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DIVISION S-2—SOIL CHEMISTRY

Sensitivity of Isotopically Exchangeable Phosphate in Soil Suspensions to the Supporting Solution

C. Morel* and J. Torrent

ABSTRACT

The isotopically exchangeable quantity (E_i) of phosphate measured in 1:10 soil/solution suspensions with deionized water has been identified as the reserve of plant-available phosphate in agricultural soils. We studied the effects of two supporting solutions, 0.01 M CaCl_2 and deionized water, on E_i values in 27 calcareous agricultural soils. For three soils, E_i was also measured after adding increasing phosphate quantities as KH_2PO_4 , and equilibrating for 24 h, to assess changes in E_i with phosphate concentration in solution (C_p). In unamended and phosphate-enriched soils, $C_p(\text{CaCl}_2)$ was smaller than and related to $C_p(\text{H}_2\text{O})$. The initial rapidly and the subsequent slowly isotopically exchangeable phosphate were both affected by the use of CaCl_2 solution. Since both the rapid and slow isotopically exchangeable phosphate are C_p dependent, the overall effect of CaCl_2 solution was analyzed considering two components: (i) a nonspecific effect attributed to the decrease in C_p and (ii) a specific effect attributed to phosphate reactions (i.e., adsorption or precipitation) in calcareous soils. Modifications in E_i are the result of both nonspecific and specific effects. The change in E_i due to the use of 0.01 M CaCl_2 instead of deionized water varies with the soil sample, and can be positive, negative or nil depending on the time of exchange. For instance, after 24 h of exchange, the ratio $\{[E_{24}(\text{CaCl}_2) - E_{24}(\text{H}_2\text{O})]/100/E_{24}(\text{H}_2\text{O})\}$ ranged from -30 to 340% for the 27 soils. The 0.01 M CaCl_2 solution thus introduces complex and unpredictable changes in isotopic exchanged phosphate, and its use is not recommended to estimate plant-available phosphate in soil.

DESCRIBING PLANT-AVAILABLE PHOSPHATE requires the measurement of the so-called Intensity and Quantity factors (Dalal and Hallsworth, 1977; Olsen and Khasawneh, 1980; Ozanne, 1980). The I factor refers to the chemical potential of phosphate in solution, usually estimated by C_p . Since the phosphate in solution, which is absorbed by plants via mass flow, represents only 1 to 5% of the plant phosphate uptake, 95 to 99% of the phosphate absorbed by plants comes from soil constituents. The Q factor refers to this phosphate reserve that can replenish soil solution phosphate in response to phosphate uptake by roots.

The Q factor within the total phosphate content of agricultural soils has been measured using isotopic labeling procedures applied to soil-plant systems and soil suspensions. With this approach, exchangeable phosphate in soils, i.e., soil phosphate having the same isotopic composition ($^{32}\text{PO}_4/^{31}\text{PO}_4$ ratio) as phosphate in soil solution, is labeled with radioisotopes. The isotopic

composition of phosphate absorbed by plants after 2 to 3 mo of cropping in greenhouse pot experiments is measured. In parallel, the isotopic composition of phosphate in solution of 1:10 soil/solution suspension with deionized water is measured for similar periods of exchange in laboratory experiments (Fardeau and Jappe, 1976). The similarity between both isotopic compositions of phosphate in plants and phosphate in soil solution has been reported for temperate (Fardeau and Jappe, 1976; Morel and Fardeau, 1991; Morel and Plenchette, 1994) and tropical (Frossard et al., 1994) agricultural soils, and for crop species varying in their mycorrhizal dependency (Morel and Plenchette, 1994). From 95 to 99% of phosphate absorbed by plants from the soil solid phase has the same isotopic composition as solution phosphate. This is, by definition, the isotopically exchangeable phosphate. Therefore, isotopically exchangeable phosphate is plant-available phosphate for different combinations of agricultural soils and crop species (Morel and Plenchette, 1994).

The E_i was initially determined after a defined period of exchange (Russell et al., 1954). However, E_i was found to be dependent on the time of exchange. Fardeau (1981, 1993) described the increase in E_i with time of exchange at a defined C_p level by the following relationship:

$$E_t = E_{1\text{min}} t^n \quad [1]$$

where $E_{1\text{min}}$ is the isotopically exchangeable phosphate after 1 min and n is a constant dependent on the soil sample and ranges from 0 to 0.5. This equation emphasizes the two-step nature of phosphate exchange between the liquid and solid phases of soil. There is an immediate isotopic exchange within the $E_{1\text{min}}$ pool followed by a slow time-dependent phase of exchange. The parameter estimates of Eq. [1] are determined for a short period (usually 100 min) and can be used successfully to predict E_i values for longer periods of exchange (Fardeau and Jappe, 1976; Fardeau, 1981). Equation [1] has been validated in many soil types (Tran et al., 1988; Salcedo et al., 1991; Morel et al., 1994). Functions were recently proposed to take into account the increase in E_i when C_p increases (Morel et al., 1994, 1995a,b). The parameter estimates of the E_i to C_p relationships were little affected by periods of equilibration ranging from 0.4 to 10 d (Morel et al., 1995b) or by long-term cultivation practices (Morel et al., 1994). In the above studies, the dependence of E_i with time and C_p was studied in 1:10 soil/solution suspension with deionized water. However, other supporting solutions (especially 0.01 M CaCl_2) have been used to determine both C_p and E_i values (McAuliffe et al., 1948; Russell et al., 1954; Dalal and Hallsworth, 1977; Le Mare, 1982).

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Table 1. Selected properties of the French soils.

Soil	Particle size			pH (H ₂ O)	Organic C	CaCO ₃ equivalent	Exchangeable cations			Total P
	Sand	Silt	Clay				Ca	Mg	K	
	%						g kg ⁻¹			mg kg ⁻¹
1	2	77	21	8.0	10.9	2	3.19	0.06	0.17	610
2	10	65	25	7.9	12.7	22	6.34	0.15	0.24	700
3	10	72	18	8.5	8.5	42	nd	0.24	0.22	nd†

† nd = not determined.

The purpose of this study was to evaluate possible effects of using 0.01 M CaCl₂ on E_t . The parameters describing the E_t - C_p relationship were determined and compared for soil suspensions prepared with either deionized water or 0.01 M CaCl₂. The comparison was done in calcareous soil samples that provide (with other soils of high base saturation) the conditions under which the use of dilute CaCl₂ solution is seemingly appropriate.

MATERIAL AND METHODS

Soil Samples

Soil samples were collected from the 0- to 20-cm layer of three French calcareous loamy Alfisols and from the Ap horizon of 24 Spanish calcareous Inceptisols and Vertisols containing widely different quantities of clay, carbonates, and Fe oxides. Characteristics of the French soils are shown in Table 1. The Spanish soils were thoroughly described in Solis and Torrent (1989a,b). All soil samples were air dried and sieved (<2 mm) before analysis.

Isotopically Exchangeable Phosphate at a Defined Soil Solution Phosphate

The quantities of E_t were determined in deionized water and 0.01 M CaCl₂. After equilibrating 10 g of soil with 99 mL

of deionized water or 0.01 M CaCl₂ for 16 h, 1 mL of carrier-free ³²P (0.1–1 MBq mL⁻¹) solution (R) was added at time zero and thoroughly mixed with a magnetic stirrer (≈200 revolutions per minute). About 2 mL of soil suspension were sampled with a plastic syringe after 1, 10, and 100 min and filtered through 0.2-μm membrane filters. The radioactivity (r_t) remaining in the filtered solution at time t was counted with a liquid scintillation cocktail. The C_p was determined after the last sampling by the ammonium molybdate–ascorbic acid method (John, 1970).

The determination of E_t is based on the assumption that in any fraction of E_t , the isotopic composition of phosphate measured after addition and exchange of carrier-free ³²PO₄ ions is identical to the isotopic composition of phosphate in soil solution. The above hypothesis results in the relationship:

$$R/E_t = r_t/10C_p \quad [2]$$

where 10 is the solution/soil ratio. For $t < 4$ mo, the r_t/R ratio is related to t by the following equation (Fardeau, 1981, 1993):

$$r_t/R = (r_{1\text{min}}/R)t^{-n} \quad [3]$$

where $r_{1\text{min}}/R$ is the proportion of ³²P remaining in soil solution after 1 min of isotopic exchange and n is an index describing the ³²P disappearance from solution with time. Equation [1] is obtained by combining Eq. [2] and [3], where $E_{1\text{min}} = 10C_p/(r_{1\text{min}}/R)$.

Table 2. P concentration in solution (C_p), radioactivity remaining in solution after 1 min ($r_{1\text{min}}/R$), n exponent ($E_t = E_{1\text{min}}t^n$), and isotopically exchangeable P after 1 min ($E_{1\text{min}}$) for all soils and supporting solutions.

Soil	C_p		$r_{1\text{mm}}/R$		n		$E_{1\text{mm}}$	
	H ₂ O	CaCl ₂	H ₂ O	CaCl ₂	H ₂ O	CaCl ₂	H ₂ O	CaCl ₂
	mg P L ⁻¹		mg P kg ⁻¹					
Spanish soils†								
1	0.020	0.011	0.14	0.07	0.34	0.34	1.4	1.6
2	0.042	0.015	0.14	0.05	0.30	0.31	2.9	2.9
3	0.035	0.007	0.11	0.03	0.31	0.32	3.2	2.2
4	0.048	0.016	0.20	0.08	0.30	0.30	2.4	2.1
5	0.053	0.021	0.20	0.10	0.31	0.32	2.7	2.2
6	0.065	0.021	0.22	0.10	0.30	0.33	3.0	2.2
7	0.031	0.012	0.25	0.10	0.32	0.33	1.3	1.2
8	0.40	0.10	0.41	0.21	0.20	0.23	9.3	5.0
9	0.029	0.012	0.13	0.05	0.28	0.31	2.3	2.7
10	0.121	0.029	0.19	0.06	0.21	0.26	6.5	4.5
11	0.026	0.013	0.16	0.08	0.34	0.39	1.6	1.6
12	0.021	0.009	0.11	0.05	0.35	0.38	1.9	2.0
13	0.017	0.011	0.16	0.07	0.42	0.40	1.0	1.7
14	0.007	0.009	0.22	0.10	0.33	0.36	0.3	0.9
15	0.037	0.22	0.29	0.12	0.28	0.32	1.3	1.8
16	0.035	0.015	0.16	0.08	0.36	0.37	2.1	1.9
17	0.004	0.009	0.07	0.05	0.37	0.38	0.6	2.3
18	0.063	0.020	0.29	0.08	0.21	0.25	2.2	2.6
20	0.035	0.018	0.20	0.08	0.34	0.35	1.8	2.2
21	0.079	0.040	0.33	0.11	0.21	0.25	2.4	3.6
22	0.013	0.012	0.14	0.11	0.36	0.25	0.9	1.8
23	0.005	0.006	0.10	0.04	0.36	0.36	0.5	1.6
24	0.041	0.020	0.23	0.09	0.25	0.28	1.8	2.3
25	0.016	0.013	0.21	0.08	0.34	0.35	0.8	1.7
French soils								
1	0.10	0.051	0.21	0.08	0.26	0.29	4.8	6.3
2	0.28	0.12	0.25	0.11	0.20	0.26	11.0	11.3
3	0.15	0.06	0.48	0.27	0.25	0.30	3.2	2.2

† Spanish soil number is the same as in Solis and Torrent (1989a,b).

Fig. 1. Relationship between phosphate concentration in solution (C_p), ^{32}P radioactivity remaining in solution after 1 min (r_{1mn}/R), isotopically exchangeable phosphate after 1 min (E_{1mn}), and the n exponent for soil suspensions in 0.01 M CaCl_2 or deionized water. The regression lines are: $C_p(\text{CaCl}_2) = 0.005 + 0.31C_p(\text{H}_2\text{O})$ (Fig. 1a); $r_{1mn}/R(\text{CaCl}_2) = -0.015 + 0.50r_{1mn}/R(\text{H}_2\text{O})$ (Fig. 1b); $E_{1mn}(\text{CaCl}_2) = 0.79 + 0.73E_{1mn}(\text{H}_2\text{O})$ (Fig. 1c); and $n(\text{CaCl}_2) = 0.08 + 0.81n(\text{H}_2\text{O})$ (Fig. 1d). As Fig. 1a and 1c have log-log scales, plots of linear regressions are nonlinear.

Assessment of the Isotopically Exchangeable Phosphate to Solution Phosphate Relationship

For the four French soils, six levels of phosphate were added as KH_2PO_4 to deionized water and 0.01 M CaCl_2 suspensions (10 g of soil in 10 mL of solution) so that phosphate concentrations in soil solution after a given equilibration time ranged from 0.01 to 10 $\text{mg PO}_4\text{-P L}^{-1}$. Phosphate additions up to 300 $\text{mg PO}_4\text{-P kg}^{-1}$ of soil were required. Each phosphate addition was carried out in duplicate. All suspensions were gently mixed for 5 min and equilibrated for 24 h at $22 \pm 3^\circ\text{C}$ without shaking to avoid soil particle abrasion. Before determining C_p , E_{1mn} , and n , suspensions were diluted with 90 mL of deionized water or 0.01 M CaCl_2 (to a soil/solution ratio of 1:10) and gently mixed overnight.

According to Eq. [1], the effect of C_p on phosphate exchange was assessed considering changes in the E_{1mn} and n values with C_p . The E_{1mn} to C_p relationship was described by a Freundlich equation (Morel et al., 1994, 1995a,b):

$$E_{1mn} = \nu C_p^w \quad [4]$$

where ν is the phosphate exchanged after 1 min at $C_p = 1 \text{ mg PO}_4\text{-P L}^{-1}$ and w is a constant describing the nonlinear increase in E_{1mn} with C_p .

The n to C_p relationship was described by (Morel et al., 1994, 1995b):

$$n = p - q \log(C_p) \quad [5]$$

where p is the n value at $C_p = 1 \text{ mg PO}_4\text{-P L}^{-1}$ and q a constant describing the nonlinear decrease in n with increasing C_p .

Statistical Analysis of the Data

For all soils and supporting solutions, the parameter estimates of Eq. [3], [4], and [5] were obtained using nonlinear, least-squares parameter optimization (Proc NLIN) of SAS software (SAS Institute, 1991). For a given soil, the comparison between the parameter estimates of Eq. [4] and [5] obtained either in CaCl_2 solution or deionized water was made using the maximum likelihood test (Huet et al., 1992). The linear regressions were obtained with the regression procedure (Proc. REG) of SAS.

RESULTS

Soil Solution Phosphate in Unamended Soil

In the 27 unamended calcareous soils, the phosphate concentration in solution obtained with deionized water

Fig. 2. Isotopically exchangeable phosphate after 1 min (E_{1mn}) in the three phosphate-amended French soils as a function of phosphate concentration in solution (C_p) for soil suspensions in 0.01 M CaCl_2 or deionized water. Lines represent Eq. [4] ($E_{1mn} = \nu C_p^w$) whose parameter estimates are in Table 3.

$[C_p(\text{H}_2\text{O})]$ ranged from 0.004 to 0.379 (mean = 0.065) $\text{mg PO}_4\text{-P L}^{-1}$ (Table 2). Differences in $C_p(\text{H}_2\text{O})$ values between agricultural soil samples are usual and attributed to soil types and agricultural practices (Fardeau, 1993; Morel et al., 1994, 1995a).

The phosphate concentration in solution in the suspension prepared with 0.01 M CaCl_2 [$C_p(\text{CaCl}_2)$] ranged from 0.006 to 0.120 (mean = 0.026) $\text{mg PO}_4\text{-P L}^{-1}$ (Table 2). The average of the $C_p(\text{H}_2\text{O})/C_p(\text{CaCl}_2)$ ratio was about 2.5, with maximum and minimum values of 5.0 and 0.4, respectively. A linear relationship [$C_p(\text{CaCl}_2) = 0.005 + 0.31 C_p(\text{H}_2\text{O})$, $R^2 = 0.90$] describes $C_p(\text{CaCl}_2)$ as a function of $C_p(\text{H}_2\text{O})$ (Fig. 1a).

Immediately Isotopically Exchangeable Phosphate in Calcium Chloride and Deionized Water Suspensions

The $r_{1mn}/R(\text{CaCl}_2)$ were lower than the $r_{1mn}/R(\text{H}_2\text{O})$ values (Table 2). A linear relationship [$r_{1mn}/R(\text{CaCl}_2) = -0.015 + 0.50 r_{1mn}/R(\text{H}_2\text{O})$, $R^2 = 0.87$] describes changes in $r_{1mn}/R(\text{CaCl}_2)$ with $r_{1mn}/R(\text{H}_2\text{O})$ values (Fig. 1b).

The $E_{1mn}(\text{CaCl}_2)$ values ranged from 1.2 to 11.3 mg

$\text{PO}_4\text{-P kg}^{-1}$, with an average value of 2.8 $\text{mg PO}_4\text{-P kg}^{-1}$ (Table 2). The $E_{1mn}(\text{H}_2\text{O})$ values ranged from 0.5 to 9.3 $\text{mg PO}_4\text{-P kg}^{-1}$, with an average value of 2.7 $\text{mg PO}_4\text{-P kg}^{-1}$. A linear relationship [$E_{1mn}(\text{CaCl}_2) = 0.79 +$

Table 3. Regression constants of the P exchanged after 1 min vs. C_p ($E_{1mn} = \nu C_p^w$) and the time dependence of isotopic exchange vs. C_p [$n = p + q \log(C_p)$ where n is the exponent of $E_i = E_{1mn} t^n$] for the three P-amended French soils. The ν constant is in milligrams P per kilogram. The w , p , and q constants are dimensionless.

Soil reference	Solution	(ν , w)	(p , q)
1	H_2O	(26, 0.75) a†	(0.16, 0.039) a
	CaCl_2	(41, 0.65) b	(0.16, 0.042) a
2	H_2O	(27, 0.75) a	[(0.16, 0.041)]‡
	CaCl_2	(42, 0.64) b	(0.15, 0.036) a
3	H_2O	(15, 0.88) a	(0.16, 0.041) a
	CaCl_2	(18, 0.80) b	[(0.15, 0.037)]
			(0.16, 0.046) a
			(0.15, 0.048) a
			[(0.16, 0.048)]

† For each soil, the (ν , w) estimates or (p , q) estimates followed by different letters are significantly different ($P < 0.05$).

‡ [(p , q)] estimates obtained by regrouping data from both H_2O and CaCl_2 solutions.

Fig. 3. Relationships between n ($E_t = E_{1mn}^n$) and phosphate concentration in solution (C_p) for soil suspensions of the three phosphate-amended French soils in 0.01 M CaCl_2 or deionized water. Lines represent Eq. [5] [$n = p - q \log(C_p)$] whose parameter estimates are in Table 3.

$0.73E_{1mn}(\text{H}_2\text{O})$, $R^2 = 0.78$] describes changes in $E_{1mn}(\text{CaCl}_2)$ with $E_{1mn}(\text{H}_2\text{O})$ values (Fig. 1c).

For a given soil to which increasing phosphate quantities were added, the $E_{1mn}(\text{CaCl}_2)$ and $E_{1mn}(\text{H}_2\text{O})$ values increased with increasing soil solution phosphate, irrespective of the supporting solution (Fig. 2). Both changes in $E_{1mn}(\text{H}_2\text{O})$ and $E_{1mn}(\text{CaCl}_2)$ values with $C_p(\text{H}_2\text{O})$ and $C_p(\text{CaCl}_2)$, respectively, are closely described by Eq. [4] for all phosphate-enriched soils (Table 3, $R^2 > 0.98$ for all E_{1mn} to C_p curves). These results are similar to those obtained for other Canadian and French soils (Morel et al., 1994, 1995a,b).

For each soil, the (v, w) pair in Eq. [4] was significantly affected by the supporting solution (Table 3). The v values were from 27 to 69% greater, while the w values were from 10 to 20% smaller in the CaCl_2 solution than in deionized water for the three French soils (Table 3).

Slowly Isotopically Exchangeable Phosphate in Calcium Chloride and Deionized Water Solution

For the 27 unamended soils, the $n(\text{CaCl}_2)$ values are higher than $n(\text{H}_2\text{O})$ values (Table 2). A linear relation-

ship [$n(\text{CaCl}_2) = 0.08 + 0.81 n(\text{H}_2\text{O})$, $R^2 = 0.91$] described the $n(\text{CaCl}_2)$ and $n(\text{H}_2\text{O})$ values (Fig. 1d).

For a given phosphate-enriched soil, the increase in C_p value induced a decrease in the n value irrespective of supporting electrolytes (Fig. 3). The n to C_p relationships were closely fitted to Eq. [5] for all phosphate-enriched soils and supporting solutions. The (p, q) pair estimate is not significantly different in CaCl_2 and deionized water solutions (Table 3). Therefore, the increase in n values using the CaCl_2 solution compared with deionized water (Fig. 1d) can be solely explained by the lower soil solution phosphate that occurs with CaCl_2 .

DISCUSSION

Isotopic Exchange of Phosphate in Soil and Deionized Water

The reactivity of phosphate in solution with phosphate on the soil solid phase consists of, initially, a fast reaction, followed by a slow continuing reaction (Barrow and Shaw, 1975; Fardeau, 1993). This two-step process is attributed to, among other factors, adsorption onto sites of different affinity for phosphate, diffusion

Fig. 4. Variations in the phosphate concentration in solution (C_p), isotopically exchangeable phosphate after 1 min (E_{1mn}), and $n(E_i = E_{1mn}t^n)$ for soil suspensions in 0.01 M CaCl_2 and deionized water, with respect to $C_p(\text{H}_2\text{O})$ for unamended soils and phosphate-amended French soils. The value of $C_p(\text{H}_2\text{O})$ is plotted on a log scale. The linear regressions are: $C_p(\text{CaCl}_2) - C_p(\text{H}_2\text{O}) = -0.01 - 0.56C_p(\text{H}_2\text{O})$ (Fig. 4a); $E_{1mn}(\text{CaCl}_2) - E_{1mn}(\text{H}_2\text{O}) = 0.06 - 4.30C_p(\text{H}_2\text{O})$ (Fig. 4b).

into soil microaggregates, and various precipitation reactions. The isotopic exchange method mathematically describes each step by taking into account the gross phosphate exchange between solution and solid phase whatever the origin of preexisting phosphate associated with soil constituents and added phosphate. The rapid phosphate exchange corresponds to a dilution of the introduced ^{32}P with phosphate in solution and phosphate associated with soil surfaces that has an immediate ability to exchange with phosphate in solution (Fardeau and Marini, 1968). This phosphate quantity is estimated by the quantity of isotopically exchangeable phosphate in 1 min (E_{1mn}) in soils of temperate areas (Salcedo et al., 1991). For a given soil, the description of E_{1mn} to C_p relationship by the Freundlich equation (Morel et al., 1994, 1995a,b) is consistent with the hypothesis of an affinity term decreasing when E_{1mn} increases, as reported by Barrow (1978) for phosphate sorption curves.

The slow isotopic phosphate exchange is described by a power function of time (Eq. [1]). The n exponent quantifies the relative importance of the slow exchange with a high n describing greater quantities of slow phos-

phate exchange. With increasing C_p , phosphate on the soil solid phase increases in addition to phosphate in solution. The decrease in n with increasing C_p (found in this [Fig. 3] as well as other studies: Fardeau, 1993; Morel et al., 1994, 1995b) reflects the decrease in phosphate diffusion to the soil solid phase during slow exchange with increasing phosphate in solution and on the soil solid phase.

Effect of Calcium Chloride Solution on Phosphate Isotopic Exchange

The use of CaCl_2 solution instead of deionized water results in significant changes in C_p , E_{1mn} , and n values (Fig. 1). Since both E_{1mn} and n values are C_p dependent (Fig. 2 and 3), the assessment of the specific effect of the CaCl_2 solution on E_{1mn} and n requires that effects of a decrease in C_p on E_{1mn} and n values be distinguished from the interactions. This was done by (i) studying changes in the $C_p(\text{CaCl}_2) - C_p(\text{H}_2\text{O})$, $E_{1mn}(\text{CaCl}_2) - E_{1mn}(\text{H}_2\text{O})$, and $n(\text{CaCl}_2) - n(\text{H}_2\text{O})$ values with the $C_p(\text{H}_2\text{O})$ values (Fig. 4), and also (ii) comparing the

Fig. 5. Relationship between the isotopically exchangeable phosphate after 24 h (E_{24h}) for soil suspensions in 0.01 M CaCl_2 and deionized water for the 27 unamended soils. The E_{24h} values were calculated from Eq. [5] and parameters in Table 2. Line shown is 1:1.

$E_{1mn}-C_p$ and $n-C_p$ relationships obtained for the two supporting solutions in phosphate-enriched soils (Fig. 2 and 3).

The effect of the CaCl_2 solution on C_p is fully explained as a function of the $C_p(\text{H}_2\text{O})$ values (Fig. 4a) since the $C_p(\text{CaCl}_2) - C_p(\text{H}_2\text{O})$ values closely fitted ($R^2 = 0.99$) by a linear regression [$C_p(\text{CaCl}_2) - C_p(\text{H}_2\text{O}) = -0.01 - 0.56C_p(\text{H}_2\text{O})$] for all unamended and phosphate-enriched soils (42 samples). The greater $C_p(\text{H}_2\text{O})$, the greater the decrease in $C_p(\text{CaCl}_2)$. This result is explained by an increase in phosphate sorption in 0.01 M CaCl_2 (Ryden and Syers, 1975; Helyar et al., 1976).

The effect of the 0.01 M CaCl_2 solution on E_{1mn} (Fig. 4b) is explained ($R^2 = 0.90$) by C_p since $E_{1mn}(\text{CaCl}_2) - E_{1mn}(\text{H}_2\text{O})$ related to $C_p(\text{H}_2\text{O})$ values by a linear regression [$E_{1mn}(\text{CaCl}_2) - E_{1mn}(\text{H}_2\text{O}) = 0.06 - 4.30C_p(\text{H}_2\text{O})$, $n = 42$] for unamended and phosphate-enriched soils (Fig. 4b). At low $C_p(\text{H}_2\text{O})$ values, the variation is positive and becomes increasingly negative when $C_p(\text{H}_2\text{O})$ values increase. These results might be explained by the phosphate reactions occurring in calcareous soils. At low $C_p(\text{H}_2\text{O})$ values, the reaction of phosphate in solution with CaCO_3 is likely to be orthophosphate adsorp-

Fig. 6. Time-dependent isotopically exchangeable phosphate ($E_t = E_{1mn}t^n$) for four soil suspensions in deionized water or 0.01 M CaCl_2 . The four soils are the Spanish soils referenced as 2, 8, 10, and 17 in Solis and Torrent (1989a,b) and represent the variability of the E_t to t relationships found in the 27 unamended soils.

tion. Higher Ca activity in solution decreases the negative potential of the Ca-P surfaces and enhances surface phosphate adsorption (Ryden and Syers, 1975). At higher $C_P(\text{H}_2\text{O})$ values, the 0.01 M CaCl_2 solution may promote the formation of Ca-phosphate-carbonate complexes or precipitation of Ca phosphates on the surface of CaCO_3 (Freeman and Rowell, 1981; Avnimelech, 1980; Salingar and Kochva, 1994) before measuring isotopic exchange. These precipitates do not exchange as readily as phosphate solid phases in deionized water. As a result, the rapid phosphate exchange decreases (the $E_{1\text{mn}}$ value decreases) in CaCl_2 , whereas the slow phosphate exchange increases (the n value increases).

The $n(\text{CaCl}_2) - n(\text{H}_2\text{O})$ values were not explained by $C_P(\text{H}_2\text{O})$ values (Fig. 4c). The same conclusion is obtained by comparing, for a defined soil, the $n-C_P$ relationship in the two supporting solutions (Fig. 3). The increase in $n(\text{CaCl}_2)$ compared with $n(\text{H}_2\text{O})$ is only due to the decrease in $C_P(\text{CaCl}_2)$ compared with $C_P(\text{H}_2\text{O})$ since parameter estimates of both $n-C_P$ relationships are not significantly different. Therefore, the CaCl_2 solution relative to the deionized water has no specific effect on the slow exchange process as described by the n to C_P curve. The variability in the $n(\text{CaCl}_2) - n(\text{H}_2\text{O})$ value is likely to be influenced by various soil properties.

Comparison between Isotopically Exchangeable Phosphate in Calcium Chloride and Deionized Water: Agronomic Significance

Although Eq. [1] is determined for 100 min, it successfully predicts E_i values up to 3 mo of exchange (Fardeau, 1981; Fardeau and Jappe, 1976). For the 27 unnamed soils, the relationship between isotopically exchangeable phosphate after 24 h (which is a very common exchange time in the literature) in CaCl_2 [$E_{24\text{h}}(\text{CaCl}_2)$] and deionized water [$E_{24\text{h}}(\text{H}_2\text{O})$] is shown in Fig. 5. The ratio $E_{24\text{h}}(\text{CaCl}_2) - E_{24\text{h}}(\text{H}_2\text{O})$ to $E_{24\text{h}}(\text{H}_2\text{O})$ ranged from -30 to 343%.

Differences in $E_{24\text{h}}$ induced by the supporting solution underline the need to adopt a standardized method for measuring isotopically exchangeable phosphate and caution against direct comparisons between data obtained by different researchers. Furthermore, differences in E_i values obtained using the two supporting solutions also depend on the period of exchange (Fig. 6). For instance, if the rate of change of E_i is extrapolated over 10 000 min (≈ 1 wk), the difference between $E_i(\text{CaCl}_2)$ and $E_i(\text{H}_2\text{O})$ varies with time. The plots of $E_i(\text{CaCl}_2)$ and $E_i(\text{H}_2\text{O})$ with time for four Spanish soils, selected to be representative of the variability found in all soils, show that the $E_i(\text{CaCl}_2) - E_i(\text{H}_2\text{O})$ value can be negative, positive, or nil depending on the time of exchange (Fig. 6). It seems, consequently, there is no way to easily relate results obtained with the different supporting solutions since the CaCl_2 solution affects the isotopic phosphate exchange process by: (i) decreasing soil solution phosphate [the greater the $C_P(\text{H}_2\text{O})$ value, the greater the decrease is]; (ii) decreasing the rapid exchange of phosphate between liquid and solid phases

[also, the greater the $C_P(\text{H}_2\text{O})$ value, the greater the decrease is]; and (iii) increasing the importance of slow relative to rapid phosphate exchange.

Two of the above effects are mainly controlled by the phosphate concentration in soil solution, which is by nature highly variable since it depends on soil types, pedogenetic evolution, and agricultural practices. The result of these effects and their interactions is a wide and unpredictable variability among soils for E_i obtained either in 0.01 M CaCl_2 or deionized water.

Finally, these results have significant agronomic implications. The isotopic phosphate exchange method using deionized water gives an estimate of the reserve of plant-available phosphate in soils (Fardeau and Jappe, 1976; Morel and Fardeau, 1991; Morel and Plenchette, 1994; Frossard et al., 1994). This study shows that the 0.01 M CaCl_2 solution modifies directly and indirectly (through soil solution phosphate) both rapid and slow phosphate exchange. The resulting overall effect varies with soil types and agricultural practices, obscuring the significance of E_i measured in deionized water. To adequately estimate the reserve of plant-available phosphate, use of 0.01 M CaCl_2 solution should be avoided.

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