Does long contact with the soil improve the efficiency of rock phosphate? Results of isotopic studies

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Abstract. The effect of incubation on the fate of phosphorus in four phosphatic fertilizers (diammonium phosphate and three rock phosphates) applied to four weakly acid to acid soils was studied. Percent utilisation of fertilizer P by the crop was measured by isotopic labelling and the level and quality of available soil P following addition of fertilizer was measured by the isotopic dilution kinetics method. Percent utilisation of fertilizer P decreased as time of contact between fertilizer and soil increased. The quantity of available soil P increased immediately after applying fertilizer but then decreased. The efficiency of P from rock phosphate was not increased by application long before sowing the crop. From practical viewpoint it is important to apply P fertilizer as near as possible to the time of planting in order to reduce the negative effects of P fixation by the soil.

Introduction

The interval between application of P fertilizer and crop uptake of P may be from a few weeks to four or five months. When heavy dressings are used to build up soil P status of low P soils, the interval may be much increased (a year or more) [27]. There are many reports on the fate of fertilizer P in soils during so-called incubation [32], digestion [10] or ageing [6, 26, 35].

Absolute efficiency of a fertilizer cannot be defined [5]; all we can do is use relative efficiency, i.e. measurement of the availability of one fertilizer relative to another or to soil nutrient. Measurement of this requires that there be a response to fertilizer P in crop yield or in P uptake. There may also be a response in available soil P content as measured by different methods.

In field or greenhouse experiments with water-soluble compounds such as diammonium phosphate or superphosphate, fertilizer P efficiency measured

by crop response decreases with time of contact with the soil [6, 8]. Similarly, PO_4 ion concentration in the soil solution [3], P extracted by chemical reagents [22] or anionic resin [47] and isotopically exchangeable P [38] all decrease with time. These findings support the view that P fertilizer should be spread just before sowing the crop [21] so that P can be taken up before it has completely reacted with the soil.

On the contrary, it has been recommended that water-insoluble P fertilizers like rock phosphate should be mixed into the soil long before sowing [11, 45] on the assumption that acid soils 'digest' rock phosphates making the P plant-available; If this was so, available P in a soil-fertilizer system should first increase with time up to a maximum and then decline. Experimental results on this point have been variable. Sometimes rock phosphate has been as good as or somewhat inferior to soluble fertilizer; sometimes it has been without effect. Laboratory measurements of PO_4 concentration or of isotopically exchangeable P have shown that these decrease with time of contact with the soil so that they do not support early spreading and incorporation of rock phosphate.

The aim of our work was to improve understanding of the effect of time of contact between soil and P fertilizer (mainly rock phosphates) and so to propose practical recommendations. Various isotopic determinations were made in the greenhouse and laboratory with four different soils, three insoluble and one water-soluble P fertilizers

Materials and methods

Soils.
No P had been applied over at least the past two years to the fields from which the four soils were sampled. Physical and chemical properties of the soils are given in Table 1. By US standards [41] they are high in available P but by French [25] (2% citric acid) or UK [12] (extractable P-Olsen) standards, they are low.

P-fertilizers.
Four P-fertilizers were chosen: diammonium phosphate (DAP), as a water-soluble P source, and three commercial rock phosphates as water insoluble forms. These latter fertilizers consisted of a Tunisian source (Tu), a North Carolina rock phosphate (CNC) and its calcined equivalent (CC). Particle size was 0–63 μm. Some of their chemical components are given in Table 2.

Table 1. Soil analyses

Soil	1	2	3	4
pH -H_2O	6.6	6.1	5.7	5.2
Total P (ppm P)	367	851	726	435
Available Olsen	19	14	19	17
P (ppm) Dyer	51	38	37	37
Langmuir K	0.24	0.28	0.49	1.01
parameters b (ppm P)	135	102	125	122
Textural class	Silt L.	Loam	Silt L.	Loam
Mechanical Clay	22.8	15.8	22.2	18.9
analysis Silt	52.8	46.6	55.8	36
(%) Sand	24.4	22.0	37.6	45.1
C/N	10.7	10.5	8.4	10.5
Organic carbon %	2.1	2.4	2.6	2.6
Exch. K (ppm K)	180	120	84	85
Exch. Ca (ppm Ca)	2840	1240	1000	560

The application rate was $66 mg P kg^{-1}$ soil corresponding to about $200 kg P ha^{-1}$ in a soil whose density was $1.5 g (cm^3)^{-1}$ and the plough depth 20 cm.

Unlabelled fertilizers were used for laboratory tests. For greenhouse experiments, the rock phosphates were labelled by neutron activation in a nuclear plant ($2.5.10^{13} n cm^{-2} s^{-1}$) and the DAP was labelled by laboratory synthesis [9, 18]. The use of irradiated P-fertilizers has sometimes been criticized [33]. We consider this criticism unjustified for the following reasons: firstly, we have shown [14, 18] that the percent of P utilisation by crops is the same for an irradiated labelled or an unlabelled fertilizer. Secondly, the presence of some other radio-isotopes, such ^{45}Ca formed during the irradiation process, is of a great interest for understanding the process of transformation of rock phosphates in soils. Thirdly, in one of the proposed alternative methods [33] used to avoid irradiation, the quantity of soluble P added as a carrier to the $^{32}PO_4$ ions and added to the soil is of the same order of magnitude as the available quantity already in the soil; such an addition of P can modify the biological response to a greater extent than the chemical or structural modifications of apatite caused by irradiation.

Table 2. Characteristics of phosphate fertilizer

Fertilizer type	DAP	CNC	Tu	CC
Total P (%)	20.1	13.1	12.4	13.8
P soluble in 2% formic acid. (%)	20.1	9.7	7.6	3.4

Ageing of phosphate fertilizers in soils.
The ageing of phosphate fertilizers in the soils was achieved by incubation under wet conditions at a temperature above 20 °C. For greenhouse experiments, each labelled fertilizer was mixed with 12 kg dry soil, sieved at 2 mm, at a rate of 66 mg P kg^{-1} soil. In each treatment without DAP, NH$_4$, as chloride, was added at 60 ppm. After mixing, the soils were put in pots each holiday 1 kg soil. Six pots of each treatment were wetted to field capacity and maintained in the greenhouse for a month at 20–25 °C; these were considered as the incubated or aged pots. Six other pots were kept under dry conditions and were considered as being non incubated. There were 240 pots altogether: 4 soils, 2 ageing periods (0 and 1 month), 5 fertilizer types (one control and 4 fertilizers) and 6 repetitions for each treatment.

For laboratory analysis, unlabelled fertilizer was mixed with dry soils at the same rate. Part of the mixture was wetted to field capacity and incubated in plastic vials: the other part was maintained under dry conditions as unincubated soil.

Analytical methods for availability of fertilizer P.
Fertilizers P availability was measured either by pot experiments or laboratory tests.

(a) Pot experiments and crop response. After one month of incubation, all pots were sown simultaneously with one gram of *Lolium perenne* seed. Seven days after sowing and at each cutting, 50 ppm N as KNO$_3$ were added to each pot. Three cuts were taken at one month intervals. Shoots were analysed for dry matter content and for radioactive and stable phosphorus contents.

Two types of calculations were used for the analysis of these measurements:
– Percent of P utilisation of the various fertilizers. If R is the total ^{32}P in the fertilizer and r and ^{32}P content of crops, the percent of P utilisation (PU) is calculated as:

$$PU \% = \frac{r}{R} * 100 \tag{1}$$

– Phosphorus derived from fertilizer (Pdff %). The expression first used in a previous experiment with ^{32}P labelled fertilizers [23], designates the proportion of the nutrient in plants that is derived from fertilizer. The major interest of this value is that it is more independent of the cultural conditions

than the PU %. It can be calculated by two equivalent formulae:

$$\text{Pdff \%} = \frac{\text{Specific radioacitivity of P in crop}}{\text{Specific radioactivity of P in fertilizer}} \cdot 100 \qquad (2)$$

or

$$\text{Pdff \%} = \frac{\text{Percent of P utilisation} \cdot \text{Rate of application}}{\text{Total P in crop}} \qquad (3)$$

(b) Laboratory tests. Isotopic dilution kinetics. Phosphorus extracted by a chemical procedure is called 'available P'. In fact, correlation between 'available' P and the phosphorus taken up by crops can only be obtained under standard conditions; there is no proof that the phosphorus extracted from soil by a chemical is the same as that taken up by plants. We therefore prefer to use a method which can provide information on truly available phosphate ions. The only way this type of information can be obtained is by using isotopic dilution kinetics. It has been established that the available pool of phosphorus is the isotopically exchangeable pool of PO_4 [15, 17] and this determination is made without addition of any chemical mobilizing or immobilizing the soil phosphate [37]. Isotopic dilution kinetics were determined as follows: 10 g soil were mixed in 99 ml water over night to obtain a steady-state soil-solution system. One ml of ^{32}P as carrier-free $^{32}PO_4$ ions was then injected at time zero into the system and well mixed with a magnetic stirrer (200 revolutions per minute). At time t = 1, 10 and 100 minutes, about 100 ml of the labelled mixture were sampled with a syringe and the solution immediately separated from soil using a millipore filter (0.2 μm pore size). Radioactivity, r, remaining in the solution at each time, t, was measured and the quantity of phosphate ions in solution, M_1, which remained constant during all the experiment since the soil-solution system was in a steady-state and the ^{32}P added without carrier, was determined after the last sampling of the isotopic exchange. It has been previously established [15, 17] that the evolution of r with time, during the interval 0.5 mn-3 months, can be described as:

$$r = r_1 \cdot t^{-n} \qquad (4)$$

r_1 is the radioactivity remaining in solution at the time t = 1 mn and n an empirical parameter varying from 0 to 0.5 depending on soils and treatments

in a given soil. In such an experiment, the isotopically exchangeable soil phosphorus, E, can be calculate by the formula:

$$\frac{r}{M_1} = \frac{R}{E} \qquad (5)$$

assuming that, at any time, the specific radioactivity of phosphate ions in the soil-solution equals the specific radioactivity of all the phosphate ions present in an exchangeable form in the soil-solution system. From equation (4), the latter relationship becomes:

$$E = \frac{M_1 \cdot R}{r_1} \cdot t^n = E_1 \cdot t^n \qquad (6)$$

From this equation it can be seen that: i) exchangeable soil phosphorus increases with the exchange time. It means that the choice of 24 h [31], 3 d [44] or 21 d [25] retained by different authors is not really justified. ii) a clear knowledge of the exchangeable soil phosphorus depends, at least, on the determination of r_1/R, M_1 and n.

In addition, using a double isotopic dilution method, we also measured a quantity, M_2, of phosphate ions which are soil-linked but as accessible for nutrition as the quanitity M_1 present in solution.

This determination was carried out as follows: an isotopic dilution experiment was performed as previously, but without sampling in a 250 ml centrifuge tube. After an isotopic exchange period of 100 mn or more, this tube was centrifuged at 20,000 g or more, the supernatant discarded, and its radioactivity content, r_{100} measured. This supernatant was immediately replaced by a similar supernatant obtained in a similar manner (same soil, soil-solution ratio and agitation time) as previously but without $^{32}PO_4$ labelling. A new instantaneous isotopic exchange took place between the labelled phosphate ions of the soil and the unlabelled phosphate ions of the new solution. The radioactivity, r'_{100} returning into the solution was immediately measured after millipore filtration. It has been previously demonstrated [17] that the quantity M_2 is given by:

$$M_2 = M_1 \cdot \frac{r'_{100}}{r_{100} - r'_{100}} \qquad (7)$$

A more complete picture of the available soil P therefore requires the knowledge of:

- M_1, the phosphate ion concentration in the soil-solution which is the intensity factor described by White and Beckett [49].
- r_1/R and n which are related to the fixing capacity of the soil for phosphate ions.
- $M_1 + M_2$, the quantity of phosphate ions of the soil-solution system which is, in any circumstances, the source of P for crop nutrition and corresponds to the quantity factor [49].

Results and discussion

Crop response

Crop data of the three cuttings are summed together: dry matter yield and P uptake are given in Table 3 and the percentage of P utilisation of the various fertilizers in Table 4. Statistical analysis was confined to the different treatments for a given soil; soils were not compared.

(a) Results without ageing. Only DAP significantly increased dry matter production in three out of four soil. This results seem to contrast with much published data where all fertilizers used, including rock phosphates, had positive effects in soils said to be poor in available P. Two main reasons can explain this apparent discrepancy:
- Firstly, most of the published data on the positive effect of rock phosphates were obtained in soils poor in available phosphorus. While the soils used in the experiments described here are poor in available P according to the French methods (Dyer and/or Joret-Hebert) and their associated standards [25], they appear medium or high in available P according to Olsen method [4].
- Secondly, the values of the percent of P utilisation of the various fertilizers, which is varied from 0.5 to 16.8% (Table 4) contribute to the explanation of the differences observed between water-soluble and water-insoluble forms of P fertilizers. It can be seen that: i)fertilizer P given in water soluble form was taken up to a greater extent than when given in a water insoluble form. ii)the rating of the fertilizers was the same for all the soils: DAP > CNC > Tu > CC, but the rate of P uptake depended on soil physical and chemical properties.

These results also stimulate some other comments. In soil 1, where pH water was 6.6, less than 2% of the phosphorus applied as rock phosphate was taken up in three months. This additional result confirms those previously observed: pH 6.1 seems to be the upper soils limit for significant

Table 3. Dry matter (DM kg^{-1} soil) and P uptake (mg P kg^{-1} soil) for incubated (I) and non incubated soils (NI)

Soil	treatment	Control		DAP		CNC		Tu		CC	
		DM	P	DM	P	DM	P	DM	P	DM	P
1	NI	2.8_a	12.2_m	2.8_a	14.3_n	2.3_b	10.7_p	2.6_a	12.7_m	2.2_b	9.8_p
	I	2.0_b	8.2_q	2.5_a	13.6_{mn}	2.0_b	9.0_{pq}	2.5_a	10.9_p	2.4_a	9.3_{pq}
2	NI	2.5_{ac}	12.7_m	3.6_b	20.9_n	2.8_a	15.2_p	3.0_a	15.3_p	2.7_a	13.8_{mp}
	I	2.7_a	10.4_q	3.0_a	15.2_p	2.9_a	15.9_p	2.5_{ac}	12.3_m	2.4_c	12.1_m
3	NI	3.7_a	15.7_m	4.7_b	25.6_n	3.6_a	20.7_p	3.7_a	20.1_p	3.5_a	16.4_m
	I	3.2_c	12.2_q	3.4_c	14.9_m	3.1_c	16.3_m	3.2_c	14.8_m	3.3_c	16.0_m
4	NI	2.5_a	10.1_m	3.2_b	15.4_n	2.1_c	10.8_m	2.4_a	11.4_m	2.2_c	9.6_m
	I	2.1_c	7.5_p	2.4_a	8.4_p	2.3_{ac}	10.5_m	2.2_c	9.3_{mp}	2.3_{ac}	8.7_{mp}

(For each soil, numbers followed by the same letter do not differ significantly at P = 0.01)

Table 4. Percent of P utilization of the fertilizer by crop, P.U.% for incubated (I) and non incubated soils (NI)

Soil treatment		DAP	CNC	TU	CC
1	NI	8.2_a	2.0_b	1.0_c	0.5_d
	I	8.0_a	1.6_e	1.1_c	0.6_d
2	NI	7.5_a	3.5_b	1.3_c	1.1_d
	I	7.9_a	3.3_b	1.3_c	0.9_d
3	NI	16.8_a	8.4_b	6.2_c	3.1_d
	I	6.2_c	6.6_c	3.9_e	3.3_d
4	NI	10.8_a	5.1_b	3.7_c	1.5_d
	I	3.9_c	5.2_b	2.9_e	1.5_d

(For each soil, numbers followed by the same letter do not differ significantly, P = 0.01)

utilisation of rock phosphate independent of geographical and geological origins.

The Carolina and Tunisian rock phosphate whose solubilities in formic acid at 2% was of the same order of magnitude, were more efficiently absorbed by crops than the calcined Carolina rock phosphates whose formic solubility was lower. This result agrees with others published recently [32, 33] concerning the correlation between solubility in formic acid and availability of rock phosphates. It can also be concluded, in agreement with studies on Gafsa rock phosphate [34], that calcination of apatite to destroy organic matter, an industrial process for phosphoric acid production, has a negative effect on its agronomic efficiency.

(b) Results with ageing of fertilizers in soils. i) After the ageing period there was no significant effect of fertilizers on dry matter yield except for soil 1 and 4 with DAP. ii) The rating for the percent P utilisation of the fertilizers remained the same in all soils as without ageing. iii) In neutral soils, pH = 6.6, the percentage of P utilisation of rock phosphate remained very low. In the two weakly acid soils, the percent P utilisation for the water soluble form and for the better rock phosphate (CNC) were of the same order of magnitude. Compared with the data obtained without ageing, these results can be explained either by a decrease in the availability of the water soluble form, or by an increase in the availability of rock phosphate. At the same time, soil incubation in wet conditions decreased dry matter yield and phosphorus uptake even for control soils which can be explained by an alteration of the physical properties of soils such as soil packing, which can greatly reduce root growth and development [9]. The choice between the two hypothesis can be made on the basis of the Pdff% values (Table 5). The decrease in the Pdff% values during the wet conditions, as compared with dry conditions, of the water soluble form showed the decay in the efficiency

Table 5. Phosphorus derived from fertilizer, Pdff % in incubated (I) and non incubated soils (NI)

Soil treatment		DAP	CNC	TU	CC
1	NI	37.8_a	12.3_b	5.2_c	3.4_d
	I	38.8_a	11.7_b	6.6_c	4.2_d
2	NI	33.6_a	15.2_b	5.6_c	5.3_c
	I	34.3_a	13.6_b	6.9_d	4.9_c
3	NI	43.3_a	26.8_b	20.3_c	12.5_d
	I	27.5_b	26.7_b	17.4_e	13.6_d
4	NI	46.2_a	31.2_b	21.4_c	10.3_d
	I	30.6_b	32.7_b	20.5_c	11.3_d

(For each soil, numbers followed by the same letter do not significantly differ P = 0.01)

of this form. During the same period, the Pdff% values for rock phosphates were not increased; it can therefore be concluded that the efficiency of rock phosphates was not increased by soil digestion, even in the acid soils. The similar percentage P utilisation for DAP and rock phosphate after one month of wet incubation was due only to a decrease in the efficiency of the DAP and rock phosphate after one month of wet incubation was due only to a decrease in the efficiency of the DAP. The same results also show the very weak contribution of rock phosphate to plant nutrition in soils with a pH above 6.1 (soils 1 and 2).

Soil phosphorus analysis after P fertilizer addition

(a) Results without ageing period (Table 6 and 7).. In comparison with the control soil, addition of DAP significantly increased M_1, $M_1 + M_2$ and r_1/R but none of the rock phosphates really modified these parameters. Thus, in these soils and in agreement with other data [16, 18], water-soluble forms of fertilizers can increase the quantity and availability of the available pool of soil phosphorus.

(b) Results with ageing (Table 6 and 7).. After the incubation period DAP increased the various parameters in only three out of four soils. There were no significant differences between control soils and soils given rock phosphates. The labile pool of P and its availability, determined by isotopic dilution kinetics method, were therefore not increased by digestion of the rock phosphates in the soils.

From the comparison of the data observed with and without incubation it can be deduced that:

– Incubation decreased the efficiency of DAP for all the soils M_1, $M_1 + M_2$ and r_1/R being decreased. This was obvious in soil 4, where all the

Table 6. Effect of P-fertilizer types on the pool of free phosphate ions (ppm P) in incubated (I) and non incubated soils (NI)

Soil treatment		Control		DAP		CNC		TU		CC	
		M_1	$M_1 + M_2$	M_1	$M_1 + M_2$	M_1	$M_1 + M_2$	M_1	$M_1 + M_2$	M_1	$M_1 + M_2$
1	NI	2.0_a	11.9_m	29.0_b	55.1_n	1.9_a	11.6_m	1.4_c	10.0_m	1.7_a	14.7_n
	I	2.7_d	9.8_m	12.4_e	23.2_p	2.2_a	10.0_m	2.1_a	8.5_m	2.2_a	6.0_q
2	NI	2.6_a	5.5_m	16.5_b	30.3_n	2.7_a	8.1_p	1.8_c	4.1_m	2.0_c	6.5_m
	I	1.6_c	2.9_r	4.9_d	7.0_m	1.9_c	4.1_s	1.4_e	2.3_r	1.3_e	3.9_{rs}
3	NI	1.4_a	5.2_m	13.1_b	16.3_n	2.0_{ac}	4.2_m	1.3_a	3.7_m	1.1_a	4.0_m
	I	1.9_c	8.0_n	3.8_d	8.4_n	2.5_e	12.9_p	2.2_{ce}	7.9_n	1.2_a	3.9_m
4	NI	0.9_a	3.4_m	19.0_s	25.1_n	1.9_c	4.4_m	1.1_a	4.1_m	0.9_a	1.4_p
	I	0.4_d	1.9_p	0.6_{ad}	1.4_p	0.6_{ad}	2.2_p	0.5_d	2.0_p	0.4_d	2.1_p

(For each soil, numbers followed by the same letter do not significantly differ P = 0.01)

Table 7. Effect of P fertilizer types on isotopic dilution kinetics parameters in incubated (I) and non incubated soils (NI)

Soil treatment		Control		DAP		CNC		TU		CC	
		r_1/R	n	r_1/R	n	r_1/R	n	r_1/R	n	r_1/R	n
1	NI	0.22_a	0.24_m	0.51_b	0.11_n	0.19_a	0.25_m	0.18_a	0.27_m	0.19_a	0.26_m
	I	0.19_a	0.21_m	0.38_c	0.12_n	0.23_a	0.24_m	0.23_a	0.24_m	0.19_a	0.21_m
2	NI	0.38_a	0.29_m	0.59_b	0.17_n	0.39_a	0.32_m	0.32_c	0.32_m	0.35_c	0.34_m
	I	0.47_d	0.30_m	0.64_b	0.36_p	0.49_d	0.30_m	0.45_d	0.28_m	0.49_d	0.28_m
3	NI	0.20_a	0.33_m	0.48_b	0.19_n	0.26_c	0.31_m	0.22_a	0.22_m	0.19_a	0.34_m
	I	0.23_a	0.31_m	0.39_d	0.27_p	0.32_e	0.28_p	0.29_p	0.29_m	0.23_a	0.32_m
4	NI	0.33_a	0.42_m	0.75_b	0.15_n	0.41_c	0.35_p	0.34_a	0.34_p	0.34_a	0.37_p
	I	0.21_d	0.38_p	0.56_e	0.32_p	0.29_f	0.31_p	0.28_g	0.33_p	0.4_c	0.35_p

(For each soil, numbers followed by the same letter do not significantly differ P = 0.01)

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treatments gave identical results. In this soil, the most acidic, neither the water-soluble nore the insolube P forms of fertilizers increased the available soil phosphorus when applied at agronomic rates. This can easily explained, for water-soluble P forms, by the quick reactions of phosphate ions with with aluminium and iron compounds [43] which are always present in acid soils.
–   Incubation induced some modifications in soil fertility even in control soils.

Comparison of crop response and soil analysis

Soil fertility was slightly modified during an incubation period under wet conditions for all the control soils; this result was observed both in pot experiments (Table 3) and from analyses (Table 6 and 7). It could be explained by changes in the structural and/or chemical properties of the soils but not by an earlier input of P fertilizer since these soils were taken from unfertilized fields. Structural modifications can affect root development, this being increased or decreased, for example, by soil packing [9]. Chemical changes would also affect P fertility: observations in grassland ecosystems have indicated a seasonal increase (or decrease) in available P, as estimated by the Olsen method [29]. So it may be that incubation in wet and warm conditions, can modify chemical P fertility of the soil as may change between winter and spring or between spring and summer according to the area. It is known that during incubation, transformations by mineralization or reorganisation of organic compounds occur [30]; the newly formed products can affect, as can many organic compounds, the phosphorus fixing capacity of soils [19, 24]. Moreover, the nitrification process with occurs in many circumstances and produces protons [20], can either dissolve phosphates [40] and increase P fertility or, in more acid soils, dissolve Al and decrease P solubility and thus P chemical fertility. In the present experiments soil analysis revealed a decrease in soil P fertility in three soils (1, 2 and 4) and an increase in one soil (3) (Table 6: values of M_1 and $M_1 + M_2$). It can be assumed that organisation dominated in soils 1, 2 and 4 and that mineralization of organic P occurred in soil 3. The quantities appearing (soil 3) and disappearing (soil 2 and 4) in the pool of the free phosphate ions during incubation were about 2 or 3 ppmP. After one month incubation, the input of 66 ppmP of water-insoluble P form (about $200 \, kg \, P \, ha^{-1}$) increased the $M_1 + M_2$ phosphate ions pool from 0 (soils 3 and 4) to 13 ppm P (soil 1), so the 2 or 3 ppm P correspond to a fertilization of about $50 \, kg \, P \, ha^{-1}$. This result is sufficient to explain why one year we can observe a crop response to P fertilization in a given field, while in a following year there is no response.

Incubation, i.e. an increase in contact time between soil and fertilizer under wet conditions, did not increase fertilizer availability even for rock phosphates which disagrees with generally held ideas: phosphorus in plants derived from fertilizer decreased with incubation time and soil P fertility was not increased.

Many authors have concluded from field [13] or pot [28] experiments that rock phosphate and water-soluble phosphate forms are similarly efficient for dry matter production. The yields obtained in the present study with soil 4 (Table 3, 4 and 5) using DAP and CNC, the better rock phosphate, provide good examples to discuss such reported equal efficiency. It is true that, after incubation, dry matter yields with DAP and CNC were of the same order of magnitude and that soil analysis, namely for phosphate ion concentration in the soil solution (Table 6) explained these results. However without incubation dry matter yields obtained with these two fertilizers differed significantly, as did phosphate ion concentration in the soil solution. It can therefore be said that the efficiency of the water-soluble form was decreased following reactions with soils components.

In general, it can be concluded that the efficiency for crop production of P fertilizers greatly depends on their contact time with soils and that all P fertilizers lead, with time, to the same level of P fertility, which in turn does not differ from that of the native soil [36]. The speed of the return to the equilibrium state depends on the nature of the soil components. From one Rothamsted experiment [48], it can be concluded that the residual effect of P fertilizers on crop yield can be observed after 50 years or more, but in the majority of field experiments phosphate applications do not remain effective for more than 2 or 3 years and further applications are therefore needed [2]. These last comments and our observations, are in accordance with data concerning the residual effect of fertilizers determined by the decrease, with time, of the available soil phosphorus estimated by the L-value method [36]. A half-life of P fertilizers was defined from these data and varied with soils. However, as the decrease in phosphate ion concentration is most probably fitted to a power function [3] rather to an exponential function, it would be more accurate to calculate and mean sojourn time rather than an half-life which is related only to the exponential function [46]. Finally, there is an apparent contradiction between soil analysis and crop P response namely for soil 4 in the case of an addition of rock phosphate as CNC, particularly in the absence of incubation, but also with an incubation period. In this soil CNC increased P uptake but did not increase available soil phosphorus. The increase of P uptake is explained by the value of the percentage of P utilization (Table 4) which is 5.2%, i.e. $66 \times 0.052 = 3.4\,mg\,P\,kg^{-1}$ soil. An explanation of these results could be: unlike the water-soluble form

which quickly reacts with soil components and becomes unavailable like the major part of the soil P, rock phosphates remain in their native form in these weakly acid soils and their phosphate ions do not react with soils. They consequently keep a low, but constant, efficiency, nearly 1% of P utilization at each cutting in the present study and this very low effect does not give significant differences for isotopic dilution parameters.

Conclusions

(i) The immediate effect of a P fertilizer on dry matter yield and P uptake, estimated in pot experiments with labelled fertilizers, depends on both the fertilizer type and on the contact period between soil and fertilizer. The availabilities of both water soluble and insoluble forms decrease with increased contact time between soil and fertilizer. The rate of this decrease is higher for soluble P than for insoluble P but it also depends on the fixing capacity of the soil. In agricultural practice, therefore the contact period between soil and fertilizer should be as short as possible, even for rock phosphate.

(ii) The residual effect of P fertilizer, i.e. its ability to increase either the quantity of the available P or to increase its availability, depends also on the fertilizer type and on the contact time with soil, as is shown by determination of the isotopic dilution kinetic parameters. As for the pot experiment, the available quantity decreases with time of contact both for soluble and insoluble forms. These soils analyses confirm results from pot experiments that contact between soil and P fertilizer should be as short as possible.

In order to reduce losses of phosphate fertilizers into unavailable forms, farmers should attempt to supply phosphorus when the plants need it.

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