotope exchange using a radioactive isotope of phosphorous. Using the correct mathematical analysis of the kinetics of heterogeneous isotope exchange, the rate of phosphate exchange was established under steady state condition. The distribution of radioactivity in equilibrium provided information on the reversibility or irreversibility of phosphate sorption. The results revealed that during a relatively short incubation period, the water-soluble/exchangeable phosphorous quantity, namely the portion of phosphate which can easily be taken up by plants, was proportional to the added phosphorous quantity. The tightly sorbed phosphorous quantity, however, reached a limit, suggesting that the reactants leading to tight sorption are consumed. The exchange rate of phosphorous between the soil and the solution was found to be proportional to the phosphorous quantity in the soil solution, showing that the rate-determining step of the heterogeneous isotope exchange process was the diffusion of phosphate ions.

1. Introduction

The nutrient cycle of soils is driven mainly by the concentration of macro and micro nutrients in the soil solution which itself is influenced by the interactions between the solid phase of soil and the soil solution. These interactions are especially important in those cases where nutrients, such as phosphate anion, can strongly bind on some soil components. The phosphate anions that precipitate with different cations (e.g., iron, calcium, aluminum) or react with soil organic components, are called tightly sorbed phosphate (Mansell et al., 1977; Sparks, 1989). Another portion of phosphate is known to be weakly and fastly sorbed (Barrow and Shaw, 1975) and can be dissolved in the soil solution. The weakly sorbed phosphate converts to tightly sorbed phosphate in a relatively slow process (Shuai et al., 2014).

Reactions between phosphate and soil components can reach a steady state. At steady state, the chemical forms of phosphate present in the solution will influence (1) the nature of the interaction between soil components and soil solution, (2) the phosphate concentration of the soil solution, and (3) consequently, the efficiency of phosphate fertilizers. The quantity of water soluble phosphate and the rate of desorption and phosphate exchange between the soil and soil solution at steady state will affect the optimal fertilization rate. Soil types, phosphate quantities, incubation times, and crop species have an effect on the proportion of water-soluble/exchangeable phosphate. Since the quantity of phosphate in the soil solution significantly influences the nutrient uptake by plants, the information gained can be utilized in practice to plan phosphate fertilization. The optimal phosphate fertilization is especially important because of decreasing reserves of raw phosphate which, according recent estimates, are sufficient for approximately 70 years. A great part of soil phosphorous cannot be utilized by plants. For this reason, novel studies on phosphorous mobilization processes become increasingly important, including the kinetics and equilibrium of the mobilization process from soil as well as the pathways of phosphorous in the complex system of the soil, soil solution and plants.

Attempts to describe the different phosphate species in soils taking into account the surface complexation, the mechanistic model of the transformation of slightly and tightly sorbed

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phosphate, the single and multiple extraction methods, have recently been summarized by Shuai et al. (2014). Moreover, the authors have developed a new method for estimating the ratio of the different phosphate species and tested their model in cropping experiments.

Heterogeneous isotope exchange of phosphate ions using a radioactive isotope of phosphorous can elucidate phosphate sorption processes on the soil exchange complex, and has been investigated mainly by two research teams led by Fardeau and Frossard (e.g., Di et al., 1997; Fardeau et al., 1985, 1991; Frossard and Sinaj, 1997; Frossard et al., 2002; Randriamanantsoa et al., 2013). The heterogeneous isotope exchange allows to determine the rate of phosphate exchange under steady state condition. Thus, the following empirical rate equation has been formulated expressing the ratio of the radioactivity remaining in solution (r_t/R) as a function of time (t):

$$\frac{r_t}{R} = m\left(t + m^{1/n}\right)^{-n} + \frac{r_\infty}{R} \qquad (1)$$

where R is the total radioactivity introduced into the solution, r_∞ is the radioactivity of the solution after the isotopic equilibrium has been reached; m and n are fitting parameters related to soil samples. The parameter m is a coefficient which accounts for immediate physical–chemical reactions and is usually considered to be equivalent to the fraction of radioactivity remaining in solution after 1 min ($m = r_{1\mathrm{min}}/R$). The value r_∞/R and $m^{1/n}$ is assumed to tend to 0 (Fardeau et al., 1991). The parameter n accounts for slower physical–chemical reactions and describes the rate of disappearance of the tracer from the solution after 1 min (Frossard and Sinaj, 1997).

The determination of $r_{1\mathrm{min}}/R$ (the ratio of phosphate isotopically exchanged within 1 min) is a fast method for the evaluation of the ratio of free phosphate instantaneously available to plants (Frossard et al., 2002) since $r_{1\mathrm{min}}/R$ is considered to be inversely proportional to the adsorption capacities of soils (Sentran et al., 1988; Frossard et al., 1992). The intervals of r_1/R characterize the fixation of phosphate (Fardeau, 1996). The exchange reaction, however, is regarded as a continuous process; the quantity of the exchangeable phosphate depends on time, but ultimately (at infinite time) all mineral phosphate can leach into the soil solution (Di et al., 1997).

The experimental technique used seems to be adequate to measure the heterogeneous isotope exchange. Namely, the distribution of phosphate is governed by the mixing entropy (no chemical changes, Eq. (3)). However, the fact is that Eq. (1) is formal, therefore, does not well represent the mechanism of heterogeneous isotope exchange and its mathematical interpretation is also difficult, for example, there is a problem with the dimensions: time, of course, has a dimension, but m, expressed by the ratio of activities, is obviously dimensionless. In addition, the boundary condition of complete dissolution of the mineral phosphate is not chemically right because of the low solubility of some metal phosphates (such as aluminum, iron phosphates). Moreover, even if the complete dissolution would be feasible, the conditions of heterogeneous isotope exchange cannot be fulfilled because during the heterogeneous isotope exchange there should be no chemical reactions (including dissolution), only the different isotopes of the same elements should exchange.

As a conclusion, the method using the exchange ratio at 1 min can well be used in practice, but its physical–chemical meaning is questionable.

In order to resolve these discrepancies, in this study, we intended to describe a way how to evaluate the sorption processes of phosphate with a correct mathematical analysis under steady state conditions (Sheppard, 1948; Solomon, 1949; Kónya and Nagy, 2012).

In this paper the results of two sets of experiments should be shown: soil samples were incubated at different phosphate quantities; in one set the phosphate added to the soil was not radioactive. In this case, the heterogeneous isotope exchange should be studied by adding radioactive phosphorous isotope via the soil solution. In the other set of experiments, the soil was incubated with radioactive phosphate, and after the incubation the dissolution of radioactive phosphate should be studied. The comparison of the results with the non-radioactively and radioactively incubated soils should provide information on the ratio of the weakly to tightly sorbed/precipitated phosphate sorption.

2. Experimental

The sorption of phosphate ion was studied using a brown forest soil collected in Keszthely, Hungary (Table 1).

Two sets of experiments were done:

Set 1 Radioactive incubation of soil: The soil was incubated for three weeks with solutions containing 0, 40, 80, 160, 320 μg phosphorous as KH_2PO_4 labeled with radioactive ^{32}P isotope/g soil. The quantity of the radioactive phosphorous was $<10^{-8}$ μg/g soil. After the incubation, 1 g of the soil samples was weighed into a beaker, suspended in 200 cm^3 tri-distilled water and stirred at 200 rpm. At different times (2, 4, 6, 8, 10, 12, 15, 20, 25, 30, 45, 60, 90, and 120 min), 1.2 cm^3 aliquot samples were taken and filtered by a cellulose nitrate membrane filter with 0.45 μm pore size (Sartorius). The error from the sampling was about 7%. After the filtration, the radioactivity of 1 cm^3 of the solution was measured by the liquid scintillation method (see later). In this way, the dissolution of phosphate ions taken up by the soil during the three week incubation period was studied. The ratio of radioactive phosphate in the solution (y) and soil (x) was expressed related to the total added phosphate; $y + x = 1$. (NB. In Eq. (1), $r_t/R = y$).

Set 2 Non-radioactive incubation of soil: The soil was incubated for three weeks with solutions containing 0, 40, 80, 160, 320 μg phosphorous as KH_2PO_4/g soil. After the incubation, 1 g of the soil samples was weighed into a beaker, suspended in 200 cm^3 tri-distilled water and stirred at 200 rpm for 2 h. The result of the non-radioactive incubation showed that this time was usually long enough to reach the equilibrium of the water-soluble/exchangeable phosphate between the solution and soil. Then the carrier-free radioactive phosphate solution labeled with ^{32}P isotope was added

Table 1
Main properties of brown forest soil Keszthely, Hungary.

pH (water)	pH (KCl)	Hydrolytic acidity	Hygroscopic water %	$CaCO_3$ %	Humus %	Total salt %
7	6.6	2.5	2.2	0	1.6	0.03

Clay %	Sand %	Silt %	Total P μg/g	AL-P_2O_5 μg/g	Olsen P_2O_5 μg/g	AL-K_2O μg/g	T meq/100 g
21.9	36.3	41.8	500	38	40	118	18.33