Soil Isotopically Exchangeable Phosphorus: A Comparison between E and L Values

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ABSTRACT

This study was designed to explain the apparent discrepancies often reported in the literature between E and L values, two parameters obtained from isotopic exchange experiments and commonly used to quantify available soil phosphate. The E and L values of the surface horizons of 10 soils from tropical, mediterranean, and temperate regions were determined. The L value was measured from a 13-wk pot experiment with common bentgrass (*Agrostis capillaris* L.) where the available soil P was labeled with $^{32}PO_4$ ions in the presence of a carrier (25–50 mg ^{31}P kg^{-1} soil). To determine the E value, the isotopic exchange kinetic experiment was carried out on each soil. Carrier-free $^{32}PO_4$ was added to the soil–solution system at a steady state and the quantity of isotopically exchangeable soil phosphate at time t, $E(t)$, was calculated from the kinetic equation describing the decrease of radioactivity in solution with time. Results showed that L values determined after 13 wk were not significantly different from $E(t)$ values extrapolated to the same period (t = 131 040 min). It was concluded that (i) the L value is a particular point of the kinetic equation and (ii) isotopically exchangeable phosphate is the available P for common bentgrass. A strict equality between $E(13wk)$ and L values was not, however, reached for all samples. Possible causes for the differences were: (i) an overestimation of the water-soluble phosphate due to the presence of silica and (ii) disturbance of the steady state following a too large uptake of phosphate by the crop or the application of too large quantities of carrier compared with the initial quantity of exchangeable soil phosphate.

T HE QUANTITY, at a given time, of phosphate ions in the soil solution is much lower than the quantity of P eventually taken up by a crop (Larsen, 1967). Hence, a large proportion of the bioavailable soil phosphate is located on the soil solid phase. Every chemical method used to extract a quantity of P that correlates with the quantity of P taken up by a crop under standard conditions provides only crude prediction of plant yield and P uptake (Bolland and Gilkes, 1992). A reason is that chemical reagents extract only a fraction of the available P together with significant amounts of unavailable forms of P (Fardeau et al., 1988). Therefore, in order to accurately characterize the available soil phosphate, a method that does not modify the equilibrium between the various P compartments is necessary.

Theoretically, the isotopic exchange method allows the determination of an unknown quantity of a given compound present in a complex mixture without extracting it from the mixture (Sheppard, 1962; Shipley and Clark, 1972). In this approach, only a small fraction of the compound is required to determine the unknown quantity. The first described procedure to determine soil available P was measurement of the isotopically ex-

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changeable soil phosphate, i.e., the E value. This procedure was based on measurement of the specific activity ($^{32}PO_4/^{31}PO_4$) of phosphate ions in the soil solution after an addition of $^{32}PO_4$ (Wiklander, 1950; Barbier and Tyszkiewicz, 1952; Fried, 1964). The isotopic equilibrium between soil P and P in solution was assumed to occur for a duration of exchange ranging from 4 h, to 3 wk, and to infinity (Scott Russell et al., 1954; Jose and Krishnamoorthy, 1972; Fardeau et al., 1985; Frossard et al., 1986; Triboï and Gachon, 1988; Barrow, 1990; He et al., 1991). But in some instances, especially in highly P fixing soils, E values have been shown to overestimate the soil available P because of overestimation of ^{31}P concentration in the solution (see, e.g., Wolf et al., 1986; Salcedo et al., 1991). In order to overcome this difficulty, Larsen (1952) proposed another procedure for measuring the quantity of isotopically exchangeable soil phosphate, the L value, based on the specific activity of a plant grown on a soil whose available P has been labeled with $^{32}PO_4$ ions. The major interest of this method is that plants take up P, by definition, the available soil phosphate (Fried, 1964).

The E and L values have been compared many times (Scott Russell, 1959; Gachon, 1966; Jose and Krishnamoorthy, 1972; Ipidmidum, 1973; Fardeau and Jappé, 1976; Roche, 1983; Gachon, 1988). Various statistical relations have been published, some being contradictory. Different durations for isotopic exchange were used ranging from 4 h to infinity for the E value and between 1 and 3 mo for L values. In a previous study Fardeau and Jappé (1976) showed that the L value measured on a loamy soil was not different from the E value calculated after the same exchange time.

The aim of this study was to show, with examples, that using the equation given by Fardeau et al. (1985), similar E and L values could be obtained provided that E values are extrapolated to an exchange time identical to that considered for the measurement of L values. Despite this, discrepancies may still be observed between these two parameters, and we address some of the reasons accounting for these discrepancies.

MATERIALS AND METHODS

Soil Samples

The surface horizons of 10 soils were selected for this study: two Vertisols and three Ultisols from tropical regions; two Mollisols from a mediterranean region; and a Mollisol, an Inceptisol, and an Alfisol from a temperate region. Before analysis, all the samples were air-dried, ground, and sieved at 2 mm. Identification and some properties of the samples are listed in Table 1.

Phosphate Additions

All soils, except Samples 3 and 4, were fertilized at the rate of 100 mg P kg^{-1} soil in the form of diammonium phosphate (Samples 1, 2, 5, 6, 7, and 8) or monocalcium phosphate

Table 1. Origin and selected properties of the studied soil samples.

Identification	Soil order†	pH_{H_2O}	Clay	Silt	Sand	TOC‡	CaCO₃	Fe_d§	Al_o¶
				%				g kg⁻¹ soil	
1	Mollisol (Morocco)¹	7.9	32.1	53.5	14.4	18.9	35.4	1.08	0.22
2	Mollisol (Morocco)¹	8.2	47.7	33.5	7.8	21.7	39.8	1.52	0.23
3	Mollisol (France)¹	7.8	29.9	21.0	49.2	20.2	16.1	2.94	0.13
4	Inceptisol (France)¹	7.8	43.3	42.3	14.3	13.6	1.6	2.32	0.15
5	Alfisol (France)²	5.3	23.5	55.3	21.2	15.6	0	22.0	1.6
6	Vertisol (Sénégal)²	7.6	56.3	40.0	13.7	6.6	0	10.2	1.00
7	Vertisol (Cameroon)²	7.4	50.1	27.9	22.0	7.4	0	7.60	1.20
8	Ultisol (Burkina Faso)²	5.3	9.2	23.4	67.4	3.3	0	5.0	0.40
9	Ultisol (Mali)³	5.3	20.6	14.6	65.2	6.1	0	nd#	nd
10	Ultisol (Togo)³	6.5	26.0	41.0	33.0	20.9	0	nd	nd

† Data extracted from (1) Arakrak (1989), (2) Pena Cervantes (1989), and (3) Paul (1988).
‡ TOC = total organic carbon.
§ Fe_d = dithionite-citrate-bicarbonate extractable Fe.
¶ Al_o = oxalic acid-oxalate extractable Al.
# nd = not determined.

(Samples 9 and 10). Samples 1, 2, 3, 4, 5, 6, 7, 8, and their fertilized counterparts were incubated for 4 wk at 28 °C and at 80% of their water-holding capacity. Samples 9 and 10 were not incubated.

Determinations of Isotopically Exchangeable Soil Phosphate

The E and L values were determined after 4 wk of incubation for all samples except Samples 9 and 10, where determinations were made just after the P application.

Pot Trials: L Values

The L values were determined using $^{32}PO_4$ ions in the presence of a carrier (Larsen, 1952; Truong and Pichot, 1976). Exchangeable soil P was labeled with a quantity, R, of $^{32}PO_4$ of 18.5 MBq kg⁻¹ soil. The quantity R was added with a quantity, Q, of carrier (between 25 and 55 mg $^{31}PO_4$ kg⁻¹ soil as KH_2PO_4) to avoid the sorption of $^{32}PO_4$ on vacant sites (Amer et al., 1955; Truong and Pichot, 1976; Barrow, 1991). A nutrient solution (N, K, and micronutrients) was added and, after distribution of the soil in pots, common bentgrass was sown. Aerial parts were harvested 4, 8, and 13 wk after sowing. Dry matter and ^{31}P and ^{32}P contents were measured. Five replicates were made for each soil and each treatment.

Since $^{32}PO_4$ ions were added with a carrier, the P taken up by the crop was derived from three sources: (i) from the soil available P, (ii) from the fertilizer, and (iii) from the carrier (KH_2PO_4). The quantity of P derived from the soil, enriched or not with a fertilizer, P_{soil}, present in the three harvests was calculated. Let p_1, p_2, and p_3 be the quantities of ^{31}P (mg P kg⁻¹) and r_1, r_2, and r_3 be the quantities of ^{32}P (MBq kg⁻¹) of the aerial parts of the bentgrass at the first, second, and third harvests. The total quantity of plant P derived from the carrier ($P_{carrier}$) is calculated by

$$P_{carrier} = Q(r_1 + r_2 + r_3)/R \qquad [1]$$

Hence

$$P_{soil} = (p_1 + p_2 + p_3) - P_{carrier} \qquad [2]$$

Values of P_{soil} were obtained with a mean coefficient of variation of 7%.

The L Values were calculated with the experimental data obtained at the third harvest, where the P derived from the seeds was negligible (Truong and Pichot, 1976).

$$L = Q\left[\frac{(R/Q)}{(r_3/p_3)} - 1\right] \qquad [3]$$

Under our experimental conditions, L values were obtained with a mean coefficient of variation of 4.4%.

Soil-Solution Systems: Isotopic Exchange Kinetics of Phosphate Ions and E Values. The experimental procedure, conducted on a soil-solution system in a steady state with a soil/solution ratio of 1:10, has been described (see, e.g., Fardeau et al., 1991; Salcedo et al., 1991; Frossard et al., 1992). Four or five samplings of the soil solution were made between 1 and 100 min after the addition of the radioactive tracer. Each experiment was conducted with carrier-free $^{32}PO_4$ ions. When a quantity, R, of carrier-free $^{32}PO_4$ ions is added to a soil solution system in a steady state, an isotopic exchange between ions in solution and some ions of the soil solid phase takes place. The quantity of radioactivity, $r(t)$, remaining in solution decreases with time, $t(min)$, according to the following theoretical equation (Fardeau et al., 1985):

$$\frac{r(t)}{R} = \frac{r(1)}{R}\left\{t + \left[\frac{r(1)}{R}\right]^{1/n}\right\}^{-n} + \frac{r(\infty)}{R} \qquad [4]$$

Where $r(1)$ and $r(\infty)$ are the radioactivity (MBq) remaining in the solution after 1 min and infinity, respectively, and n is a parameter obtained from the isotopic exchange kinetic experiment. In this experiment, n is calculated as the slope of the regression equation between $\log[r(t)/R]$ and $\log(t)$ (Fardeau and Jappé, 1978).

The ratio $r(\infty)/R$ is the maximum possible dilution of the isotope. It is approximated by the ratio of the water-soluble P to the total inorganic P (P_{inorg}) of the soil (Fardeau, 1993).

$$\frac{r(\infty)}{R} = \frac{10\ c_P}{P_{inorg}} \qquad [5]$$

where c_P is the water-soluble P (mg P L⁻¹). The factor 10 arises from the fact that 10 g of soil are suspended in 100 mL of water.

To characterize the isotopic exchange of phosphate ions between soil and solution, the following parameters must be determined: $r(1)/R$, n, c_P, and P_{inorg}. Moreover the $r(1)/R$ ratio is highly correlated to the soil P-fixing capacity. Soils with a $r(1)/R < 0.2$ have a high P-fixing capacity, while soils with a $r(1)/R > 0.4$ have a low P-fixing capacity (Fardeau, 1981; Morel et al., 1989; Frossard et al., 1993).

The quantity, $E(t)$ (mg P kg⁻¹ soil), of isotopically exchanged P at time t is calculated assuming that (i) $^{31}PO_4$ and $^{32}PO_4$ ions have the same fate in the system and (ii) whatever the time t, the specific activity of the phosphate ions in the soil solution is identical to that of the isotopically exchanged phosphate ions in the whole system.

$$\frac{r(t)}{c_P\,10} = \frac{R}{E(t)} \qquad [6]$$

Therefore

$$E(t) = 10\,c_P\,\frac{R}{r(t)} \qquad [7]$$

In some instances, especially for soils with n values lower than 0.2, the theoretical Eq. [7] can be simplified (Fardeau et al., 1985). The simplified equation is similar to the empirical kinetics equation previously published (Wiklander, 1950):

$$E(t) = 10\,c_P[R/r(1)]t^n \qquad [8]$$

Phosphorus Analysis

The water-soluble P was colorimetrically measured on an aliquot of the solution (Murphy and Riley, 1962). The total P was measured after an attack with hot concentrated $HClO_4$ for soils and after calcination of the plants (4 h at 550 °C). Mineral P (P_{inog}) was extracted with 1 M H_2SO_4 for 17 h (Saunders and Williams, 1955). Phosphorus-32 was measured by liquid scintillation counting.

RESULTS AND DISCUSSION

Total and Mineral Phosphorus

The total P content ranged from 89 mg P kg^{-1} soil in Sample 8 to 1919 mg P kg^{-1} in Sample 3 (Table 2). The proportion of mineral P varied from 82% of the total P in sample 3 to 33% in Sample 10.

Phosphorus Exported by *Agrostis* and *L* Values

The quantities of P taken up by bentgrass that were derived from the soil available P (P_{soil}) varied from 4.8 mg P kg^{-1} soil in Sample 9 to 44 mg P kg^{-1} soil in Sample 5 (Table 2). The L values ranged from 12 mg P kg^{-1} soil in Sample 7 up to 278 mg P kg^{-1} soil in Sample 5. These results show that a Mollisol (Sample

1), the two Vertisols (Samples 6 and 7), and the three Ultisols (Samples 8, 9 and 10) could be considered as severely P limited according to Roche et al. (1980).

The addition of water-soluble P led to strong P_{soil} and L increases. The L value increases ranged from 78 to 100 mg P kg^{-1} soil, i.e., most of the added P remained isotopically exchangeable after 13 wk. This result seems contradictory to numerous studies that have shown that a significant fraction of added P becomes almost unexchangeable (see, e.g., Larsen, 1967; Barrow and Shaw, 1975).

Isotopic Exchange Kinetics Parameters

The $r(1)/R$ ratio of the unfertilized samples varied from 0.02 and 0.03 in Samples 7 and 6 and up to 0.41 in Sample 8 (Table 2). The high P-fixing capacity of the two Vertisols (Samples 6 and 7) was related to their high clay content. The low P-fixing capacity of the Ultisols (Samples 8, 9, and 10) was a consequence of their low clay and Fe and Al oxide content (Frossard et al., 1992).

The concentration, c_P, of phosphate ions in the solution ranged from 0.007 mg P L^{-1} in Sample 7 to 1.12 mg P L^{-1} in Sample 3 (Table 2). Water-soluble P contents higher than 0.1 mg L^{-1} were observed in cultivated soils receiving heavy P fertilization (Samples 2, 3, 4, and 5).

The quantity of phosphate isotopically exchangeable within 1 min, $E(1\text{min})$, was calculated (Table 2). The value of $E(1\text{min})$ is a good approximation of the quantity of free phosphate ions in the soil–solution system available without chemical transformation to plants (Tran et al., 1988; Salcedo et al., 1991; Fardeau and Frossard, 1992). According to this parameter, Samples 1, 6, 7, 8, 9, and 10 are low in available P (Tran et al., 1988).

In all the soils, the recent application of a water-soluble P fertilizer increased $r(1)/R$, c_P, and $E(1\text{min})$ values and decreased n, as expected (Fardeau and Frossard, 1992). None of these soils remained P limited after addition of 100 mg P kg^{-1} soil.

Table 2. Soil P status of unfertilized samples and samples fertilized with water-soluble P at the rate of 100 mg P kg^{-1} soil.

Soil	Total P	Inorganic P	Pot trial P$_{soil}$ (sum of three cuts)	Pot trial L value (13wk)	$r(1)/R$	n	c_P	Calculated E(t) values E(1min)	Calculated E(t) values E(13wk)[†]	Calculated E(t) values E(13wk)[‡]
	——— mg kg^{-1} soil ———						mg P L^{-1}	——— mg kg^{-1} soil ———		
Soil 1	513	281	11.8	36	0.16	0.34	0.04	2.51	92.3	137.4
Soil 1 + P	613	295	23.6	118	0.27	0.23	0.43	15.9	149.1	239.4
Soil 2	629	363	19.4	88	0.15	0.25	0.15	10.0	124.8	190.3
Soil 2 + P	729	456	23.0	172	0.22	0.22	0.57	25.9	196.8	346.2
Soil 3	1919	1571	25.1	271	0.30	0.19	1.12	37.4	286.4	350.3
Soil 4	927	676	23.8	224	0.13	0.31	0.103	7.81	208.3	301.1
Soil 5	1058	690	44.0	278	0.13	0.36	0.115	8.56	319.4	594.6
Soil 5 + P	1158	796	62.1	378	0.22	0.31	0.375	17.1	360.1	657.7
Soil 6	265	195	5.9	44	0.03	0.27	0.008	2.67	48.3	64.2
Soil 6 + P	365	316	24.7	141	0.06	0.33	0.032	5.33	142.8	260.5
Soil 7	168	76	8.6	12	0.02	0.26	0.007	3.50	37.7	74.9
Soil 7 + P	268	198	33.9	100	0.06	0.33	0.032	7.67	62.4	91.0
Soil 8	89	34	16.9	19.5	0.41	0.24	0.036	0.88	10.3	14.9
Soil 8 + P	189	139	52.8	98	0.77	0.06	1.85	24.0	36.0	48.7
Soil 9	132	56	4.8	21.1	0.36	0.39	0.07	2.01	43.6	192.6
Soil 9 + P	232	156	44.1	111	0.54	0.19	2.52	47.2	115.2	437.8
Soil 10	332	108	11.7	34.2	0.31	0.22	0.10	3.24	30.7	43.1
Soil 10 + P	432	208	48.9	127	0.43	0.11	1.00	23.3	60.3	85.0

† $E(13\text{wk})$ values calculated using the theoretical Eq. [7].
‡ $E(13\text{wk})$ values calculated using the simplified Eq. [8].

Comparison between L and E Values

Since isotopic exchange is a time-dependent mechanism (Eq. [4]), the $E(t)$ values were calculated for a similar exchange time to that used to measure the L values, i.e., 13 wk or 131040 min.

Extrapolation of E Values to Thirteen Weeks

The $E(t)$ values were calculated (Table 2) by extrapolation of the isotopic exchange data using either the theoretical Eq. [7] or the simplified Eq. [8] previously used by Fardeau and Jappé (1976). The E value extrapolated to 131040 min (13 wk) from data obtained between 1 and 100 min is noted as E(13wk). The simplified equation always overestimated the E(13wk) values. Therefore, this equation must be avoided to estimate $E(t)$ values for times longer than 2 or 3 d, especially if n is larger than 0.2. Solving the theoretical equation (Eq. [7]) necessitates the measurement of mineral P to calculate $r(\infty)/R$ (Eq. [5]). As a consequence, mineral P must be determined for each soil if the data obtained between 1 and 100 min are to be extrapolated to evaluate the quantities of phosphate isotopically exchangeable for periods longer than 4 wk.

Comparison between E(13wk) Values and L Values

The E(13wk) values, determined with the theoretical Eq. [7], were correlated with the L values (Fig. 1). A highly statistically significant linear relation appeared between E(13wk) and L. Furthermore, the regression coefficient was not statistically different from one and the intercept was not significantly different from zero (Table 3). These results were in accordance with those previously published by Fardeau and Jappé (1976) and confirmed that the available soil phosphate is the isotopically exchangeable phosphate.

However, in one case (Sample 1), E(13wk) significantly overestimated L, while in other cases (Samples 7+P, 8+P, and 10+P) E(13wk) values were significantly lower than L values (Fig. 1).
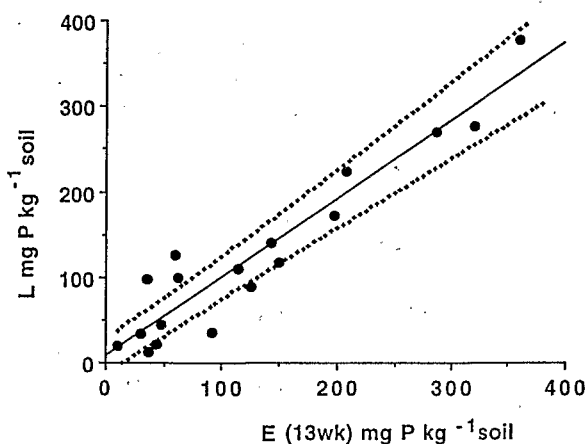

Fig. 1. Relation between $E(t)$ values extrapolated to 13 wk of isotopic exchange using Eq. [7] and L values experimentally measured after 13 wk of growth of common bentgrass. The solid line indicates the regression model while dashed lines show the confidence bands (at $P = 0.05$) for the population regression line.

Table 3. Estimation of the regression coefficients of the equation $L = aE(\text{13wk})\dagger + b$.

Estimated values		Standard deviation	Confidence limits $(P = 0.10)$	Regression coefficient (r^2)
a	0.924	0.078	0.788; 1.059	0.900
b	6.966	12.81	−15.40; 29.33	

$\dagger$ E(13wk) values calculated using Eq. [7].

As there is only one physical mechanism, the isotopic exchange of phosphate ions between the phosphate ions in solution and those located on the soil solid phase, there is only one exact value. Therefore these discrepancies are due either to experimental errors or incorrect procedures.

The two procedures differ in two aspects: (i) the fraction of the system used to determine the specific activity of the exchangeable soil phosphate is the soil solution for E(13wk) and the crop for L; and (ii) E(13wk) values were determined without carrier and L values with a carrier.

If a proper isotopic experiment is to be done, the following constraints have to be respected: (i) the tracer must be chemically and radiochemically pure, i.e., ^{32}P must be applied only as orthophosphate ions; (ii) the specific activity, i.e., $r(t)/(10\,c_P)$ or r_3/p_3, must be determined on a unique compound derived from a unique compartment, i.e., the soil solution or the plant and (iii) the system has to be maintained at a steady state. Therefore the quantity of tracer and quantity of carrier must be negligible in comparison with the quantity of the same compound present in the pool that receives the tracer and carrier. The fraction of the component taken up from a pool for the determination of the specific activity must also be negligible in comparison with the quantity of this component remaining in the pool. If one or more of these constraints is not respected, the E(13wk) and L values can be false, because each parameter of the formula $E(t) = 10\,c_P\,[R/r(t)]$ or $L = Q[(R/Q)/(r_3/p_3) - 1]$ can be modified.

E values determined without carrier can be affected by errors on R and c_P. The value of R must be the quantity of ^{32}P added as orthophosphate ions to the isotopically exchangeable pool of phosphate ions. The value of R can affect the calculation of E values in two ways: (i) the added radioactivity contains not only ^{32}P but other radioisotopes; (ii) ^{32}P is applied not only as orthophosphate ions but also as pyro- or metaphosphate ions. Under these circumstances the E(13wk) value may be lower or higher than the exact value.

To explain the overestimation of soil available P when the isotopically exchangeable P is measured with carrier-free ^{32}P in soils with a high P-fixing capacity, it has been assumed that some of the added labeled ions react with vacant sites and become sorbed instead of being truly exchanged with unlabeled ions (Amer, 1962; Amer et al., 1969; Barrow, 1991). In this case the quantity of radioactivity applied to the exchangeable pool would not be R but a smaller quantity. As a result, $r(t)$ would be lower than expected and $E(t)$ higher. As a matter of fact, this assumption seems very unlikely. The total quantity of radioactivity used for the determination of the isotopic

Table 4. Mean increases of $L(\Delta L)$ and E(13wk) [ΔE(13wk)] values after the application of 100 mg P kg^{-1} soil in a water-soluble form, and consequences on the quantity of carrier P actually applied in the exchangeable pool of phosphate (corrected Q). Corrected Q is calculated from Eq. [9].

Samples	ΔL	ΔE(13wk)	Applied Q	Corrected Q
		mg P kg soil^{-1}		
1	82.0	57.0	30.0	20.8
2	84.0	72.0	30.0	25.7
5	100.0	41.0	33.3	13.7
6	97.0	95.0	33.3	32.6
7	88.0	25.0	27.7	7.87
8	79.0	26.0	25.0	8.23
9	90.0	72.0	50.0	40.0
10	93.0	30.0	50.0	16.1
Mean	89.1	52.2	34.9	20.6

kinetic parameters of phosphate in a soil sample is about 10^5 Bq. Therefore 10^3 Bq are added per milliliter, i.e., $\approx 10^{-7}$ µg P mL^{-1} because a quantity of 37×10^8 Bq corresponds to 3.5 µg P (Pannetier, 1980). Besides, the lowest concentration of phosphate ions observed in the solution of soils with a very high fixing capacity, or natural waters in contact with sediments, is $\approx 2 \times 10^{-3}$ µg P mL^{-1}. Therefore, at the beginning of an isotopic exchange experiment in these most unfavorable cases, there is about one $^{32}PO_4$ ion in the presence of 2×10^4 $^{31}PO_4$ ions. Since $^{32}PO_4$ and $^{31}PO_4$ ions have the same fate, there is no reason for a specific adsorption of $^{32}PO_4$ ions instead of $^{31}PO_4$ ions.

The only origin left for any E(13wk) overestimation remains an error on c_P. All the reagents used to colorimetrically determine phosphate ions in the soil solution react with silica (Fardeau and Jappé, 1988; Ciavatta et al., 1990). Fardeau and Jappé (1988) have shown that with reagents used in the Murphy and Riley (1962) procedure, 500 µg Si have the same absorbance as 1 µg P. In soil solution, the Si concentration ranges between 5 and 80 mg Si L^{-1}. Therefore, in many soils it is very difficult to accurately know the P concentration in the soil solution because the greater part of the absorbance results from the presence of Si.

The L values can be affected by errors on (i) R and p_3 and (ii) Q when L is determined with a carrier. Errors on R can affect the determination of L values as they affect the determination of E values. The quantity of phosphate taken up by the crop, p_3, can also change the results of the isotopic exchange. A large uptake, compared with the small quantity of rapidly exchangeable phosphate, will modify significantly the steady state of the system. This is illustrated by the results obtained on Sample 8, in which 87% of the isotopically exchangeable phosphate was taken up (i.e., the percentage of P taken up by the crop [P_{soil}] to the L value). In this case the L value probably increased due to the desorption of very slowly exchangeable phosphate.

The value of Q can change the result of isotopic exchange. A large application of P carrier, compared with the quantity of P contained in the exchangeable pool, will modify significantly the steady state of the system. A fraction of P added as carrier may become very slowly exchangeable (Fardeau, 1993). In this case,

the specific activity of the carrier is not modified, but r_3 decreases. Hence, L calculated with Eq. [3] is higher than the exact value. This explains why L increases more rapidly than E(13wk) (Table 4). The mean increase in E(13wk) [ΔE(13wk)] after an addition of 100 mg P kg^{-1} soil is about 52 mg P kg^{-1} soil. This is a more realistic value than the mean increase in $L(\Delta L)$, which is close to 89 mg P kg^{-1} soil. If ΔE(13wk) represents a realistic increase in exchangeable P after 13 wk of isotopic exchange and ΔL overestimates this increase because of a lower exchangeability of the added carrier, then ΔE(13wk)/ΔL can be considered a corrective factor (<1) and the following equation can be used to recalculate the amount of carrier remaining really exchangeable (corrected Q):

$$\text{corrected } Q = \text{applied } Q \ \Delta E(13 \text{ wk})/\Delta L \quad [9]$$

The use of this equation shows that the mean quantity of carrier that was actually applied to the pool of exchangeable ions in our experiment was not 34.9 but 20.6 mg P kg^{-1} soil (Table 4).

CONCLUSIONS

This study has demonstrated that the L value is a single point of the kinetic equation describing $E(t)$, and the isotopically exchangeable phosphate is the major source of available soil phosphate for bentgrass. In addition, from a practical view point, we showed that isotopic methods must be conducted with much rigor for proper interpretation.

The chosen procedure will be the one that offers the most important volume of results considering the chosen objectives. The measurement of the L value is pertinent because it allows for obtaining biological data. However, the use of a P carrier should be avoided. The isotopic exchange kinetic method allows the simultaneous determination of the three parameters necessary for characterizing soil available P: the intensity factor (c_P), the quantity factor [$E(t)$] and the buffer capacity [$R/r(1)$] (Dalal and Hallsworth, 1977; Fardeau and Frossard, 1992). This study demonstrated that $E(t)$ values can be extrapolated up to 13 wk, which is a period relevant to the nutrition of annual crops. The most difficult measurement remains that of c_P, a problem that can be overcome by preconcentrating solution P on an anionic resin prior to its determination (Salcedo et al., 1991).

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