



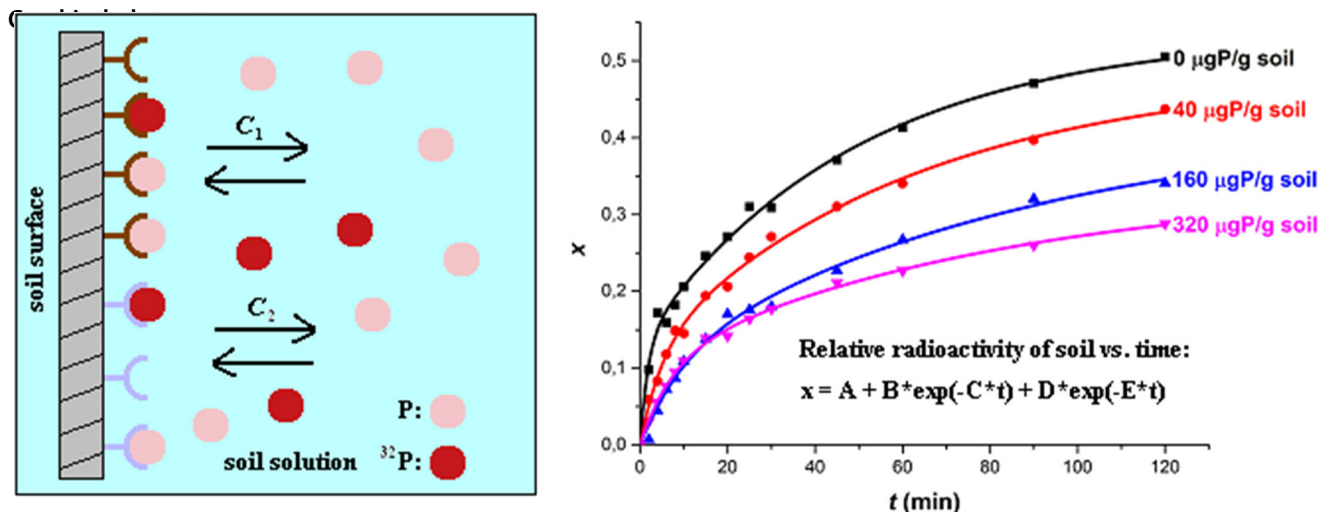
Study of phosphate sorption on rendzina soil by heterogeneous isotopic exchange: a biexponential kinetic model

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Abstract

Phosphate sorption on rendzina soil was studied by P-32 heterogeneous isotopic exchange under a steady-state. There are two types of sorbed phosphate, namely strongly and weakly bonded phosphate, the latter being able to exchange with phosphate ($\text{H}_2^{32}\text{PO}_4^-$) ions in the soil solution. The experimental kinetic data was not fitted by the one exponential kinetic model. Starting from this observation, a new kinetic model is established by assuming two types of weakly bonded phosphate, which take part in the two parallel exchange processes. A biexponential kinetic equation is obtained, which fits the experimental data much better than the one exponential equation.



Keywords Heterogeneous isotopic exchange · Biexponential kinetic model · Weakly bonded phosphate · Phosphate sorption on soil · Langmuir isotherm · Kinetic equation

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Introduction

Phosphorus is an essential nutrient for plants, which is taken up from the soil solution in the form of phosphate ions [1, 2]. Phosphate ions can be sorbed on a soil by different mechanisms, namely weakly and tightly sorbed phosphate [3, 4], the tightly sorbed phosphate being significant. Weakly sorbed phosphate can get back to the

Table 1 Kinetic equations for heterogeneous isotopic exchange (x is the dimensionless relative radioactivity of soil, t is time in min)

	Name	Formula	Parameters
Empiric equations	Series of exponential terms [5]	$x = A_0 - A_1 \cdot e^{-a_1 \cdot t} - \dots - A_n \cdot e^{-a_n \cdot t}$	$A_0, A_1, \dots, A_n, a_1, \dots, a_n$ empiric constants
	Edgington [5]	$1 - x = \left(\frac{t+\gamma}{\gamma}\right)^{-b}$	γ, b empiric constants
	Fardeau [1, 6]	$\frac{r}{r_0} = m \cdot \left(t + m^{\frac{1}{n}}\right)^{-n} + \frac{r_\infty}{r_0}$	r_0 : total radioactivity r : radioactivity in the solution at t time r_∞ : radioactivity in the solution at infinite time m, n : empiric constants
Compartmental models	Modified Elovich [7]	$\theta = \frac{1}{B} \cdot \ln\left(\frac{t+k}{k}\right) + \theta_0$	B, k : constants derived from rate constant and activation energy of sorption θ : fraction of equilibrated sites
	Kónya et al. [3]	$x = \frac{m_2}{m_1+m_2} \cdot \left[1 - e^{-\frac{m_1+m_2}{m_2} \cdot \frac{C}{m_1} \cdot t}\right]$	m_1 and m_2 : amounts of P in the soil solution and on the solid phase in μg C : steady-state rate in $\mu\text{g}/\text{min}$
Mechamistic models	Imre [8, 11]	$x = A_3 - A_1 \cdot e^{-a_1 \cdot t} - A_2 \cdot e^{-a_2 \cdot t}$	A_1, A_2, A_3, a_1 and a_2 : constants derived from the probabilities of transfer of radioactive species between the solution, the surface and the Paneth exchange layer
	Barrow [9]	$\Delta\theta = k_1^* \Delta t (1 - \theta) - k_2^* \Delta t \theta - \Delta M$	θ : fraction of exchanged sites M : amount of penetrated P k_1^* and k_2^* : rate constants dependent on surface potential

solution via desorption, so it is potentially available for plants, while tightly sorbed phosphate is hardly desorbed.

Weakly sorbed phosphate ions can be exchanged by phosphate ions in the soil solution, kinetic behavior can be examined by radioisotope (^{32}P) heterogeneous isotopic exchange [1]. In this process the phosphate ions sorbed on the solid phase exchange with the radiolabelled phosphate ions in the soil solution, the driving force is the increase of mixing entropy, while there is no change in enthalpy. The main advantage of this method is that kinetics can be examined even if there is steady-state for sorption and desorption. In this case the total amounts of phosphate ions in the soil solution and the solid phase do not change, but the amounts of radiolabelled phosphate in the soil solution is deminishing because of the exchange process, and the rate of heterogeneous isotopic exchange is proportional to the steady-state rate of sorption and desorption. Models and equations describing the kinetics of heterogeneous isotopic exchange (Table 1) can be classified into three main groups, including empiric equations (such as the series of exponential terms [5], the two constant equation by Edgington [5] and the empiric formula used by Fardeau et al. [1, 6]), compartmental models (including the modified Elovich equation by Atkinson et al. [7] and the one exponential model by Kónya et al. [3]) and mechanistic exchange models (for example the Paneth exchange and

recrystallization model by Imre [8] and the surface reaction-solid state diffusion model by Barrow et al. [9]).

The aim of this research is to establish a compartmental model for heterogeneous isotopic exchange on rendzina soil under a steady-state condition. Kinetic data has been applied at several phosphate concentrations.

Experimental

The studied soil was rendzina [Miskolc (Hungary), collected in 2019, clay and silt content: 28.36%, CaCO_3 content: 11.51%, humus content: 14.52%, $\text{pH} = 7.49$, conductivity = 695 $\mu\text{S}/\text{cm}$], the detailed description of experiments can be found elsewhere [3]. P was added to the soil samples in amounts of 0, 40, 80, 160 and 320 $\mu\text{gP}/\text{g}$ in the form of KH_2PO_4 solution, and they were incubated for 1 week, 3 weeks and 3 months at room temperature at 60% of maximum water holding capacity of soil (0 $\mu\text{gP}/\text{g}$ were the control samples, in those cases distilled water was added instead of KH_2PO_4 solution). Heterogeneous (^{32}P) isotopic exchange experiments were carried out at room temperature (25 °C) by using 1.288 g of soil sample (1 g air dried material) stirred with 210 cm^3 of distilled water for 60 min—during this time reaction mixture has reached steady-state. Then, 10 cm^3 sample was taken from the soil solution and analyzed for phosphorous concentration by

ammonium molybdate method by spectrophotometric technique [10]. 100 μl of carrier free $\text{H}_3^{32}\text{PO}_4$ radiotracer (carrier free means there it contains only ^{32}P , concentration of $^{32}\text{P} < 10^{-12}$ gP/experiment) was added to the remaining 200 cm^3 soil solution, and 1.8–1.8 cm^3 samples were taken after 2, 4, 6, 8, 10, 15, 20, 25, 30, 45, 60, 90 and 120 min. To 1–1 cm^3 -s of the samples 4–4 cm^3 of scintillation cocktail (composition see in [3]) was added, and radioactive intensities were measured by TriCarb 4810 TR Liquid Scintillation Analyser, radioactivity of ^{32}P is limited by the half-life. In order to determine the total radioactivity in the system a zero solution was also established, in which to 200 mL of distilled water 100 μL of carrier free $\text{H}_3^{32}\text{PO}_4$ radiotracer was added. 1 cm^3 of the zero solution was also taken (zero sample) and the radioactive intensities were determined as seen before.

Parameter evaluation according to the one exponential equation

First, relative radioactivities of soil were plotted versus time for each reaction mixture, and data points were fitted by the one exponential equation [3]:

$$x = A \cdot [1 - \exp(-B \cdot t)] \quad (1)$$

where x is the relative radioactivity of soil (which is dimensionless because it is the ratio of the radioactivity of the soil and the total radioactivity). x can be calculated as following: $x = 1 - \frac{I_1}{I_{\text{tot}}}$ where I_1 and I_{tot} are the intensities of the soil solution and the zero sample. $A = \frac{m_2}{m_1 + m_2}$ and $B = \frac{C}{m_1} \cdot \frac{m_1 + m_2}{m_2}$. C is the steady-state rate (in $\mu\text{g}/\text{min}$), m_1 and m_2 are the amounts of phosphorus in the soil solution and weakly sorbed on the solid phase (in μg). Fitted curves of soil samples incubated for 1 week, 3 weeks and 3 months can be seen in the Appendix in Figs. 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20.

As seen, all fitted curves show systematic deviation from experimental data points. In the middle period (in the range of 20–60 min) the experimental data are below, while at longer reaction times (over 60 min) they are above the fitted curves (Fig. 1). This reveals that more than one sites of weakly sorbed/isotopically exchangeable phosphate exist. There should be at least two different isotope exchange processes with different rates. At the initial period (up to 20 min) the faster exchange process is almost completed. According to this, a new kinetic model is established. Another compartmental model is the modified Elovich equation [7], but it's application for soil and other natural systems is not relevant, because these systems do not meet the boundary condition that the activation energy changes linearly with surface coverage.

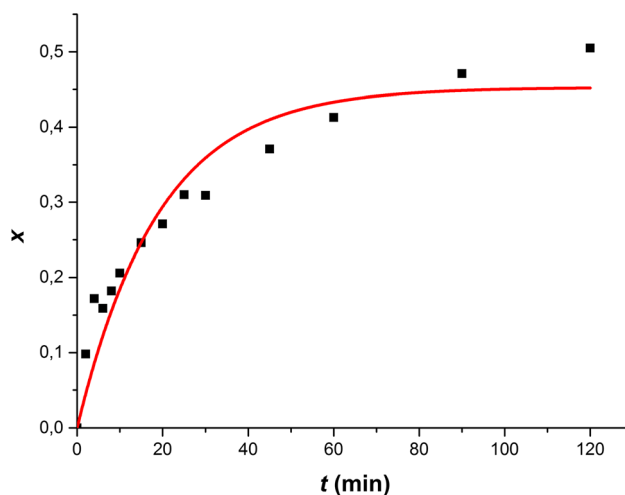


Fig. 1 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 0 $\mu\text{gP/g}$ for 1 week

Establishment of a biexponential kinetic model

The new kinetic model assumes two types of weakly sorbed phosphate, which take part in the following sorption and desorption processes:



where S_1 and S_2 are the bonding sites for the two different exchangeable phosphate compartments, and P is phosphate species (at soil solution pH it is mostly dihydrogen phosphate ion). It should be emphasised that there is no statement about the type of bonding sites or the mechanism of sorption and desorption—it can be either adsorption or ion exchange or even precipitation. The only assumption is that it must be a reversible process in order that steady-state can occur. That is why it can be said that the model is nonmechanistic.

In steady state, sorption and desorption rates are equal at both bonding sites:

$$\frac{dm_{P:L \rightarrow S_1}}{dt} = \frac{dm_{P:S_1 \rightarrow L}}{dt} = C_1 \quad (4)$$

$$\frac{dm_{P:L \rightarrow S_2}}{dt} = \frac{dm_{P:S_2 \rightarrow L}}{dt} = C_2 \quad (5)$$

where t is time (in minutes), and C_1 and C_2 are steady state rates for sorption and desorption at bonding sites S_1 and S_2 (in $\mu\text{g}/\text{min}$) and L means the soil solution. Let us be m_{2a} and m_{2b} the mass of phosphorus (in μg) sorbed at bonding sites S_1 and S_2 in steady state, m_1 the mass of phosphorus (in μg) in the soil solution and m_{2a}^* , m_{2b}^* and m_1^* are the masses of the radioactive forms (in μg). When

kinetic isotopic effect is negligible, radioactive phosphorus is exchanged in the same manner as inactive one. This means, at a given t time $\frac{m_{2a}^*}{m_{2a}} \cdot C_1$ is the desorption rate for radioactive phosphorus at bonding site S_1 . The same is valid for S_2 and for sorption rates, so the following differential equation system can be constructed:

$$\frac{dm_{2a}^*}{dt} = \frac{m_1^*}{m_1} \cdot C_1 - \frac{m_{2a}^*}{m_{2a}} \cdot C_1 \tag{6}$$

$$\frac{dm_{2b}^*}{dt} = \frac{m_1^*}{m_1} \cdot C_2 - \frac{m_{2b}^*}{m_{2b}} \cdot C_2 \tag{7}$$

After radiotracer has been added to reaction mixture, the system is closed for radioactive phosphorus, so Eq. (8) can be written:

$$m^* = m_1^* + m_{2a}^* + m_{2b}^* \tag{8}$$

where m^* is the total mass of radioactive phosphorus (in μg).

From Eqs. (6–8), the following differential equation system is obtained:

$$\frac{dm_{2a}^*}{dt} = -\left(\frac{C_1}{m_1} + \frac{C_1}{m_{2a}}\right) \cdot m_{2a}^* - \frac{C_1}{m_1} \cdot m_{2b}^* + \frac{C_1}{m_1} \cdot m^* \tag{9}$$

$$\frac{dm_{2b}^*}{dt} = -\frac{C_2}{m_1} \cdot m_{2a}^* - \left(\frac{C_2}{m_1} + \frac{C_2}{m_{2b}}\right) \cdot m_{2b}^* + \frac{C_2}{m_1} \cdot m^* \tag{10}$$

After arrangement of Eqs. (9) and (10), and parameters $A = \frac{C_1}{m_1}$, $B = \frac{C_1}{m_{2a}}$, $D = \frac{C_2}{m_1}$, $E = \frac{C_2}{m_{2b}}$ and functions $x_1 = \frac{m_{2a}^*}{m^*}$, $x_2 = \frac{m_{2b}^*}{m^*}$ are introduced, a linear differential equation system is obtained:

$$\begin{pmatrix} \frac{dx_1}{dt} \\ \frac{dx_2}{dt} \end{pmatrix} = \begin{bmatrix} -(A+B) & -A \\ -D & -(D+E) \end{bmatrix} \cdot \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + \begin{pmatrix} A \\ D \end{pmatrix} \tag{11}$$

At $t = 0 \rightarrow x_1, x_2 = 0$, the solution of the equation system is:

$$x_1 = \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot \exp\left[\frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t + K_2 \cdot \frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2}\right] \cdot \exp\left[\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t\right] \tag{12}$$

$$x_2 = \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot \exp\left[\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t + K_2 \cdot \frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2}\right] \cdot \exp\left[\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t\right] \tag{13}$$

The relative radioactivity of soil is the sum of relative radioactivities at bonding sites S_1 and S_2 (they are dimensionless):

$$x = x_1 + x_2 \tag{14}$$

So, the relative radioactivity of soil versus time according to the biexponential model is:

$$x = \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} + \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot \left(A + \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) \cdot \exp\left[\frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t + K_2 \cdot \left(D + \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) \right] \cdot \exp\left[\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t\right] \tag{15}$$

where,

$$K_1 = \frac{\frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{A \cdot E \cdot D}{A \cdot E + B \cdot D + B \cdot E}}{A \cdot D + \left(\frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right)^2}$$

and

$$K_2 = \frac{\frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{A \cdot B \cdot D}{A \cdot E + B \cdot D + B \cdot E}}{A \cdot D + \left(\frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right)^2}$$

Thus, when there are two compartments of weakly sorbed phosphate with two different steady-state rates, a biexponential kinetic equation is obtained. There are 4 independent fitting parameters namely A , B , D and E , which are derived from the 5 original parameters m_1 , m_{2a} , m_{2b} , C_1 and C_2 . A , B , D and E can be obtained from fitting, while m_1 is calculated from photometry. In the next session, the application of the new model will be discussed.

Table 2 Phosphate concentrations in the soil solution and fitting parameters of the biexponential kinetic equation

Incubation time	<i>P</i> added (μgP/g)	<i>c_P</i> /(mol/dm ³)	<i>A</i> /min ⁻¹	<i>σ(A)</i> /min ⁻¹	<i>B</i> /min ⁻¹	<i>σ(B)</i> /min ⁻¹	<i>D</i> /min ⁻¹	<i>σ(D)</i> /min ⁻¹	<i>E</i> /min ⁻¹	<i>σ(E)</i> /min ⁻¹
1 week	0	2.35•10 ⁻⁰⁶	0.0110	0.0010	0.0108	0.0018	0.0718	0.0169	0.4878	0.1467
	40	3.62•10 ⁻⁰⁶	0.0078	0.0011	0.0094	0.0023	0.0224	0.0030	0.1837	0.0509
	160	5.15•10 ⁻⁰⁶	0.0047	0.0021	0.0072	0.0057	0.0100	0.0018	0.0954	0.0512
	320	1.79•10 ⁻⁰⁵	0.0037	0.0007	0.0092	0.0028	0.0142	0.0009	0.1269	0.0218
3 weeks	0	4.22•10 ⁻⁰⁶	0.0094	0.0007	0.0086	0.0012	0.0241	0.0012	0.1451	0.0183
	40	4.55•10 ⁻⁰⁶	0.0105	0.0014	0.0868	0.0341	0.0058	0.0017	0.0061	0.0036
	80	2.26•10 ⁻⁰⁶	0.0053	0.0017	0.0058	0.0038	0.0105	0.0013	0.0782	0.0270
	160	8.09•10 ⁻⁰⁶	0.0053	0.0006	0.0129	0.0020	0.0185	0.0022	0.2288	0.0509
3 months	0	4.12•10 ⁻⁰⁶	0.0084	0.0019	0.0122	0.0043	0.0124	0.0026	0.1695	0.0957
	40	3.48•10 ⁻⁰⁶	0.0097	0.0015	0.0147	0.0029	0.0142	0.0050	0.2326	0.1572
	80	2.98•10 ⁻⁰⁶	0.0069	0.0010	0.0112	0.0023	0.0166	0.0014	0.1381	0.0300
	160	1.92•10 ⁻⁰⁵	0.0067	0.0014	0.0117	0.0029	0.0094	0.0012	0.1077	0.0410
	320	2.83•10 ⁻⁰⁵	0.0036	0.0007	0.0152	0.0034	0.0087	0.0020	0.2141	0.0992

Results and discussion

The phosphate concentrations in the soil solution determined by spectrophotometry, fitting parameters of the biexponential kinetic equation and their standard deviations and phosphate concentrations are summarized in Table 2. From the phosphate concentration in the soil solution (c_P in mol/dm³) m_1 (in μg) is calculated. The fitting parameters (which are all in min⁻¹) are the following: $A = \frac{C_1}{m_1}$, $B = \frac{C_1}{m_{2a}}$, $D = \frac{C_2}{m_1}$, $E = \frac{C_2}{m_{2b}}$, from here the steady state rates and masses of weakly sorbed phosphate at bonding sites S_1 and S_2 can be calculated as

$$C_1 = A \cdot m_1, m_{2a} = \frac{A}{B} \cdot m_1, C_2 = D \cdot m_1, m_{2b} = \frac{D}{E} \cdot m_1$$

and summarized in Table 3. The kinetic curves can be seen in Figs. 2, 3 and 4. The differences of relative radioactivities calculated from the fitted biexponential equation and measured values (d , which is also dimensionless) versus time are also plotted, which can be found in the Appendix (Figs. 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33). In Fig. 2 it is clearly seen that the order of kinetic curves from the top to the bottom is 0, 40, 160 and 320 μgP/g soil, which is in accordance with the fact that the more phosphate is in the system, the less is the ratio of the amount of weakly bonded phosphate to the amount of phosphate in the soil solution (saturation effect).

It can be seen (Fig. 5) that the new, biexponential kinetic equation obtained from the biexponential model fits much better experimental data, than the one exponential equation by Kónya et al. Data points fit well even in the middle period and at long times, where the one exponential model showed systematic deviation. The differences of

calculated and measured relative radioactivities (d) also have to be examined (Figs. 6, 22, 21, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33). As for the one exponential model, d versus time shows a maximum, which means, there is a systematic deviation. As for the biexponential model, d values scatter randomly around 0, and their values are smaller compared to one exponential fitting, which means biexponential equation obtained from the kinetic model assuming two types of weakly bonded phosphate describes appropriately the kinetics of heterogeneous isotopic exchange. The R^2 values further strengthen this assumption (Table 4). As for the biexponential model, R^2 values are all above 0.99, while in the case of one exponential model, they are between 0.95 and 0.99. This means that there are at least two different types of weakly sorbed phosphate on rendzina soil, which exchange at two different rates. However, it cannot be excluded that there are more than two types of weakly sorbed phosphate, but kinetically they can be separated only to two compartments.

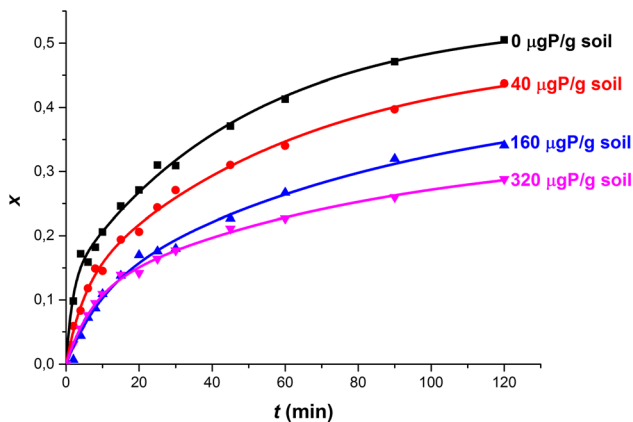
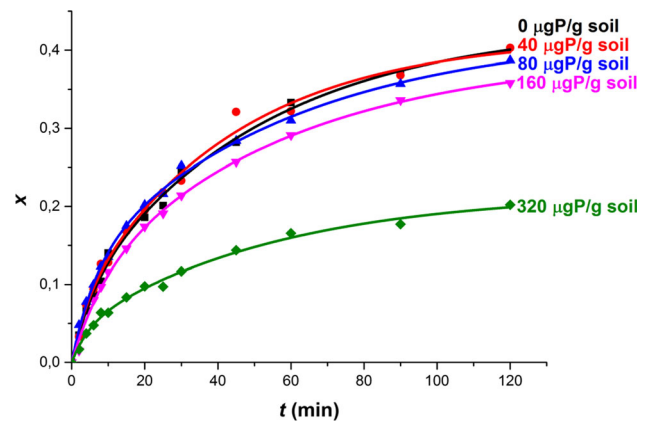
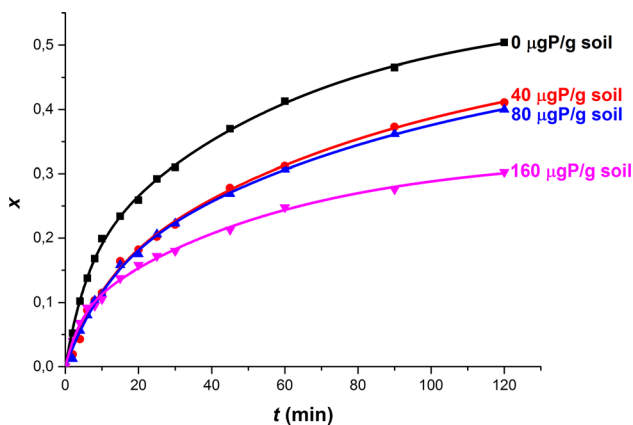
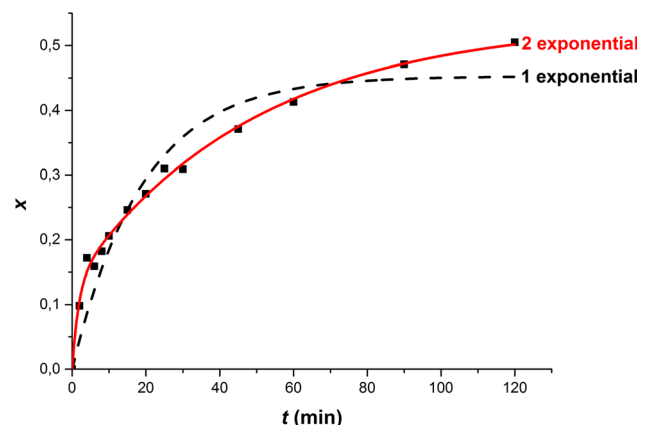
As for 1 week incubation time, the amounts of weakly sorbed phosphorus at the two different bonding sites (m_{2a} and m_{2b}) obtained from the new biexponential model have been plotted versus c_P (the concentration of phosphorus in the solution in μg/dm³) and fitted by Langmuir isotherm [Eq. (16), Fig. 7]. Fitting parameters can be found in Table 5.

$$a_P = \frac{K \cdot M \cdot c_P}{1 + K \cdot c_P} \quad (16)$$

where a_P is the amount of sorbed phosphorus on the soil surface sites S_1 and S_2 (in μgP/g), c_P is the concentration of phosphorus in the soil solution (in μg/dm³), M is the maximum value of sorbed phosphorus at bonding sites S_1

Table 3 Steady-state rates and masses of sorbed P at the two different bonding sites

Incubation time	P added ($\mu\text{gP/g}$)	$m_1/\mu\text{g}$	$m_{2a}/\mu\text{g}$	$m_{2b}/\mu\text{g}$	$C_1/(\mu\text{g}/\text{min})$	$C_2/(\mu\text{g}/\text{min})$
1 week	0	14.6	14.8	2.15	0.160	1.048
	40	22.4	18.5	2.73	0.174	0.502
	160	31.9	20.6	3.36	0.149	0.320
	320	111	44.5	12.4	0.408	1.571
3 weeks	0	26.2	28.7	4.34	0.247	0.630
	40	28.2	3.39	26.7	0.295	0.162
	80	14.0	12.7	1.88	0.074	0.147
	160	50.1	20.8	4.06	0.267	0.929
3 months	0	25.5	17.7	1.87	0.215	0.317
	40	21.6	14.2	1.32	0.208	0.307
	80	18.5	11.3	2.22	0.127	0.307
	160	119	67.6	10.4	0.793	1.117
	320	175	41.8	7.10	0.633	1.519

**Fig. 2** Biexponential kinetic curves of heterogeneous isotopic exchange on rendzina soil samples (1 week incubation time)**Fig. 4** Biexponential kinetic curves of heterogeneous isotopic exchange on rendzina soil samples (3 months incubation time)**Fig. 3** Biexponential kinetic curves of heterogeneous isotopic exchange on rendzina soil samples (3 weeks incubation time)**Fig. 5** Comparing the one exponential and the biexponential model ($0 \mu\text{gP/g}$ 1 week)

and S_2 (in $\mu\text{gP/g}$) and K is the sorption constant for bonding sites S_1 and S_2 (in $\text{dm}^3/\mu\text{g}$). In the case of 3 weeks and 3 months incubation time, m_{2a} and m_{2b} versus C_P cannot be fitted by the Langmuir or any other isotherm—

data points scatter on a very large scale. The reason for this can be that some secondary processes might occur. This can also explain the contradictory fact that the phosphate

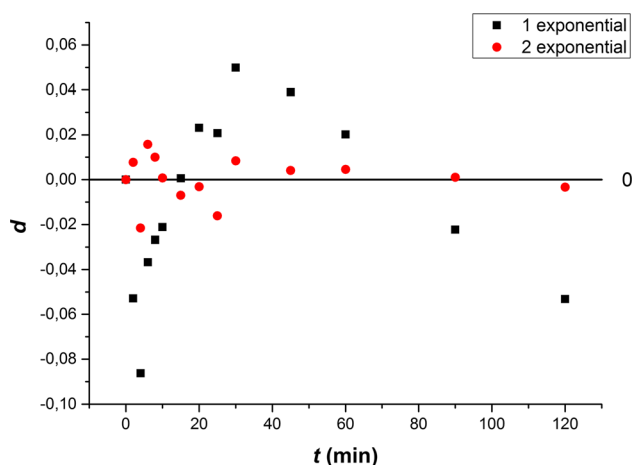


Fig. 6 Differences (d) of calculated and measured relative radioactivities (x) versus time (1 week incubation, 0 $\mu\text{gP/g}$)

Table 4 R^2 values for the 1 and 2 exponential equation fitting

Incubation time	P added ($\mu\text{gP/g}$)	R^2 (1 exponential)	R^2 (2 exponential)
1 week	0	0.9125	0.9936
	40	0.9631	0.9958
	160	0.9785	0.9917
	320	0.9677	0.9977
3 weeks	0	0.9698	0.9991
	40	0.9853	0.9966
	80	0.9865	0.9973
	160	0.9585	0.9971
3 months	0	0.9828	0.9944
	40	0.9814	0.9926
	80	0.9758	0.9978
	160	0.9889	0.9977
	320	0.9728	0.9932

concentration in the soil solution is smaller at 80 $\mu\text{gP/g}$ than at 0 or 40 $\mu\text{gP/g}$ incubation (Table 2, lines 6–8).

Conclusions

It is clearly seen that heterogeneous isotopic exchange on rendzina soil can be described by the biexponential kinetic equation obtained from a new model, which assumes two types of exchangeable phosphate. There were such biexponential kinetic equations before too, however, they were only empirical ones [5, 8]. The only exception we know about is the biexponential model by Imre [11] established for the heterogeneous isotopic exchange of lead and actinium ions sorbed on barium sulphate, but the meaning of the parameters was different, and it contained also some

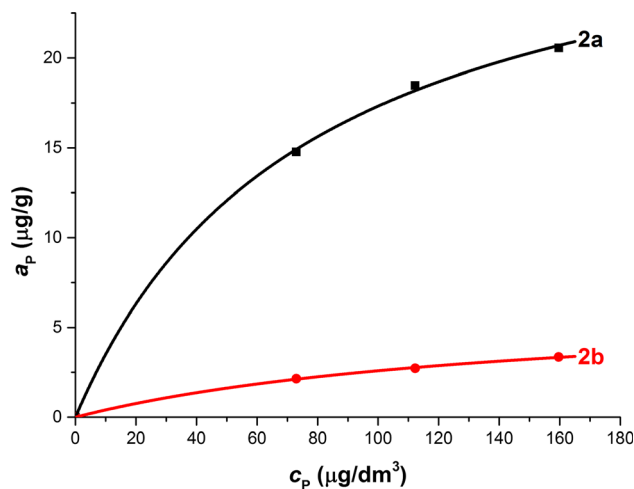


Fig. 7 Langmuir plots for soil samples incubated for 1 week (amounts of phosphorus at surface sites 2a and 2b calculated from the biexponential model)

mechanistic considerations. There is also a biexponential model by Darbee et al. similar to ours, but it was established for homogeneous isotopic exchange [12]. Earlier Kosmulski et al. already proved, that if there are several parallel exchange processes, the kinetics of heterogeneous isotopic exchange can be described by a series of exponential terms [13]. The novelty of the biexponential equation derived in the present work is that it is obtained from a kinetic model, so the parameters have physical meaning, and can be related to the two exchange processes, however, there is no assumption about the details of the mechanism of sorption and desorption, so it can be used universally. From the fitting parameters the amounts of weakly sorbed phosphorus at the two different bonding sites can be determined, and sorption isotherms can be obtained.

Normally the concentration of phosphate ions in the soil solution increases with the amount of the added phosphate during the incubation period (0, 40, 80, 160 and 320 $\mu\text{gP/g}$ soil), and the kinetic curves follow from the top to the bottom in that order—as it can be observed for 1 week incubation time (Fig. 2). When this is the case, the Langmuir isotherm can be applied (Fig. 7). However, there are cases, when the concentration of phosphate ions in the soil solution does not correlate with the amount of added phosphorus during incubation (3 weeks and 3 months incubation time, Figs. 3 and 4), in these cases the order of kinetic curves is also not unambiguous, and the Langmuir isotherm cannot be applied. The reasons for this phenomenon might be some secondary processes. It can happen, for example, that at higher amounts of added phosphorus precipitation takes places, which diminishes the amount of phosphate in the soil solution. To clear up these secondary processes, further research is demanded.

Table 5 Langmuir parameters at the two different surface sites for 1 week incubation time

Incubation time	Bonding site	K (dm ³ /μg)	σK (dm ³ /μg)	M (μg/g)	σM (μg/g)	R^2
1 week	2a	0.0130	0.0014	30.69	1.34	0.9993
	2b	0.00672	0.00072	6.45	0.38	0.9994

The new model makes possible to understand better the sorption and desorption of phosphate on soil, which is important to improve fertilizing strategies in agriculture. From the kinetic parameters of the heterogeneous isotopic exchange on soil it becomes possible to identify which components of the soil are responsible for weak phosphate bonding, and strategies can be established to prevent the transformation of phosphate to unavailable forms.

Appendix 1

See Table 6.

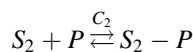
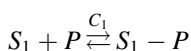
Table 6 List of physical quantities and their units

Sign	Name	Unit
C_1	Steady state rate at bonding site 2a	μg/min
C_2	Steady state rate at bonding site 2b	μg/min
m_1	Amount of phosphorus in the soil solution	μg
m_{2a}	Amount of weakly bonded phosphorus at bonding site 2a	μg
m_{2b}	Amount of weakly bonded phosphorus at bonding site 2b	μg
m^*	Total amount of radioactive phosphorus in the system	μg
m_1^*	Amount of radioactive phosphorus in the soil solution	μg
m_{2a}^*	Amount of radioactive phosphorus at bonding site 2a	μg
m_{2b}^*	Amount of radioactive phosphorus at bonding site 2b	μg
A, B, D, E	Fitting parameters of the biexponential kinetic equation	1/min
x	Relative radioactivity of the soil	1
t	Time	min
c_P	Concentration of phosphorus in the soil solution	μg/dm ³
a_P	Concentration of weakly bonded phosphorus at bonding site 2a or 2b (they are plotted on the same figure)	μg/g
K	Langmuir constant for bonding site 2a or 2b	dm ³ /μg
M	Maximum sorbed concentration of phosphorus at bonding site 2a or 2b	μg/g

Appendix 2

Complete mathematical deduction of biexponential kinetic model

Sorption–desorption processes at the two types of bonding sites:



Let us be m_{2a} and m_{2b} the mass of phosphorus sorbed at bonding sites S_1 and S_2 in steady state, and m_1 the mass of phosphorus in the soil solution, which is in equilibrium with the solid state. In steady state, sorption and desorption rates are equal at both bonding sites, so the following equations can be written:

$$\frac{dm_{P,L \rightarrow S_1}}{dt} = \frac{dm_{P,S_1 \rightarrow L}}{dt} = C_1 \quad (17)$$

$$\frac{dm_{P,L \rightarrow S_2}}{dt} = \frac{dm_{P,S_2 \rightarrow L}}{dt} = C_2 \quad (18)$$

where t is time, and C_1 and C_2 are steady state rates for sorption and desorption at bonding sites S_1 and S_2 , and

L means the liquid phase. Adding radioactive $H_3^{32}PO_4$ to the liquid phase, it will get into three forms:

m_{2a}^* , m_{2b}^* and m_1^* are the masses of radioactive phosphorus at a given t time at bonding sites S_1 , S_2 and in the liquid phase (soil solution), and m^* is the total amount of radioactive phosphorus added to the solution. The mass balance is valid for them:

$$m^* = m_1^* + m_{2a}^* + m_{2b}^* \quad (19)$$

At a given t time, $\frac{m_1^*}{m_1}$, $\frac{m_{2a}^*}{m_{2a}}$ and $\frac{m_{2b}^*}{m_{2b}}$ are the proportions of radioactive phosphorus at bonding sites S_1 , S_2 and in the liquid phase. Radioactive phosphorus goes to bonding sites S_1 and S_2 via sorption, and leaves the bonding sites via desorption, so the following differential equation system can be written:

$$\frac{dm_{2a}^*}{dt} = \frac{m_1^*}{m_1} \cdot C_1 - \frac{m_{2a}^*}{m_{2a}} \cdot C_1 \quad (20)$$

$$\frac{dm_{2b}^*}{dt} = \frac{m_1^*}{m_1} \cdot C_2 - \frac{m_{2b}^*}{m_{2b}} \cdot C_2 \quad (21)$$

m_1^* can be obtained from (19) as following:

$$m_1^* = m^* - m_{2a}^* - m_{2b}^* \quad (22)$$

So Eqs. (20) and (21) get the forms:

$$\frac{dm_{2a}^*}{dt} = \frac{m^* - m_{2a}^* - m_{2b}^*}{m_1} \cdot C_1 - \frac{m_{2a}^*}{m_{2a}} \cdot C_1 \quad (23)$$

$$\frac{dm_{2b}^*}{dt} = \frac{m^* - m_{2a}^* - m_{2b}^*}{m_1} \cdot C_2 - \frac{m_{2b}^*}{m_{2b}} \cdot C_2 \quad (24)$$

From (23) and (24) the following expressions can be obtained:

$$\frac{dm_{2a}^*}{dt} = \frac{m^*}{m_1} \cdot C_1 - \frac{m_{2a}^*}{m_1} \cdot C_1 - \frac{m_{2b}^*}{m_1} \cdot C_1 - \frac{m_{2a}^*}{m_{2a}} \cdot C_1 \quad (25)$$

$$\frac{dm_{2b}^*}{dt} = \frac{m^*}{m_1} \cdot C_2 - \frac{m_{2a}^*}{m_1} \cdot C_2 - \frac{m_{2b}^*}{m_1} \cdot C_2 - \frac{m_{2b}^*}{m_{2b}} \cdot C_2 \quad (26)$$

After rearrangement:

$$\frac{dm_{2a}^*}{dt} = \frac{C_1}{m_1} \cdot m^* - \frac{C_1}{m_1} \cdot m_{2a}^* - \frac{C_1}{m_1} \cdot m_{2b}^* - \frac{C_1}{m_{2a}} \cdot m_{2a}^* \quad (27)$$

$$\frac{dm_{2b}^*}{dt} = \frac{C_2}{m_1} \cdot m^* - \frac{C_2}{m_1} \cdot m_{2a}^* - \frac{C_2}{m_1} \cdot m_{2b}^* - \frac{C_2}{m_{2b}} \cdot m_{2b}^* \quad (28)$$

Via reduction of (27) and (28) the following expressions are obtained:

$$\frac{dm_{2a}^*}{dt} = -\left(\frac{C_1}{m_1} + \frac{C_1}{m_{2a}}\right) \cdot m_{2a}^* - \frac{C_1}{m_1} \cdot m_{2b}^* + \frac{C_1}{m_1} \cdot m^* \quad (29)$$

$$\frac{dm_{2b}^*}{dt} = -\frac{C_2}{m_1} \cdot m_{2a}^* - \left(\frac{C_2}{m_1} + \frac{C_2}{m_{2b}}\right) \cdot m_{2b}^* + \frac{C_2}{m_1} \cdot m^* \quad (30)$$

After division by m^* :

$$\frac{1}{m^*} \cdot \frac{dm_{2a}^*}{dt} = -\left(\frac{C_1}{m_1} + \frac{C_1}{m_{2a}}\right) \cdot \frac{m_{2a}^*}{m^*} - \frac{C_1}{m_1} \cdot \frac{m_{2b}^*}{m^*} + \frac{C_1}{m_1} \quad (31)$$

$$\frac{1}{m^*} \cdot \frac{dm_{2b}^*}{dt} = -\frac{C_2}{m_1} \cdot \frac{m_{2a}^*}{m^*} - \left(\frac{C_2}{m_1} + \frac{C_2}{m_{2b}}\right) \cdot \frac{m_{2b}^*}{m^*} + \frac{C_2}{m_1} \quad (32)$$

$\frac{1}{m^*}$ is constant, so it can be taken in the derivatives:

$$\frac{d \frac{m_{2a}^*}{m^*}}{dt} = -\left(\frac{C_1}{m_1} + \frac{C_1}{m_{2a}}\right) \cdot \frac{m_{2a}^*}{m^*} - \frac{C_1}{m_1} \cdot \frac{m_{2b}^*}{m^*} + \frac{C_1}{m_1} \quad (33)$$

$$\frac{d \frac{m_{2b}^*}{m^*}}{dt} = -\frac{C_2}{m_1} \cdot \frac{m_{2a}^*}{m^*} - \left(\frac{C_2}{m_1} + \frac{C_2}{m_{2b}}\right) \cdot \frac{m_{2b}^*}{m^*} + \frac{C_2}{m_1} \quad (34)$$

$x_1 = \frac{m_{2a}^*}{m^*}$ and $x_2 = \frac{m_{2b}^*}{m^*}$ are the relative radioactivities of phosphorus sorbed at sites S_1 and S_2 , in such way the following equations can be obtained:

$$\frac{dx_1}{dt} = -\left(\frac{C_1}{m_1} + \frac{C_1}{m_{2a}}\right) \cdot x_1 - \frac{C_1}{m_1} \cdot x_2 + \frac{C_1}{m_1} \quad (35)$$

$$\frac{dx_2}{dt} = -\frac{C_2}{m_1} \cdot x_1 - \left(\frac{C_2}{m_1} + \frac{C_2}{m_{2b}}\right) \cdot x_2 + \frac{C_2}{m_1} \quad (36)$$

The following notation can be introduced:

$$A = \frac{C_1}{m_1}; B = \frac{C_1}{m_{2a}}; D = \frac{C_2}{m_1}; E = \frac{C_2}{m_{2b}} \quad (37)$$

With these notations the equation system can be written in the following form:

$$\frac{dx_1}{dt} = -(A + B) \cdot x_1 - A \cdot x_2 + A \quad (38)$$

$$\frac{dx_2}{dt} = -D \cdot x_1 - (D + E) \cdot x_2 + D \quad (39)$$

It can be also rewritten in matrix representation:

$$\begin{pmatrix} \frac{dx_1}{dt} \\ \frac{dx_2}{dt} \end{pmatrix} = \begin{bmatrix} -(A + B) & -A \\ -D & -(D + E) \end{bmatrix} \cdot \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} + \begin{pmatrix} A \\ D \end{pmatrix} \quad (40)$$

First, the eigenvalues of coefficient matrix should be determined:

$$\begin{vmatrix} -(A + B) - \lambda & -A \\ -D & -(D + E) - \lambda \end{vmatrix} = [-(A + B) - \lambda] \cdot [-(D + E) - \lambda] - (-A) \cdot (-D) = 0 \quad (41)$$

$$\begin{aligned} (A + B) \cdot (D + E) + (A + B) \cdot \lambda + (D + E) \cdot \lambda + \lambda^2 - A \cdot D \\ = 0 \end{aligned} \quad (42)$$

$$\begin{aligned} \lambda^2 + A \cdot D + A \cdot E + B \cdot D + B \cdot E + (A + B) \cdot \lambda \\ + (D + E) \cdot \lambda - A \cdot D \\ = 0 \end{aligned} \quad (43)$$

$$\lambda^2 + (A + B + D + E) \cdot \lambda + (A \cdot E + B \cdot D + B \cdot E) = 0 \quad (44)$$

Using the solving formula for quadratic equations:

$$\lambda_1 = \frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \quad (45)$$

$$\lambda_2 = \frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \quad (46)$$

The \underline{u} eigenvector can be found as following:

$$\begin{bmatrix} -(A+B) - \lambda_1 & -A \\ -D & -(D+E) - \lambda_1 \end{bmatrix} \cdot \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad (47)$$

That means:

$$[-(A+B) - \lambda_1] \cdot u_1 - A \cdot u_2 = 0 \quad (48)$$

$$-D \cdot u_1 + [-(D+E) - \lambda_1] \cdot u_2 = 0 \quad (49)$$

$$\begin{aligned} -(A+B) - \lambda_1 &= \frac{-(A+B) \cdot 2}{2} \\ &= \frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{-2 \cdot A - 2 \cdot B + A + B + D + E - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{-(A+B) + (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \end{aligned} \quad (50)$$

$$\begin{aligned} -(D+E) - \lambda_1 &= \frac{-(D+E) \cdot 2}{2} \\ &= \frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{-2 \cdot D - 2 \cdot E + A + B + D + E - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \end{aligned} \quad (51)$$

From (48)–(51) Eqs. (52) and (53) can be derived:

$$\frac{-(A+B) + (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot u_1 - A \cdot u_2 = 0 \quad (52)$$

$$-D \cdot u_1 + \frac{(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot u_2 = 0 \quad (53)$$

From (52) u_2 can be expressed:

$$u_2 = \frac{-(A+B) + (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2 \cdot A} \cdot u_1 \quad (54)$$

So one possible \underline{u} eigenvector is:

$$\underline{u} = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix} = \begin{pmatrix} A \\ \frac{-(A+B) + (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \end{pmatrix} \quad (55)$$

Simillary, for \underline{v} eigenvector:

$$\begin{bmatrix} -(A+B) - \lambda_2 & -A \\ -D & -(D+E) - \lambda_2 \end{bmatrix} \cdot \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \quad (56)$$

From this Eqs. 57 and 58 can be obtained:

$$[-(A+B) - \lambda_2] \cdot v_1 - A \cdot v_2 = 0 \quad (57)$$

$$-D \cdot v_1 + [-(D+E) - \lambda_2] \cdot v_2 = 0 \quad (58)$$

$$\begin{aligned} -(A+B) - \lambda_2 &= \frac{-(A+B) \cdot 2}{2} \\ &= \frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{-2 \cdot A - 2 \cdot B + A + B + D + E + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{-(A+B) + D + E + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \end{aligned} \quad (59)$$

$$\begin{aligned} -(D+E) - \lambda_2 &= \frac{-(D+E) \cdot 2}{2} \\ &= \frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{-2 \cdot D - 2 \cdot E + A + B + D + E + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \\ &= \frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \end{aligned} \quad (60)$$

From (57)–(60) Eqs. (61) and (62) can be derived:

$$\frac{-(A+B) + D + E + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot v_1 - A \cdot v_2 = 0 \quad (61)$$

$$-D \cdot v_1 + \frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot v_2 = 0 \quad (62)$$

From (62) v_1 can be expressed:

$$v_1 = \frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2 \cdot D} \cdot v_2 \quad (63)$$

So one possible \underline{v} eigenvector is:

$$\underline{v} = \begin{pmatrix} v_1 \\ v_2 \end{pmatrix} = \begin{pmatrix} \frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{D} \\ 1 \end{pmatrix} \quad (64)$$

The general solution of a homogenous linear differential equation system is:

$$\underline{x}_H = K_1 \cdot \underline{u} \cdot \exp(\lambda_1 \cdot t) + K_2 \cdot \underline{v} \cdot \exp(\lambda_2 \cdot t) \quad (65)$$

So the homogenous solution of our system is:

$$\begin{pmatrix} x_{1H} \\ x_{2H} \end{pmatrix} = K_1 \cdot \left(\frac{A}{-(A+B)+(D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}} \right) \cdot \exp^{\frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t} + K_2 \cdot \left(\frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2D} \right) \cdot \exp^{\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t} \tag{66}$$

In order to get the solution of the inhomogenous system, the proof function method is used. It can be supposed, that there is a particular solution of the inhomogenous system in the following form:

$$\begin{pmatrix} x_1 \\ x_2 \end{pmatrix} = \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} \tag{67}$$

where P_1 and P_2 are constant. So, the differential equation system can be written:

$$\begin{pmatrix} \frac{dP_1}{dt} \\ \frac{dP_2}{dt} \end{pmatrix} = \begin{bmatrix} -(A+B) & -A \\ -D & -(D+E) \end{bmatrix} \cdot \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} + \begin{pmatrix} A \\ D \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{68}$$

Therefore:

$$-(A+B) \cdot P_1 - A \cdot P_2 + A = 0 \tag{69}$$

$$-D \cdot P_1 - (D+E) \cdot P_2 + D = 0 \tag{70}$$

P_2 can be expressed from (69):

$$P_2 = \frac{A - (A+B) \cdot P_1}{A} \tag{71}$$

Then it can be substituted for P_2 in (70):

$$-D \cdot P_1 - (D+E) \cdot \frac{A - (A+B) \cdot P_1}{A} + D = 0 \tag{72}$$

$$\frac{-D \cdot A \cdot P_1}{A} - \frac{(D+E) \cdot [A - (A+B) \cdot P_1]}{A} + \frac{A \cdot D}{A} = 0 \tag{73}$$

$$\frac{-D \cdot A \cdot P_1 - (D+E) \cdot [A - (A+B) \cdot P_1] + A \cdot D}{A} = 0 \tag{74}$$

$$\frac{-D \cdot A \cdot P_1 - (D+E) \cdot A + (D+E) \cdot (A+B) \cdot P_1 + A \cdot D}{A} = 0 \tag{75}$$

$$\frac{-D \cdot A \cdot P_1 - A \cdot D - A \cdot E + D \cdot A \cdot P_1 + D \cdot B \cdot P_1 + E \cdot A \cdot P_1 + E \cdot B \cdot P_1 + A \cdot D}{A} = 0 \tag{76}$$

$$-A \cdot E + D \cdot B \cdot P_1 + E \cdot A \cdot P_1 + E \cdot B \cdot P_1 = 0 \tag{77}$$

$$(A \cdot E + B \cdot D + B \cdot E) \cdot P_1 = A \cdot E \tag{78}$$

$$P_1 = \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \tag{79}$$

Then P_2 can be obtained from (71):

$$\begin{aligned} P_2 &= \frac{A - (A+B) \cdot \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E}}{A} \\ &= 1 - \frac{(A+B) \cdot E}{A \cdot E + B \cdot D + B \cdot E} \\ &= \frac{A \cdot E + B \cdot D + B \cdot E - A \cdot E - B \cdot E}{A \cdot E + B \cdot D + B \cdot E} \\ &= \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \end{aligned} \tag{80}$$

So the particular solution of the system is:

$$\underline{x}_p = \begin{pmatrix} P_1 \\ P_2 \end{pmatrix} = \begin{pmatrix} \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \\ \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \end{pmatrix} \tag{81}$$

After that the general solution of a linear system is:

$$\underline{x} = \underline{x}_p + \underline{x}_H \tag{82}$$

So the general solution of the system can be written as:

$$\begin{aligned} \underline{x} &= \begin{pmatrix} \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \\ \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \end{pmatrix} + K_1 \cdot \left(\frac{A}{-(A+B)+(D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}} \right) \cdot \exp^{\frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t} \\ &\quad + K_2 \cdot \left(\frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2D} \right) \cdot \exp^{\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t} \end{aligned} \tag{83}$$

Boundary condition is: $t = 0 \leftrightarrow x_1, x_2 = 0$, in consequence:

$$0 = \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot A + K_2 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \tag{84}$$

$$0 = \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot \frac{-[(A+B) - (D+E)]}{-\sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}} + K_2 \cdot D \tag{85}$$

$$0 = \frac{A \cdot E \cdot D}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot \frac{A \cdot D + K_2 \cdot D \cdot [(A+B) - (D+E)]}{\sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}} \quad (86)$$

$$0 = \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_2 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \quad (87)$$

Subtracting (87) from (86) (88) is got:

$$\frac{A \cdot E \cdot D}{A \cdot E + B \cdot D + B \cdot E} - \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_2 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} = 0 \quad (88)$$

$$\frac{A \cdot E \cdot D}{A \cdot E + B \cdot D + B \cdot E} - \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_2 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} = 0 \quad (89)$$

$$\frac{A \cdot E \cdot D}{A \cdot E + B \cdot D + B \cdot E} - \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_2 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} = 0 \quad (90)$$

From (90) K_1 can be expressed:

$$K_1 = \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{A \cdot E \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \quad (91)$$

Determination of K_2 :

$$0 = \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_1 \cdot A \cdot \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_2 \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{[(A+B) - (D+E)] - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \quad (92)$$

$$0 = \frac{A \cdot B \cdot D}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot A \cdot \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} + K_2 \cdot A \cdot D \quad (93)$$

Subtracting (93) from (92):

$$0 = \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{A \cdot B \cdot D}{A \cdot E + B \cdot D + B \cdot E} - K_2 \cdot \left(\frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right)^2 - K_2 \cdot A \cdot D \quad (94)$$

From (94) K_2 can be expressed:

$$K_2 = \frac{\frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{A \cdot B \cdot D}{A \cdot E + B \cdot D + B \cdot E}}{A \cdot D + \left(\frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right)^2} \quad (95)$$

The total relative radioactivity of the solid phase (x) can be obtained as the sum of relative radioactivities at the two sorption sites:

$$x = x_1 + x_2 \quad (96)$$

$$x_1 = \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot \frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot \exp \left(\frac{(A+B) - (D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) - \frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot \exp \left(\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) \cdot t \quad (97)$$

$$x_2 = \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} + K_1 \cdot \frac{-(A+B) + (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot \exp \left(\frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) + K_2 \cdot D \cdot \exp \left(\frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) \cdot t \quad (98)$$

From (96), (97) and (98) the kinetic equation of heterogenous isotopic exchange is obtained:

$$\begin{aligned}
 x = & \frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} + \frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \\
 & + K_1 \cdot \left(A + \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) \cdot \exp \\
 & \frac{-(A+B+D+E) + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t + K_2 \cdot \\
 & \left(D + \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right) \cdot \exp \\
 & \frac{-(A+B+D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \cdot t
 \end{aligned} \tag{99}$$

where,

$$K_1 = \frac{\frac{B \cdot D}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{A \cdot E \cdot D}{A \cdot E + B \cdot D + B \cdot E}}{A \cdot D + \left(\frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right)^2}$$

and

$$K_2 = \frac{\frac{A \cdot E}{A \cdot E + B \cdot D + B \cdot E} \cdot \frac{-(A+B) - (D+E) - \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} - \frac{A \cdot B \cdot D}{A \cdot E + B \cdot D + B \cdot E}}{A \cdot D + \left(\frac{[(A+B) - (D+E)] + \sqrt{(A+B+D+E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2} \right)^2}$$

It can be proved, that expression under squer root $(A + B + D + E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)$ is always positive:

$$\begin{aligned}
 (A + B + D + E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E) &= A^2 + B^2 + D^2 + E^2 + 2AB + 2AD + 2AE + 2BD \\
 &+ 2BE + 2DE - 4AE - 4BD - 4BE \\
 &= A^2 + B^2 + D^2 + E^2 + 2AB + 2AD - 2AE - 2BD \\
 &- 2BE + 2DE
 \end{aligned} \tag{100}$$

$$\begin{aligned}
 (-A - B + D + E)^2 &= A^2 + B^2 + D^2 + E^2 + 2AB - 2AD \\
 &- 2AE - 2BD - 2BE + 2DE
 \end{aligned} \tag{101}$$

Comparing (100) and (101) the following expression is obtained:

$$\begin{aligned}
 (A + B + D + E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E) &= (-A - B + D + E)^2 + 4AD > 0
 \end{aligned} \tag{102}$$

It is always positive because A and D are positive quantities—therefore, expression under squer root is always positive, so exponent is always a real number. As a consequence, (98) is a biexponential kinetic equation. It can also be shown that exponents are negative real numbers:

$$\frac{-(A + B + D + E) - \sqrt{(A + B + D + E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2}$$

is negative because A, B, D and E are positive and square root is also positive. As for

$$\frac{-(A + B + D + E) + \sqrt{(A + B + D + E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2}$$

$$\begin{aligned}
 \sqrt{(A + B + D + E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)} &< \sqrt{(A + B + D + E)^2} \\
 &= (A + B + D + E)
 \end{aligned}$$

, consequently,

$$\frac{-(A + B + D + E) + \sqrt{(A + B + D + E)^2 - 4 \cdot (A \cdot E + B \cdot D + B \cdot E)}}{2}$$

is always negative, too. So both exponential members have negative exponents, as a result, they are deminishing with time. As a consequence, relative radioactivity of soil shows a saturating tendency with time.

Appendix 3

See Figs. 8,9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33.

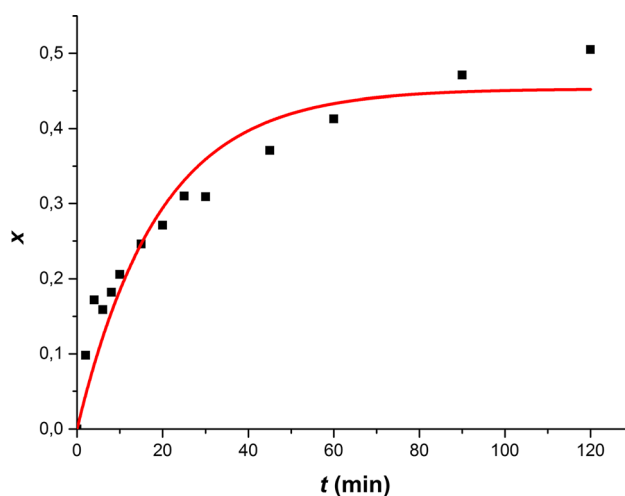


Fig. 8 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 0 µgP/g for 1 week

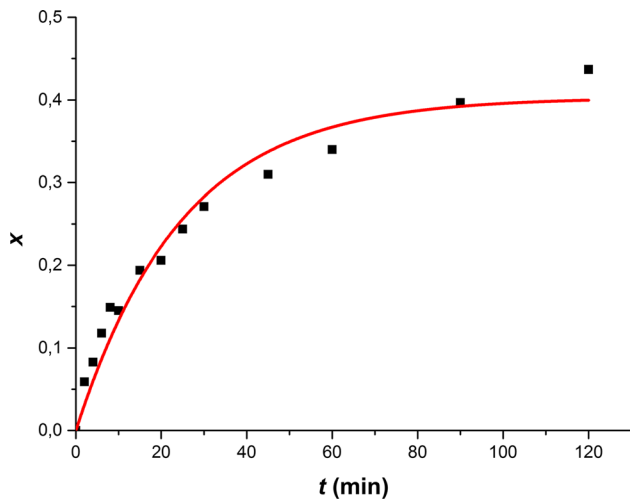


Fig. 9 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 40 µgP/g for 1 week

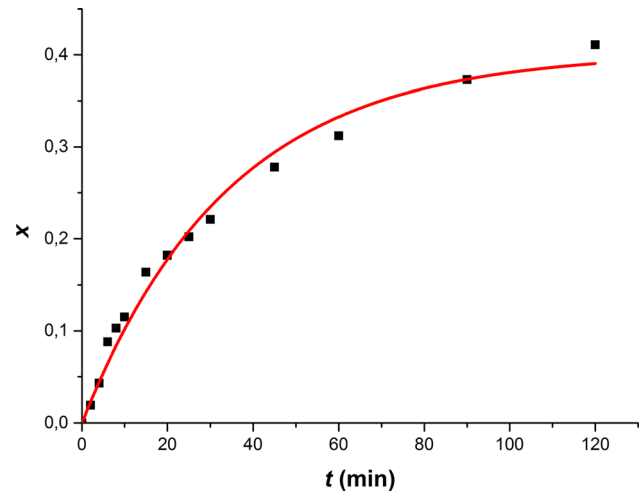


Fig. 13 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 40 µgP/g for 3 weeks

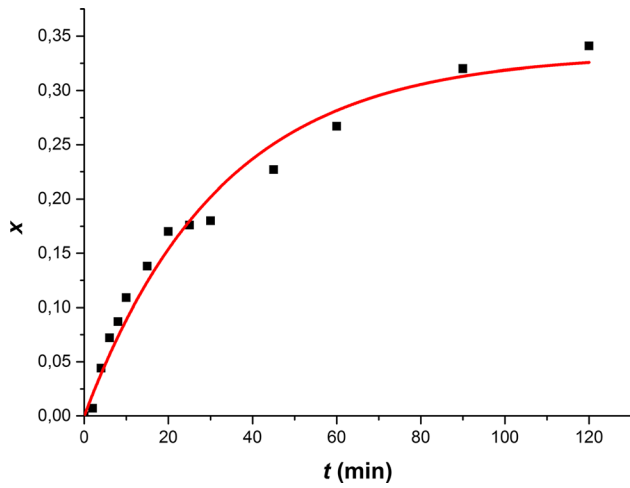


Fig. 10 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 160 µgP/g for 1 week

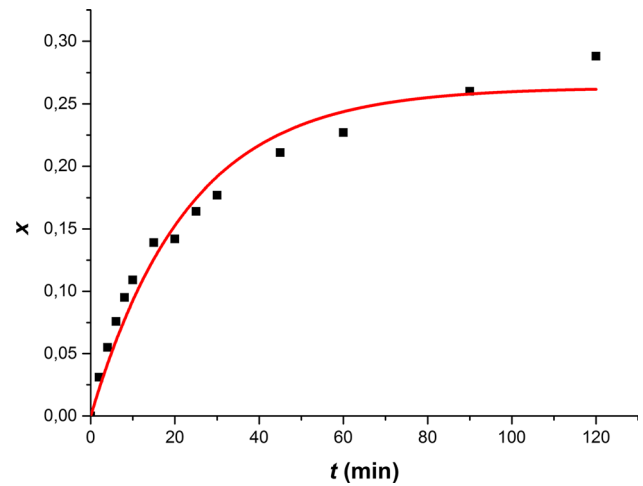


Fig. 11 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 320 µgP/g for 1 week

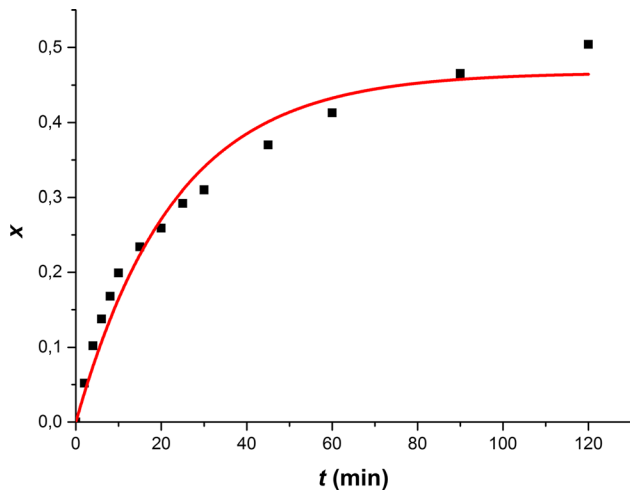


Fig. 12 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 0 µgP/g for 3 weeks

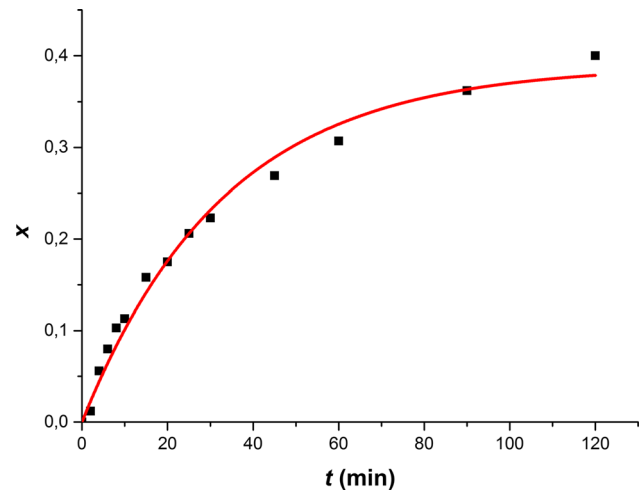


Fig. 14 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 80 µgP/g for 3 weeks

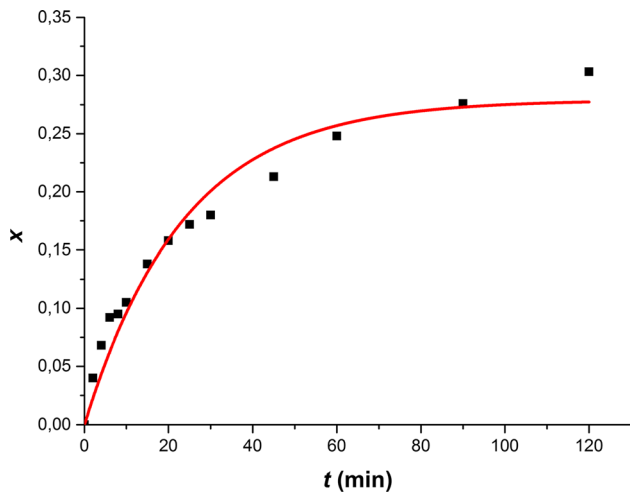


Fig. 15 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 160 $\mu\text{gP/g}$ for 3 weeks

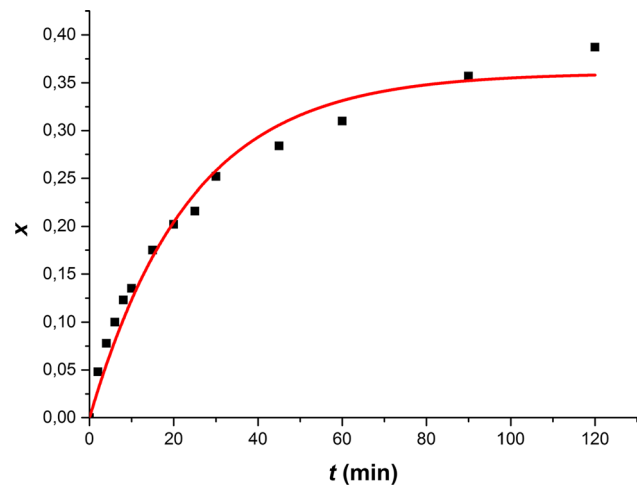


Fig. 18 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 80 $\mu\text{gP/g}$ for 3 months

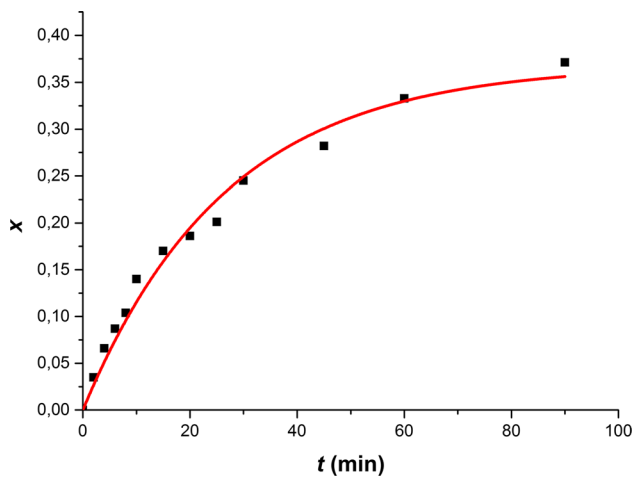


Fig. 16 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 0 $\mu\text{gP/g}$ for 3 months

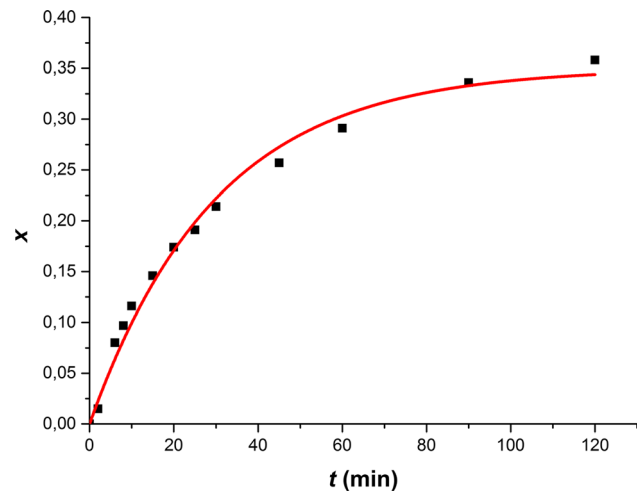


Fig. 19 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 160 $\mu\text{gP/g}$ for 3 months

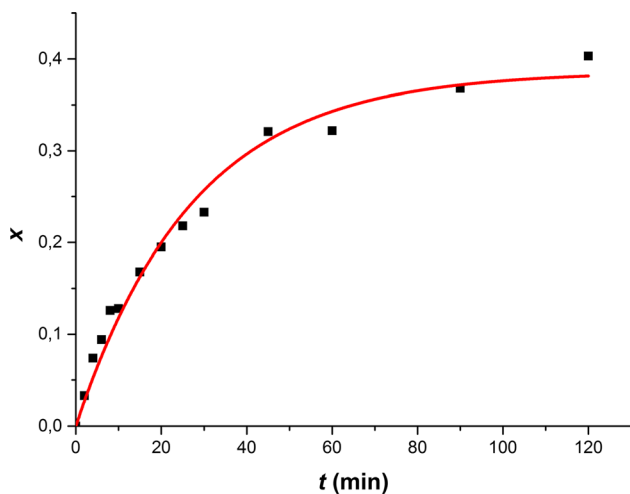


Fig. 17 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 40 $\mu\text{gP/g}$ for 3 months

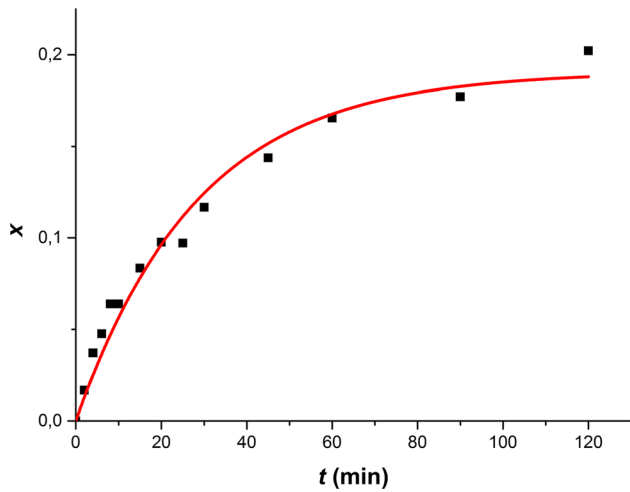


Fig. 20 One exponential kinetic curve of heterogeneous isotopic exchange on rendzina soil sample treated with 320 $\mu\text{gP/g}$ for 3 months

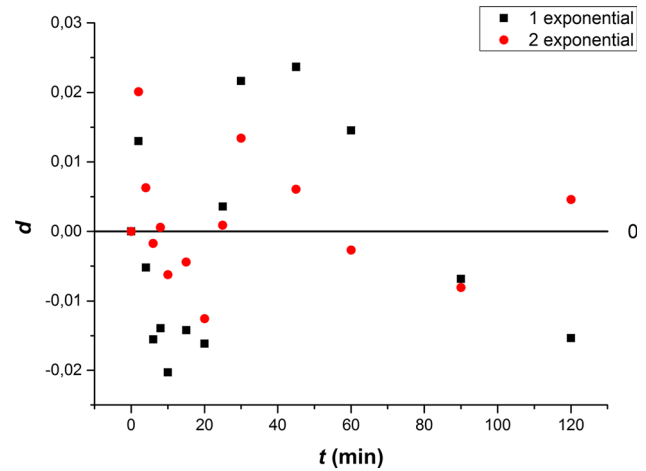


Fig. 23 Differences (d) of calculated and measured relative radioactivities (x) versus time (1 week incubation, 160 $\mu\text{gP/g}$)

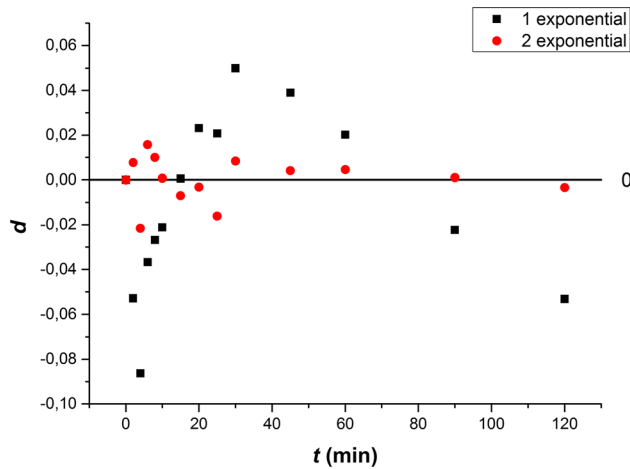


Fig. 21 Differences (d) of calculated and measured relative radioactivities (x) versus time (1 week incubation, 0 $\mu\text{gP/g}$)

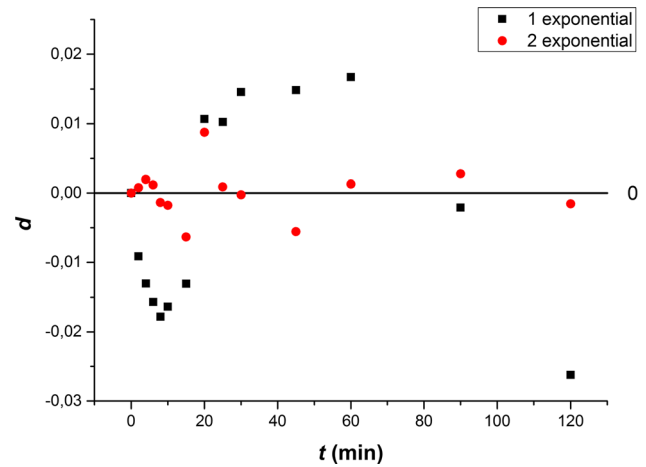


Fig. 24 Differences (d) of calculated and measured relative radioactivities (x) versus time (1 week incubation, 320 $\mu\text{gP/g}$)

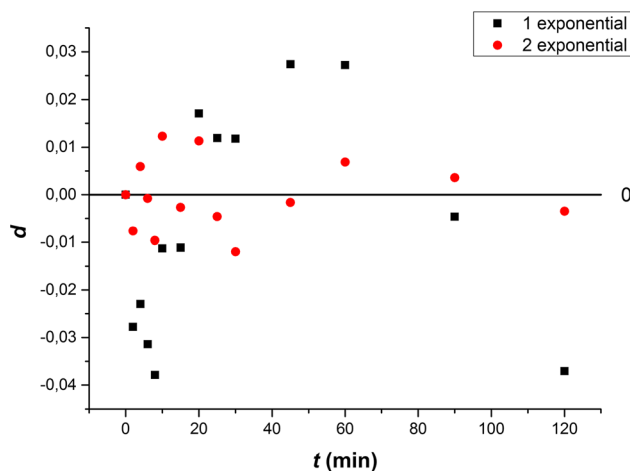


Fig. 22 Differences (d) of calculated and measured relative radioactivities (x) versus time (1 week incubation, 40 $\mu\text{gP/g}$)

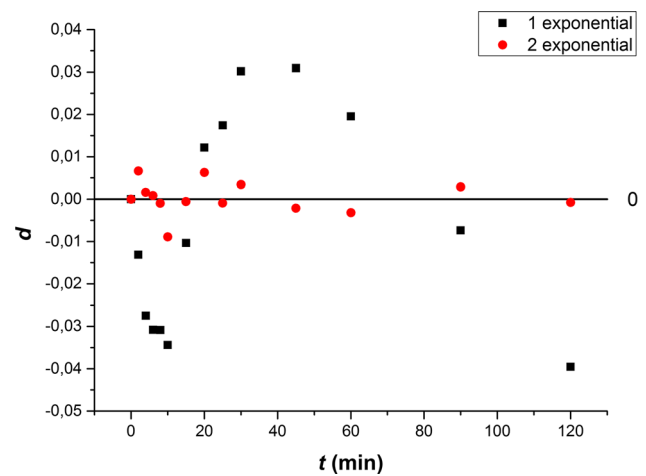


Fig. 25 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 weeks incubation, 0 $\mu\text{gP/g}$)

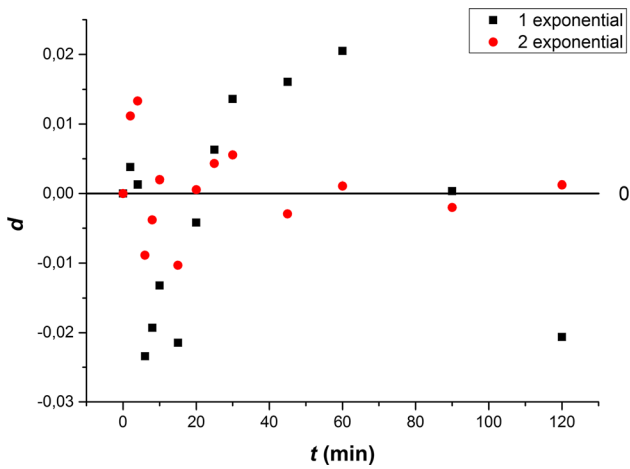


Fig. 26 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 weeks incubation, 40 $\mu\text{gP/g}$)

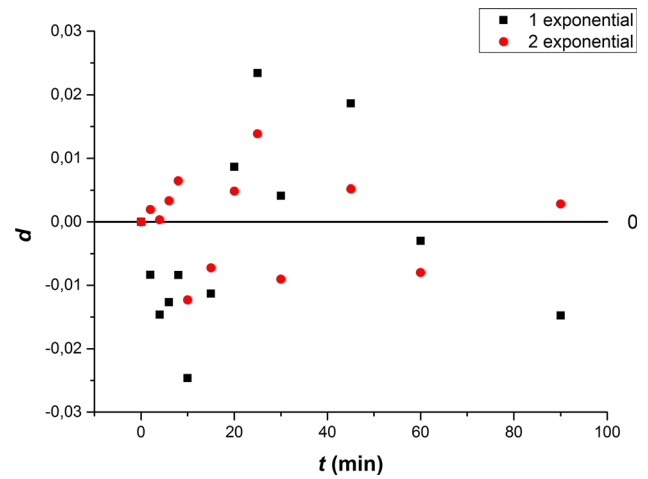


Fig. 29 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 months incubation, 0 $\mu\text{gP/g}$)

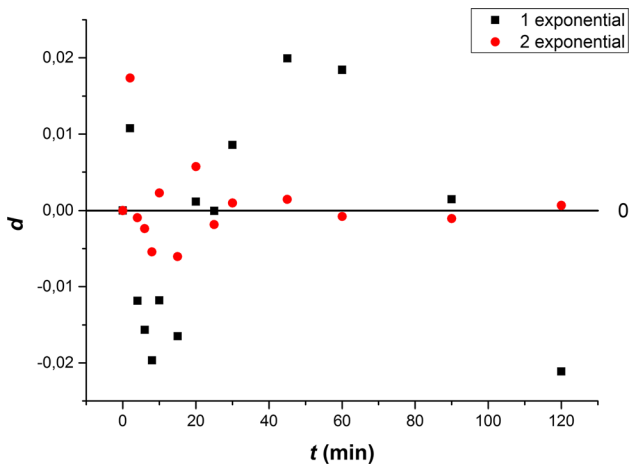


Fig. 27 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 weeks incubation, 80 $\mu\text{gP/g}$)

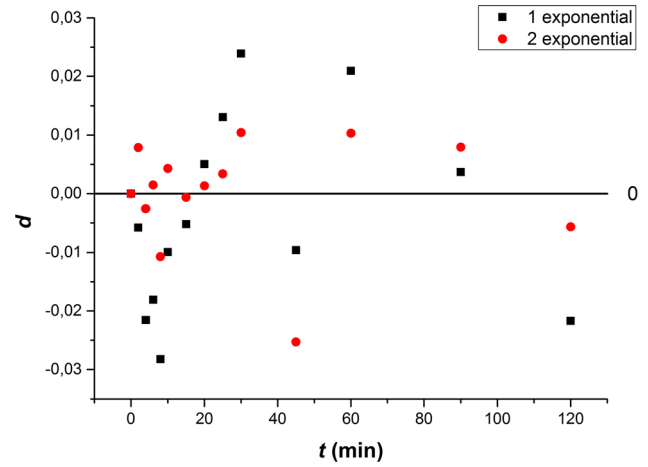


Fig. 30 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 months incubation, 40 $\mu\text{gP/g}$)

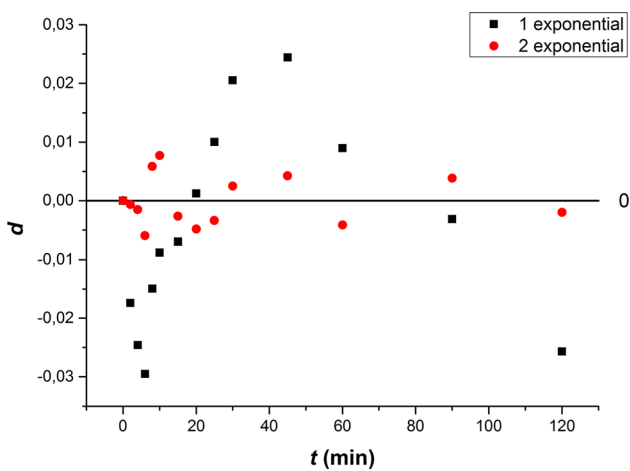


Fig. 28 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 weeks incubation, 160 $\mu\text{gP/g}$)

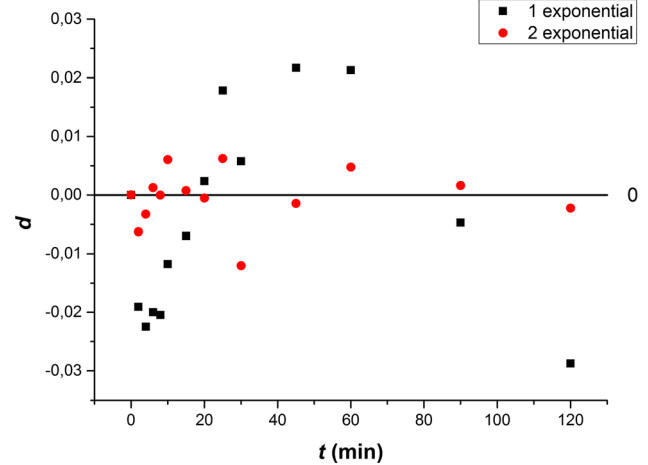


Fig. 31 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 months incubation, 80 $\mu\text{gP/g}$)

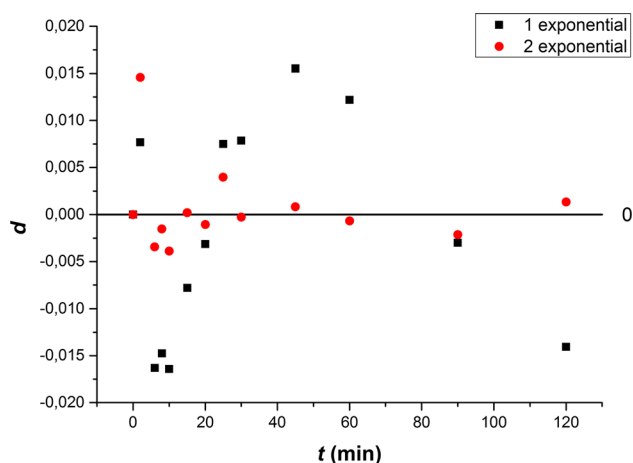


Fig. 32 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 months incubation, 160 $\mu\text{gP/g}$)

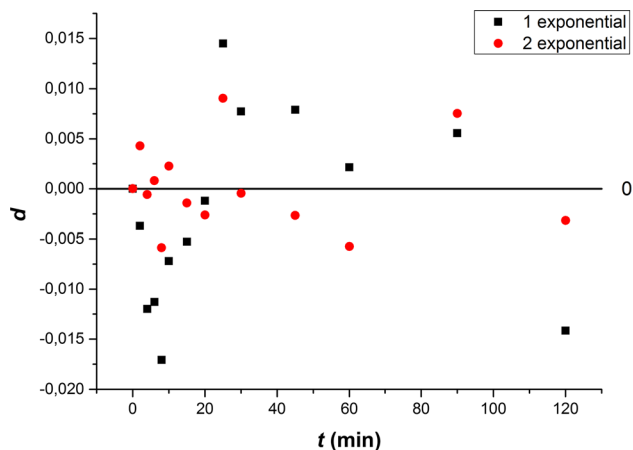


Fig. 33 Differences (d) of calculated and measured relative radioactivities (x) versus time (3 months incubation, 320 $\mu\text{gP/g}$)

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Declarations

Data availability All the data used in this article can be found in the main text of the manuscript and Appendix 3.

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