Supplementary Information

The mathematical derivation of K_m

Solution P turnover can be calculated from the model parameters *m* and *n*, which describe the loss of radioactivity in the soil solution of an isotopic exchange kinetic experiment (IEK) (Fardeau et al., 1991). An IEK experiment is comprised of three main parts. First, P exchange between a predefined amount of soil and water is brought into a thermodynamic steady-state. This is typically carried out using 10 g of soil in 99 ml of water and shaking for 16h (Oehl et al., 2001). Second, carrier-free radioactive P isotopes (^{33}P or ^{32}P) are added to the soil suspension. For example, a 1 ml solution containing between 10^5 Bq P and 10^6 Bq P is added to the soil suspension at time zero. Third, the radioactivity of the soil solution is probed over time. For example, at time (t) = 1, 4, 10, 40, and 90 min after the addition of radioisotope to the soil solution. Radioactivity is sequentially lost from the solution over time as radiolabeled P exchanges with unlabeled P located on the soil solid phase. Fardeau et al. (1991) described this rate of decline of radioactivity from the soil solution using Eq. (1):

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

where $r_{(t)}$ is the radioactivity measured at time *t*, *R* is the total amount of radioactivity added, and *m* and *n* are the model parameters determined by non-linear regression (Fardeau et al., 1991;Frossard et al., 2011).

As time progresses (increasing t), $\frac{r_{(t)}}{R}$ approaches $\frac{r_{(\infty)}}{R}$, which is set to equal the concentration of P in solution (P_w [mg kg^{-1}]) divided by the total concentration of inorganic P in the soil (P_{inorg} [mg kg^{-1}]). This is because, in theory, eventually the entire pool of inorganic P in the soil will be isotopically exchangeable.

$$\frac{r_{(\infty)}}{R} = \frac{P_w}{P_{inorg}} \qquad (2)$$

Under conditions that have obtained a thermodynamic steady-state, which is a necessary assumption of the IEK experiment, there is a constant rate of exchange between the soil solution and soil solid phases. Therefore, there is no net flux of P between soil and solution. This can be described using Eq. (3):

$$\frac{dP_w}{dt} = k_2 * P_{solid} - k_1 * P_w = 0 \qquad (3)$$

$$P_{solid} = P_{inorg} - P_w \qquad (4)$$

where P_w and P_{solid} are the concentrations of P in solution and the solid soil phase [mg kg^{-1}], and k_1 and k_2 are the respective rates of exchange [min^{-1}].

Assuming that the chemical behavior of the isotopes is the same, it is possible to quantify k_1. When carrier free radioisotopes are added to the soil solution, all radioactivity is in P_w, and the change in the concentration of radioactivity in P_w at t = 0 is a result of the loss of radioactivity from the liquid to the solid phase (since there cannot be any backflow of radioactivity yet).

$$k_1 = -\frac{dP_w/dt}{P_w} = -\left.\frac{d(\frac{r_{(t)}}{R})/dt}{\frac{r_{(t)}}{R}}\right|_{t=0} \qquad (5)$$

The terms $\frac{r_{(t)}}{R}$ and $d(\frac{r_{(t)}}{R})/dt$ in Eq. (4) can be substituted by Eq. (1) and its first derivative. This results in Eq. (5):

$$k_1 = -\left.\frac{d(\frac{r_{(t)}}{R})/dt}{\frac{r_{(t)}}{R}}\right|_{t=0} = n * \frac{m\left(t+m^{\frac{1}{n}}\right)^{-n-1}}{m\left(t+m^{\frac{1}{n}}\right)^{-n}+\frac{r_{(\infty)}}{R}} \tag{6}$$

The term $\frac{r_{(\infty)}}{R}$ can be neglected at low t values. Equation (5) can be simplified when taking into account t = 0. This results in Eq. (6).

$$k_1 = \frac{n}{m^{\frac{1}{n}}} \tag{7}$$

Fardeau derived eq. 6 using a different approach, namely stochastic analysis of Eq. (1) (Fardeau, 1996). The two approaches lead to the same result; however, we believe our derivation is more transparent for agricultural and environmental scientists. The mean soil solution P turnover rate has been called both K_m and g_m (Fardeau et al., 1991;Oberson et al., 1993;Frossard et al., 2011). Following the more common term, k_1 will be called K_m in the rest of this text.

References

Fardeau, J.-c., Morel, C., and Boniface, R.: Phosphate ion transfer from soil to soil solution: kinetic parameters, Agronomie, 11, 787-797, 1991.
Fardeau, J. C.: Dynamics of phosphate in soils. An isotopic outlook, Fertilizer Research, 45, 91-100, 10.1007/bf00790658, 1996.
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Supplementary Tables

Table 1. Isotopic exchange kinetic (IEK) properties of soils used in the meta-analysis. Reported E-values were used for validation purposes only. For data analysis, E(t) was calculated using eq. (6). All but 35 IEK experiments were conducted on dried soil samples.

Variable	Description	min	quartile 1	median	mean	quartile 3	max	sample size
P_w	phosphate ions in soil solution [mg kg^{-1}]	0.008	0.310	1.03	3.31	3.40	42.5	217
n	IEK model parameter	0.01	0.214	0.313	0.309	0.400	0.669	217
m	IEK model parameter	0.002	0.130	0.360	0.386	0.600	1.29	217
P_{inorg}	total inorganic phosphate in soil [mg kg^{-1}]	13.3	160	351	534	533	13960	170
reported E_{1min}	isotopically exchangeable phosphate ions within 1 min [mg kg^{-1}]	0.12	1.10	2.80	9.19	10.5	121	93
reported E_{1day}	isotopically exchangeable phosphate ions within 1 day [mg kg^{-1}]	13	21.5	33.1	37.9	45.9	117	37

Supplementary Figures

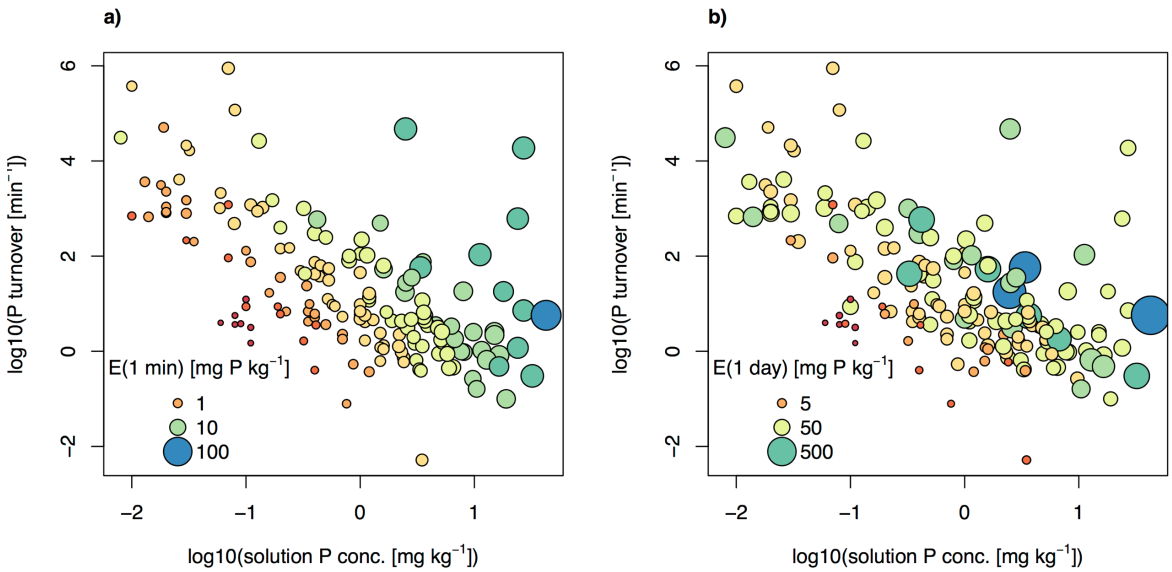

Figure 1. Soil solution P concentration (P_w) plotted vs. soil solution P turnover (K_m) for 170 soils. Isotopically exchangeable P (E(t)) at t = 1 min (a) and t = 1440 min (1 day) (b) is shown by point size and color.