Applied Radiation and Isotopes 217 (2025) 111602

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Testing a biexponential kinetic model for the heterogeneous isotopic exchange of phosphate ions on several types of soil

János Z. Vörös *, József Kónya, Noémi M. Nagy

Imre Lajos Isotope Laboratory, Department of Physical Chemistry, Institute of Chemistry, Faculty of Sciences, University of Debrecen, Egyetem tér 1., H-4032, Debrecen, Hungary

ARTICLE INFO

Keywords:
Heterogeneous isotopic exchange
Biexponential kinetic equation
Sorption isotherm
Cooperative sorption
Desorption kinetics

ABSTRACT

In this study, a new kinetic equation was applied for the heterogeneous isotopic exchange of phosphate ions on soil. Phosphate sorption on chernozem, marshy meadow and meadow soil was studied by P-32 heterogeneous isotopic exchange in steady-state. The soil samples were incubated with 5 different amounts of KH_2PO_4 for 1, 3, 13, 10, 12 and 22 weeks. Then they were equilibrated with destilled water, and after the equilibrium was reached, $H_3^{32}PO_4$ radiotracer was added to the soil solution. At different times samples were taken from the soil solution, and radioactivities were determined by liquid scintillation (LSC) technique. The concentration of phosphate ions was determined by photometry. The relative radioactivity of soil vs time could be fitted well by the biexponential kinetic equation, which assumes two types of weakly bonded phosphate. From the fitting parameters of the biexponential equation and the phosphate concentration determined by photometry the amounts of the two types of weakly bonded phosphate and their steady-state rates were determined. The amounts of weakly bonded phosphate were plotted vs phosphate concentration – data points could be fitted by a Langmuir-like representation or the S-shape sorption isotherms. The rate orders of the desorption proved to be 1 or 2; rate constants were determined. It can be concluded that in some cases cooperative sorption can occure, which can be due to hydrogen bonding between the hydrogenphosphate ions on the surface.

1. Introduction

Phosphorus is an essential nutrient for plants, which is taken up by the roots from the soil solution in the form of hydrogenphosphate or dihydrogenphosphate ions. The latter can be sorbed by the solid phase of the soil, and the sorbed phosphate can be divided into two pools namely tightly and weakly bonded phosphate (Mansell et al., 1977; Fardeau, 1996; Kónya and Nagy, 2015; Gasser et al., 2023). Tightly bonded phosphate can be desorbed only by difficulties that is why it is hardly available for plants. However, weakly bonded phosphate can be desorbed therefore it can be taken up by plants, and, mainly under laboratory conditions, it can undergo heterogeneous isotopic exchange with the phosphate ions in the soil solution (Fardeau, 1996; Kónya and Nagy, 2015). Since we do not have previous assumptions about the details of the mechanism of the fixation of phosphate on the solid phase, we consequently use the word „sorption" instead of „adsorption". Sorption can be either physisorption, chemisorption, ion exchange or even precipitation, and the surface energy can either increase or decrease. As opposed to this, the driving force of adsorption is always the deminishing surface energy (we can say it is a special case of sorption).

Several types of soil were examined by our research group via heterogeneous isotopic exchange in steady-state. According to this method, first the soil sample is stirred with a given amount of destilled water for some hours in order that the system gets in steady-state, that means, the rates of sorption and desorption become equal. After that carrier-free $^{32}PO_4^{3-}$ ions are added to the soil solution – the amount of the tracer ($<10^{-12}$ mol/dm^3) is so small compared to the total amount of phosphate, that it does not disturb the equilibrium. From this point, the heterogeneous isotopic exchange begins, and the relative radioactivity of the soil increases with time (at the beginning it is zero, because the tarcer is added to the liquid phase). The rate of the isotopic exchange depends on the rate of sorption and desorption (which are equal because the system is in steady-state). In accordance with this, the main significance of this method is, that the kinetics of sorption and desorption can be examined in equilibrium (Fardeau, 1996; Kónya and Nagy, 2015).

In the data processing of heterogeneous isotopic exchange, the

* Corresponding author. Department of Physical Chemistry, Institute of Chemistry, Faculty of Sciences, University of Debrecen, Egyetem tér 1., H-4032, Debrecen, Hungary.
E-mail address: voros.janos@science.unideb.hu (J.Z. Vörös).

https://doi.org/10.1016/j.apradiso.2024.111602
Received 1 March 2024; Received in revised form 5 November 2024; Accepted 21 November 2024
Available online 23 November 2024

Table 1
Parameters of the soil samples (Buzetzky et al., 2023).

soil type/ parameters	Chernozem Látókép	Meadow Görbeháza	marshy meadow Debrecen-Dombostanya
	Calcic Chernozem (Loamic)	Calcic Vertisols (Gleyic)	Calcic Gleysols (Arenic, Humic)
Clay and silt %	44.26	52	28.32
Hygroscopicity %	2.15	2.85	–
pH (H_2O)	6.59	8.14	8.22
pH KCl	5.57	6.97	7.37
$CaCO_3$ %	–	3	14.39
conductivity (at 100 % water holding capacity) (μS/cm)	776	4120	456
SOM %	2.38	3.25	6.39
Organic C (g/kg)	13.8	18.9	37.0
Organic N (g/kg)	1.36	1.90	3.70
total P (digestion with H_2SO_4) (mg/kg)	925	842	1044

relative radioactivities vs time are plotted and fitted by empiric (Fardeau, 1996; Probert and Larsen, 1972; Brown et al., 2020) or theoretical kinetic equations (Kónya and Nagy, 2015; Atkinson et al., 1971; Barrow, 1991). Kosmulski et al., 1983, showed that when there are several parallel exchange processes, the time dependence of the relative radioactivity can be described by a series of exponential terms. Kónya et al. developed a theoretical model which assumes that all the weakly sorbed phosphate has a given steady-state rate *C*, and based on this assumption a one exponential equation was obtained (Kónya and Nagy, 2015). The amount of phosphate in the soil solution should be determined by photometry (Murphy and Riley, 1962), and from this and the fitting parameters of the one exponential equation, the steady state rates of sorption and desorption and the amounts of weakly bonded phosphate were calculated (Nagy and Kónya, 2018; Nagy et al., 2019; Buzetzky et al., 2023). Nevertheless, in the case of rendzina soil (classification: rendzic phaeozem, hyperhumic, according to the World Reference Base (WRB) for Soil Resources (IUSS Working Group WRB, 2014)) the one exponential equation did not fit well the experimental data points, therefore a new kinetic model was established (Vörös et al., 2024). Using the new model, the weakly bonded phosphate is further divided into two pools, which take part in the heterogeneous isotopic exchange with two different steady-state rates. This leads to a biexponential kinetic equation, which fits well experimental data points in the case of rendzina soil. By fitting this equation, the steady-state rates and the amounts of phosphate ions at the two different weakly bonded phosphate pools were determined (Vörös et al., 2024). The advantage of this model is, that the amounts of bonded phosphate at the two different sites can be separately plotted vs the concentration of phosphate in the soil solution, and fitted by sorption isotherms. This means that, based on heterogeneous isotopic exchange experiments, both the kinetics and the thermodynamics of the sorption and desorption process can be examined.

In this study, we would like to test the new biexponential model on other types of humic soil as well, namely on meadow (calcic vertisols, gleyic), chernozem (calcic chernozem, loamic) and marshy meadow (calcic gleysols, arenic, humic) soils, where the one exponential equation also proved to be inappropriate. Our aim is to develop a general method for the examination of the thermodynamics and kinetics of the phosphate sorption on soil based on heterogeneous isotopic exchange experiments and the biexponential kinetic equation set up in our previous study (Vörös et al., 2024). The main advantage of this method is, that it provides a deeper insight into the mechanism of phosphate sorption because it deals with the faster and slower exchange processes separately – however this is also its main disadvantage, because the higher number of fitting parameters causes higher uncertainty in the parameter evaluation. That is why it should be tested on several types of soil in order that experimental conditions can be optimised, and further experiments can be properly engineered.

2. Materials and methods

2.1. Experimental

The studied soils were chernozem (calcic chernozem, loamic, collected in Látókép, Hungary, 2017), marshy meadow (calcic gleysols, arenic, humic, collected in Dombostanya, Hungary, 2019) and meadow (calcic vertisols, gleyic, collected in Görbeháza, Hungary, 2018); the details of the soils are presented in Table 1. The detailed description of experiments can be found also in Kónya and Nagy, 2015; Nagy et al. (2019).

P was added to the soil samples in amounts of 0, 40, 80, 160 and 320 μgP/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. These are the I1week, I3week and I3months series. During incubation the water contents of the soil samples were kept at a constant level, in order to retrieve water loss via evaporation water was added to the samples if necessary. There were performed also other experiments, where the soil samples treated with the same amounts of phosphate after 1 week, 3 weeks or 3 months were left in the same conditions for further 9 weeks: these are the K1week, K3week and K3months series. So the total incubation times are 1 week, 3 weeks and 13 weeks for the I1week, I3weeks and I3months series and 10 weeks, 12 weeks and 22 weeks for the K1week, K3weeks and K3months series.

Heterogeneous (^{32}P) isotopic exchange experiments were carried out at room temperature (25 °C) by using soil samples equivalent to 1 g air-dried soil (this means 1.300 g of chernozem, 1.254 g of marshy meadow and 1.229 g of meadow soil at 60 % of maximum water holding capacity) stirred with 210 cm^3 of distilled water for 60 min. During this time reaction mixture has reached steady-state. This means that steady-state is reached by the partial desorption of phosphate ions from the soil samples. After this, 10 cm^3 sample was taken from the soil solution and separated from the solid phase by 0.45 μm filter cyring. Then it was analyzed for phosphorous concentration by ammonium molybdate method by spectrophotometric technique (Murphy and Riley, 1962; details see later) – from this the equilibrium concentration of phosphate ions can be calculated. 100 μl of carrier free $H_3^{32}PO_4$ radiotracer (carrier free means there it contains only ^{32}P, concentration of $^{32}P < 10^{-12}$ 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. The soil solution and the solid phase were separated by 0.45 μm filter cyring. To 1-1 cm^3-s of the samples 4-4 cm^3 of scintillation cocktail (composition see in Nagy et al., 2019) 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 cm^3 of destilled water 100 μL of carrier free $H_3^{32}PO_4$ radiotracer was added. 1 cm^3 of the zero solution was also taken (zero sample) and the radioactive intensities were determined as seen before.

The scintillation cocktail was prepared as follows: 4.00 g of 2,5-diphenyloxazole was dissolved in 106 cm^3 of ethyl alcohol, then 37 cm^3 of ethylene glycol and 257 cm^3 of TRITON-X-100 was added, and the whole was filled up to 1000 cm^3 with xylene isomer mixture.

The phosphate photometry was carried out in the following way: 1 cm^3 of 10 m/m% ascorbic acid solution was added to 4 cm^3 of acidic ammonium molybdate – potassium-antimonyl-tartarate reagent, and it was filled up to 100 cm^3 with 3X destilled water. After waiting for at least 20 min, we obtained in such way „reagent 2". After this, 2.5 cm^3 of „reagent 2" was added to 2 cm^3 of soil solution or KH_2PO_4 standard solution, and it was filled up to 5 cm^3 with 3X destilled water. After

having waited for exactly 20 min, the absorbance of the solution was measured at 660 nm by Cary 3 UV–VIS spectrophotometer.

2.2. Parameter evaluation

The relative radioactivities of soil samples were plotted vs time and fitted by the biexponential kinetic equation (Vörös et al., 2024), where x is the relative radioactivity of soil (dimensionless), t is time (min), A, B, D and E are fitting parameters:

$$x = \frac{\mathbf{A}\bullet\mathbf{E}}{\mathbf{A}\bullet\mathbf{E}+\mathbf{B}\bullet\mathbf{D}+\mathbf{B}\bullet\mathbf{E}} + \frac{\mathbf{B}\bullet\mathbf{D}}{\mathbf{A}\bullet\mathbf{E}+\mathbf{B}\bullet\mathbf{D}+\mathbf{B}\bullet\mathbf{E}} + +\mathbf{K_1}\bullet\left(\mathbf{A}+\frac{-[(\mathbf{A}+\mathbf{B})-(\mathbf{D}+\mathbf{E})]-\sqrt{(\mathbf{A}+\mathbf{B}+\mathbf{D}+\mathbf{E})^2-4\bullet(\mathbf{A}\bullet\mathbf{E}+\mathbf{B}\bullet\mathbf{D}+\mathbf{B}\bullet\mathbf{E})}}{2}\right)$$
$$\bullet\exp\frac{-(\mathbf{A}+\mathbf{B}+\mathbf{D}+\mathbf{E})+\sqrt{(\mathbf{A}+\mathbf{B}+\mathbf{D}+\mathbf{E})^2-4\bullet(\mathbf{A}\bullet\mathbf{E}+\mathbf{B}\bullet\mathbf{D}+\mathbf{B}\bullet\mathbf{E})}}{2}\bullet t + +\mathbf{K_2}$$
$$\bullet\left(\mathbf{D}+\frac{[(\mathbf{A}+\mathbf{B})-(\mathbf{D}+\mathbf{E})]+\sqrt{(\mathbf{A}+\mathbf{B}+\mathbf{D}+\mathbf{E})^2-4\bullet(\mathbf{A}\bullet\mathbf{E}+\mathbf{B}\bullet\mathbf{D}+\mathbf{B}\bullet\mathbf{E})}}{2}\right)$$
$$\bullet\exp\frac{-(\mathbf{A}+\mathbf{B}+\mathbf{D}+\mathbf{E})-\sqrt{(\mathbf{A}+\mathbf{B}+\mathbf{D}+\mathbf{E})^2-4\bullet(\mathbf{A}\bullet\mathbf{E}+\mathbf{B}\bullet\mathbf{D}+\mathbf{B}\bullet\mathbf{E})}}{2}\bullet t \quad (1)$$

where

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

and

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

The relative radioactivity can be calculated as follows:

$\boldsymbol{x} = \mathbf{1} - \frac{\boldsymbol{I_1}}{\boldsymbol{I_{tot}}}$ where $\boldsymbol{I_1}$ and $\boldsymbol{I_{tot}}$ are the radioactive intesities of the soil solution and the zero sample measured by LSC technique.

The aim was to determine the amount of phosphorus in the soil solution (m_1, in μg), the amounts of phosphorus at bonding sites 2a and 2b (m_{2a} and m_{2b} in μg) and the steady-state rates at bonding sites 2a and 2b (C_1 and C_2 in μg/min). The m_1 value was obtained from the steady-state phosphate concentration in the soil solution determined by spectrophotometry. It is important to emphasize that m_1 cannot be calculated from the amounts of the added phosphate during the incubation, because it partially converts to tightly bonded phosphate, on the other hand, original untreated soil also contains some desorbeable phosphate. That is why m_1 must be determined from the sample taken from the soil solution after steady state was reached. C_1, C_2, m_{2a} and m_{2b} are calculated in the following manner (Vörös et al., 2024):

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

So the parameters C_1, C_2, m_{2a} and m_{2b} are calculated from the fitting parameters of the biexponential kinetic equation and the steady-state phosphate concentration in the soil solution determined by photometry. In order to examine the sorption equilibrium m_{2a} and m_{2b} were plotted vs m_1 and fitted by the Langmuir (Eq. (5)) or the S-shape sorption isotherm (Eq. (6)) (Liu, 2015). It is worth to emphasize that the phosphate ions at bonding sites 2a and 2b are really in equilibrium with the phosphate ions in the soil solution, this is the main advantage of this method over the traditional batch experiments. In the latter case, the amounts of sorbed phosphate are calculated as the difference between the initial and the equilibrium concentrations, but the problem is, that this difference contains not only the weakly but also the tightly sorbed phosphate, which is not in equilibrium with the phosphate ions in the soil solution – this also means, that we cannot get a real equilibrium isotherm in this way. As for heterogeneous isotopic exchange – on the contrary – the amounts of weakly bonded phosphate can be calculated and real equilibrium isotherms can be obtained. The novelty of our biexpontnial kinetic equation is, that the amounts of two different types of weakly bonded phosphate can be calculated, and their isotherms can be examined separately.

The Langmuir behaviour assumes that there is no cooperation between the sorbed phosphate ions, in other words, the affinity of phosphate to the surface does not depend on if there is already sorbed phosphate on the surface or not. At first sight this can be contradictious, because hydrogenphosphate ions have negative charges which causes negative feedback due to repulsion, however this contradiction can be resolved. On one hand, it is not sure that the bonding sites are directly beside each other – it can also occur that they are separated from each other for example, via soil organic matter: in this case the electrostatic interactions between the sorbed ions are not significant. On the other hand, if the mechanism is ion exchange, it can be proved that at certain conditions the Langmuir isotherm can be applied (Misak, 1993).

It can be mathematically proved that Langmuir isotherm is always concave. However, in some cases we experienced that data points at smaller concentrations fit rather on a convex curve, which can be explained by positive cooperativity, this means that the sorption of a phosphate ion on the surface promotes the sorption of another one. This is also contradictious at first sight, since we are rather awaiting for a negative feedback due to electrostatic repulsion. But in the case of hydrogen-phosphate ions hydrogen bonds can be formed, which can be stronger than the electrostatic repulsion. The potential energy of electrostatic repulsion calculated from the Coulomb law is in the range of a few 10 kJ/mol, while the P-O-H…O-P hydrogen bond energy is between 63 and 167 kJ/mol (Desiraju and Steiner, 2001). So hydrogen bonds can overcompensate the electrostatic repulsion, and as a consequence, positive feedback can occur. It can be modeled in such way, that there are two steps of phosphate sorption: the first step is the sorption on a surface site where there is no phosphate (Eq. (3)), and the second step is the sorption at a surface site, where there is already a sorbed phosphate ion (Eq. (4)). This model is the simplification of the cooperative n-layer sorption model (Liu, 2015) to two layers – this simplification should be done because of the relative small number of data points compared to the number of fitting parameters. Two equilibrium constants (K_1 and K_2) belong to the two steps, and it is proved that the isotherm has convex part if $K_2 > K_1$ (see the details in Appendix1). We tested both the Langmuir and the S-shape sorption isotherm in all series, and decided

Table 2
Kinetic parameters of phosphate sorption on chernozem soil (m_1 is the amount of phosphate in the soil solution in steady-state in μgP, m_{2a} and m_{2b} are the amounts of weakly bonded phosphate at bonding sites 2a and 2b in μgP, C_1 and C_2 are the steady-state rates at bonding sites 2a and 2b in μgP/min; green color means that the standard errors are less than 50 % of the value of the parameters, and yellow color means that the standard errors are between 50 % and 100 %).

Series	P added (μgP/g)	m_1 / μg	m_{2a} / μg	m_{2b} / μg	C_1 / (μg/min)	C_2 / (μg/min)
I1week	0	0.000	0.000	0.000	0.0000	0.0000
	40	32.110	10.973	8.359	0.2916	10.5783
	80	46.500	10.578	4.252	0.6189	31.2438
	160	82.910	14.532	9.807	0.2562	6.7008
	320	177.03	65.100	38.223	0.4479	42.3580
I3weeks	0	15.930	7.995	6.698	0.1462	3.7813
	40	70.850	31.644	29.173	1.3136	22.0464
	80	75.510	22.331	22.111	0.7959	10.1825
	160	94.810	24.918	49.980	0.7869	40.5910
	320	123.040	32.516	41.105	0.9339	36.5687
I3months	0	3.000	1.674	0.673	0.0381	0.4861
	40	5.070	2.228	1.587	0.0407	0.7947
	80	4.980	2.182	1.504	0.0570	1.7362
	160	2.610	0.952	0.403	0.0230	0.3925
	320	29.140	7.122	4.968	0.3060	2.3268
K1week	0	17.700	10.507	4.876	0.2004	36.8040
	40	29.600	13.090	6.573	0.3330	4.2414
	80	46.800	19.085	11.203	0.4502	57.6487
	160	93.500	27.351	22.342	0.6078	16.9029
	320	200.000	56.112	54.524	1.0420	38.9660
K3weeks	0	17.040	9.931	4.587	0.2830	1.8575
	40	22.750	12.257	7.249	0.2530	5.6579
	80	27.600	10.403	8.659	0.2967	6.5942
	160	45.250	16.979	12.724	0.5389	10.0754
	320	79.350	18.909	19.729	0.8927	20.8151
K3months	0	16.600	20.289	5.366	0.1698	2.1328
	40	30.300	17.025	5.546	0.4278	2.8212
	80	45.700	21.718	13.357	0.4209	5.3391
	160	100.200	39.142	15.045	1.7144	45.5499
	320	211.300	65.652	34.150	1.4411	279.9598

Table 3
Parameters of the isotherms of phosphate sorption on chernozem soil.

Series	I3weeks		I3months		K3weeks	
Bonding site	2a	2b	2a	2b	2a	2b
Isotherm type	Langmuir	Langmuir	Langmuir	S-shape	Langmuir	Langmuir
M (μg/g)	48.5	205	13.31	2.671	26.55	75.2
σM (μg/g)	19.3	510	1.18	0.085	3.83	14.6
K_1 (dm^3/μg)	0.0030	0.00047	0.0079	0.000013	0.00654	0.00090
σK_1 (dm^3/μg)	0.0027	0.0014	0.0012	0.0038	0.00215	0.00022
K_2 (dm^3/μg)	–	–	–	48.9	–	–
σK_2 (dm^3/μg)	–	–	–	14359	–	–

Table 4
Desorption rate orders and rate constants of phosphate sorption on chernozem soil.

Series	I3weeks		I3months		K3weeks	
Bonding site	2a	2b	2a	2b	2a	2b
Order	1	1–2	1–2	1	2	1–2
k_{d1st} (min^{-1})	0.0341	0.474	0.0145	0.529	–	0.452
σk_{d1st} (min^{-1})	0.0026	0.185	0.0028	0.083	–	0.084
k_{d2nd} ($\mu g^{-1} min^{-1}$)	–	0.00775	0.00399	–	0.00225	0.0303
σk_{d2nd} ($\mu g^{-1} min^{-1}$)	–	0.00430	0.00043	–	0.00016	0.0051

based on the R^2 value which one is appropriate to the given data series. In the main text we present only the appropriate isotherms, but in Appendix2 all the R^2 values for the fittings for all series can be found and all the graphs are included in the Supplementary.

$$S + P \rightleftharpoons SP \quad (3)$$

(3)

$$SP + P \rightleftharpoons SP_2 \quad (4)$$

(4)

The Langmuir isotherm:

$$a_P = \frac{K \bullet M \bullet c_P}{1 + K \bullet c_P} \quad (5)$$

Table 5
Kinetic parameters of phosphate sorption on marshy meadow soil (m_1 is the amount of phosphate in the soil solution in steady-state in µgP, m_{2a} and m_{2b} are the amounts of weakly bonded phosphate at bonding sites 2a and 2b in µgP, C_1 and C_2 are the steady-state rates at bonding sites 2a and 2b in µgP/min; green color means that the standard errors are less than 50 % of the value of the parameters, and yellow color means that the standard errors are between 50 % and 100 %).

Series	P added (µgP/g)	m_1 / µg	m_{2a} / µg	m_{2b} / µg	C_1 / (µg/min)	C_2 / (µg/min)
I1week	0	17.152	15.438	2.588	0.2796	1.1867
	40	0.596	0.300	0.042	0.0072	0.0381
	80	36.209	11.250	3.509	0.2567	0.4754
	160	38.711	11.455	4.261	0.1990	1.1718
	320					
I3weeks	0	0.000	0.000	0.000	0.000	0.000
	40	6.789	2.211	0.732	0.0343	0.0766
	80	29.539	10.453	0.774	0.2561	0.5163
	160	46.572	12.907	1.284	0.3116	0.8495
	320	173.252	23.973	12.259	0.3742	1.2890
I3months	0	0.000	0.000	0.000	0.0000	0.0000
	40	22.512	11.129	1.904	0.2179	1.0112
	80	509.925	191.390	75.580	2.1723	9.5050
	160	630.087	207.165	38.011	2.7346	3.7175
	320	46.096	13.286	4.056	0.1659	0.2503
K1week	0	19.415	9.453	3.674	0.1299	0.9457
	40	21.440	11.848	2.209	0.2680	1.3125
	80	230.274	34.292	79.753	9.8419	1.6557
	160	53.242	19.572	6.779	0.2550	1.4210
	320	71.466	21.830	8.960	0.5481	8.5623
K3weeks	0	0.000	0.000	0.000	0.0000	0.0000
	40	0.000	0.000	0.000	0.0000	0.0000
	80	0.000	0.000	0.000	0.0000	0.0000
	160	28.586	10.926	4.333	0.2496	3.0439
	320	67.535	16.587	15.047	0.5376	5.5028
K3months	0	0.238	0.201	0.061	0.0038	0.0364
	40	2.859	1.774	0.589	0.0252	0.1315
	80	37.996	16.990	7.056	0.4035	4.6063
	160	25.728	10.175	4.816	0.2112	2.0335
	320	67.178	24.529	12.527	0.4037	4.3504

Table 6
Parameters of the isotherms of phosphate sorption on marshy meadow soil.

Series	I3weeks		K1week		K3months	
Bonding site	2a	2b	2a	2b	2a	2b
Isotherm type	Langmuir	S-shape	Langmuir	Langmuir	Langmuir	Langmuir
M (μg/g)	34.10	8791.6	38.22	54.8	93.5	6153
σM (μg/g)	1.76	24787300	3.77	81.0	34.5	28490
K_1 (dm^3/μg)	0.00273	0.00000036	0.00382	0.00054	0.00107	0.0000061
σK_1 (dm^3/μg)	0.00031	0.00101	0.00072	0.00093	0.00051	0.0000281
K_2 (dm^3/μg)	–	0.00201	–	–	–	–
σK_2 (dm^3/μg)	–	0.0131	–	–	–	–

Table 7
Desorption rate orders and rate constants of phosphate sorption on marshy meadow soil.

Series	I3weeks		K1week		K3months	
Bonding site	2a	2b	2a	2b	2a	2b
Order	1	1	1	2	1	1
k_{d1st} (min^{-1})	0.0184	0.113	0.0196	–	0.0190	0.421
σk_{d1st} (min^{-1})	0.0020	0.034	0.0029	–	0.0014	0.055
k_{d2nd} ($\mu g^{-1}min^{-1}$)	–	–	–	0.0881	–	–
σk_{d2nd} ($\mu g^{-1}min^{-1}$)	–	–	–	0.0169	–	–

where a_P is the amount of sorbed phosphorus on the soil surface sites 2a or 2b (in μgP/g), c_P is the concentration of phosphorus in the soil solution (in μg/dm^3), M is the maximum value of sorbed phosphorus at bonding sites 2a or 2b (in μgP/g) and K is the sorption constant for bonding sites 2a or 2b (in dm^3/μg).

The S-shape sorption isotherm:

$$a_P = \frac{K_1 \bullet M \bullet (c_P + 2 \bullet K_2 \bullet {c_P}^2)}{1 + K_1 \bullet c_P + K_1 \bullet K_2 \bullet {c_P}^2} \quad (6)$$

where a_P is the amount of sorbed phosphorus on the soil surface sites 2a or 2b (in μgP/g), c_P is the concentration of phosphorus in the soil solution (in μg/dm^3), M is the maximum value of sorbed phosphorus at bonding sites 2a or 2b (in μgP/g), K_1 and K_2 are the first and the second sorption constants for bonding sites 2a or 2b (in dm^3/μg). In order to easily compare the sorption processes of the different sorption sites, in Tables 3, 6 and 9 the K parameter of the Langmuir equation is also written as K_1 (we can realize that Eq. (5) is a special case of Eq. (6), where $K_2 = 0$). As we can see, the S-shape sorption isotherm contains 3 fitting parameters: this means that in this study it can be used only for qualitative purposes due to the relative low amount of raw data related to the number of fitting parameters (we have 5–6 data points for an isotherm).

Based on the parameters obtained from the fitting of the biexponential kinetic equation, kinetic investigations for the desorption were also done – according to this C_1 vs m_{2a} and C_2 vs m_{2b} were plotted. Since the system is in steady-state, C_1 and C_2 are the rates of both the sorption and the desorption, so they can be used to determine the rate orders and parameters of the desorption. This underlines the main advantage of heterogeneous isotopic exchange experiments: it is the only method that makes it possible to examine kinetics while the system is in equilibrium. The results for the three different soils are unfolded in the following subsessions.

Since our system is a natural one, scattering of the data points can be relatively high, that is why we used both in the case of sorption isotherms and that of kinetic investigations only the data of the heterogeneous isotopic exchange experiments where the magnitude of the standard error of the fitting parameters was not higher than that of the data value. In Tables 2, 6 and 10 the rows where the standard error of the fitting parameters is less than 50% of the value of the parameter are marked with green background color. It is marked with yellow background color where the standard error is bigger than 50% but still acceptable, this means it is not bigger than the magnitude of the data value. These two groups are judged to be useful for the isothermic and kinetic investigations; the rest, where the magnitude of standard error is higher than that of the data value, are unacceptable. There were also a few cases where the scattering of the data points was so large that they could not be fitted at all: these are the empty rows in Table 5, 8, 12 and 13.

3. Results

3.1. Chernozem soil

The fitted kinetic curves of the heterogeneous isotopic exchange for the series I1week, I3weeks, I3months, K1week, K3weeks and K3months can be seen in Fig. 1, the fitting parameters and their standard error can be found in Table 11 (Apendix2) and the results (m_1, m_{2a}, m_{2b}, C_1, C_2) in Table 2. Normally the order of the kinetic curves from above to the bottom is 0, 40, 80, 160 and 320 μgP/g, but when cooperative sorption occurs (as we later will see), this order can change. Sometimes there are overhanging points (for example Fig. 1 E), if there is only one such point at a kinetic curve, than it is excluded from the parameter evaluation. Since soil-water is a natural system, there always can occur some unexpected problem, for example the aggregation or disaggregation of soil particles, which alters the surface. That is why kinetic curves have to be selected, and only those have to be used fo further calculations, where the fitting is reliable.

In the I3weeks, I3months and the K3weeks series there are enough experiments with standard errors not higher than the magnitude of the parameters, so these series are judged to be suitable to obtain sorption isotherms (Fig. 2) and to examine the kinetics of desorption (Fig. 3). The parameters of the sorption isotherms are summarised in Table 3, and the rate orders and rate constants of desorption in Table 4.

It can be seen that in the K3weeks series the sorption process can be described at both bonding sites by the Langmuir isotherm (Eq. (5)) (Fig. 2 C). However, in the case of I3weeks, neither of the bonding sites can be described properly by any type of sorption isotherm because of the large scattering of data points (Fig. 2 B). The reason for this can be, that the incubation time is too small, and the soil surface did not have enough time to be regenerated after the treatment with KH_2PO_4. In the I3months series only the 2a bonding site shows Langmuir characteristics (Fig. 2 A 2a curve), while the sorption at bonding site 2b can be described by the S-shape sorption isotherm (Eq. (6)) with $K_2 > K_1$ (Fig. 2 A 2b curve, Table 3 column 5). This would mean, that the sorption of phosphate ions at bonding site 2b shows positive cooperativity, so the sorption of a phosphate ion promotes the sorption of another one. But this conclusion should be treated with caution because, as we can see in Fig. 2 A, the distribution of data points is very uneven, and they are missing in the middle parts of the curves.

As a summary, it can be concluded that in the case of K3weeks series both types of bonding sites have Langmuir characteristics, while at the I3weeks and 13months series the isothermic behaviour of the bonding sites is highly uncertain.

Table 8
Kinetic parameters of phosphate sorption on meadow soil (m_1 is the amount of phosphate in the soil solution in steady-state in μgP, m_{2a} and m_{2b} are the amounts of weakly bonded phosphate at bonding sites 2a and 2b in μgP, C_1 and C_2 are the steady-state rates at bonding sites 2a and 2b in μgP/min; green color means that the standard errors are less than 50 % of the value of the parameters, and yellow color means that the standard errors are between 50 % and 100 %).

Series	P added (μgP/g)	m_1 / μg	m_{2a} / μg	m_{2b} / μg	C_1 / (μg/min)	C_2 / (μg/min)
I1week	0	7.218	4.966	1.323	0.0334	0.2065
	40	20.520	9.924	6.789	0.2179	10.0800
	80	53.096	26.927	30.553	0.5097	20.3768
	160	82.656	21.885	27.470	0.9224	164.2388
	320	143.26	29.926	70.199	0.7808	66.7392
I3weeks	0	0.000	0.000	0.000	0.0000	0.0000
	40	8.716				
	80	9.282	4.493	2.676	0.0862	3.2132
	160	60.849				
	320	153.895				
I3months	0		0.000	0.000	0.0000	0.0000
	40	32.106	27.711	15.671	0.2125	12.8245
	80	70.149	35.308	38.633	0.4770	26.6860
	160	52.574				
	320	187.241	26.366	218.102	12.4983	103.5310
K1week	0	20.250	21.426	3.467	0.2582	2.0369
	40	35.110	31.783	8.901	0.4663	5.4982
	80	59.210	32.138	15.176	0.7324	9.6181
	160	114.210	51.169	26.176	1.4276	17.4901
	320	220.100	69.621	34.836	1.4593	29.7641
K3weeks	0	21.720	20.798	7.208	0.3527	4.8062
	40	38.820	23.275	12.105	0.6335	6.1087
	80	57.600	35.673	11.491	0.7862	9.9792
	160	106.390	33.792	20.814	2.1587	123.9178
	320	193.590	86.696	48.553	2.4179	95.0701
K3months	0	30.000	37.300	5.500	0.2238	5.8254
	40	41.200	25.271	5.871	0.4425	3.6441
	80	62.300	31.200	9.994	0.5869	8.7874
	160	108.540	56.526	15.879	1.5228	23.6183
	320	201.700	74.902	33.042	2.2853	30.4587

Table 9
Parameters of the isotherms of phosphate sorption on meadow soil.

Series	I1week		K1week		K3weeks		K3months	
Bonding site	2a	2b	2a	2b	2a	2b	2a	2b
Isotherm type	Langmuir	S-shape	Langmuir	S-shape	Langmuir	Langmuir	Langmuir	Langmuir
M (μg/g)	41.34	45.23	93.7	21.03	206.3	10758	118.4	34699
σM (μg/g)	7.89	0.46	12.1	0.83	41.8	447525	35.3	3467000
K_1 (dm^3/μg)	0.00452	0.000178	0.00232	0.00106	0.00075	0.0000047	0.00163	0.00000092
σK_1 (dm^3/μg)	0.00219	0.000063	0.00067	0.00026	0.00023	0.00019	0.00092	0.000092
K_2 (dm^3/μg)	–	0.0397	–	0.00544	–	–	–	–
σK_2 (dm^3/μg)	–	0.0150	–	0.00194	–	–	–	–

Table 10
Desorption rate orders and rate constants of phosphate sorption on meadow soil.

Series	I1week		K1week		K3weeks		K3months	
Bonding site	2a	2b	2a	2b	2a	2b	2a	2b
Order	1	1	1	1–2	1	1	2	1
k_{d1st} (min^{-1})	0.0226	0.910	0.0219	0.425	0.0223	0.675	–	1.009
σk_{d1st} (min^{-1})	0.0020	0.058	0.0020	0.086	0.0020	0.096	–	0.098
k_{d2nd} ($\mu g^{-1}min^{-1}$)	–	–	–	0.0117	–	–	0.000419	–
σk_{d2nd} ($\mu g^{-1}min^{-1}$)	–	–	–	0.0029	–	–	0.000032	–

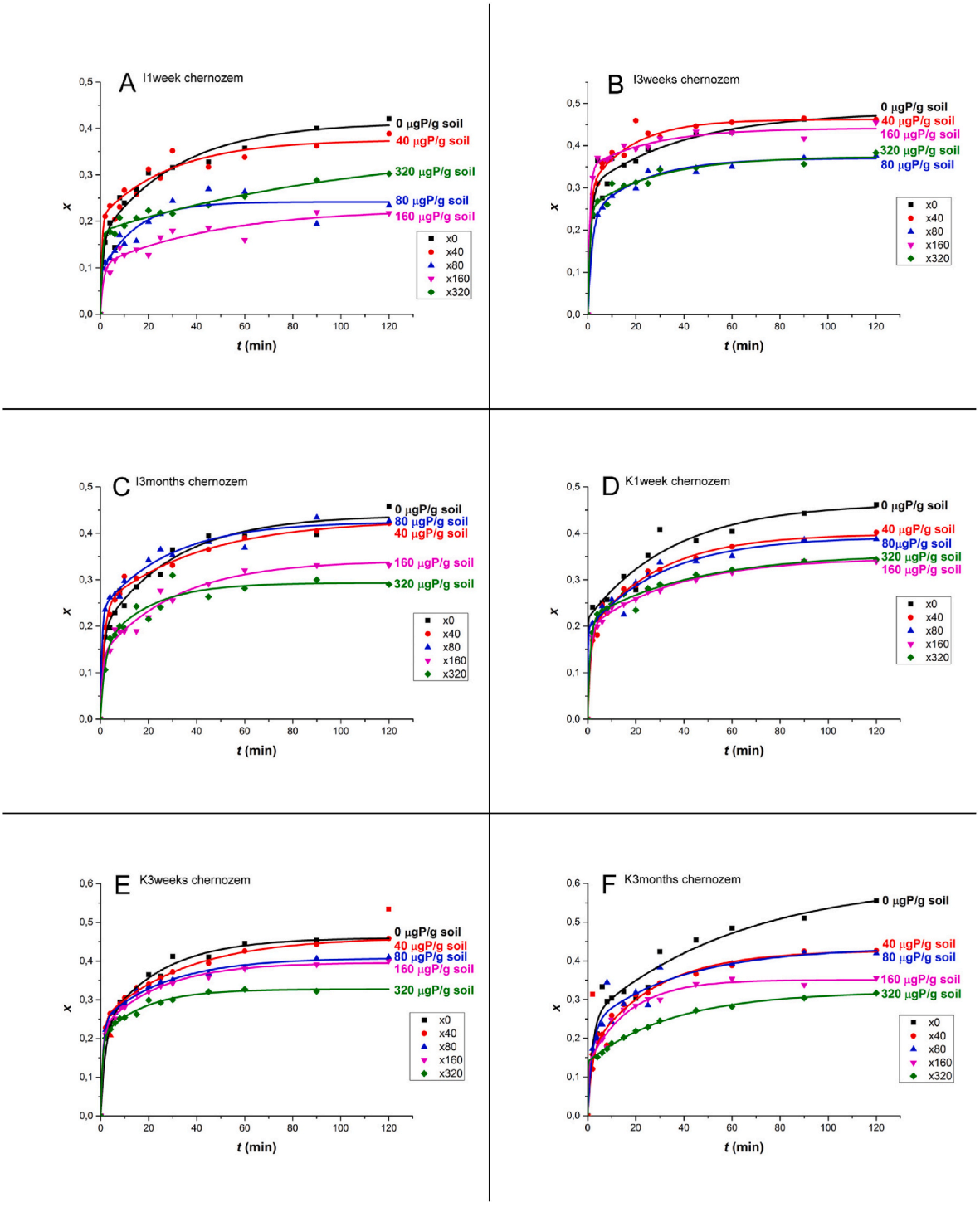

Fig. 1. Biexponential kinetic curves of heterogeneous isotopic exchange on chernozem soil; A: I1week, B: I3weeks, C: I3months, D: K1week, E: K3weeks, F: K3months (*x* is the relative radioactivity of soil, *t* is time).

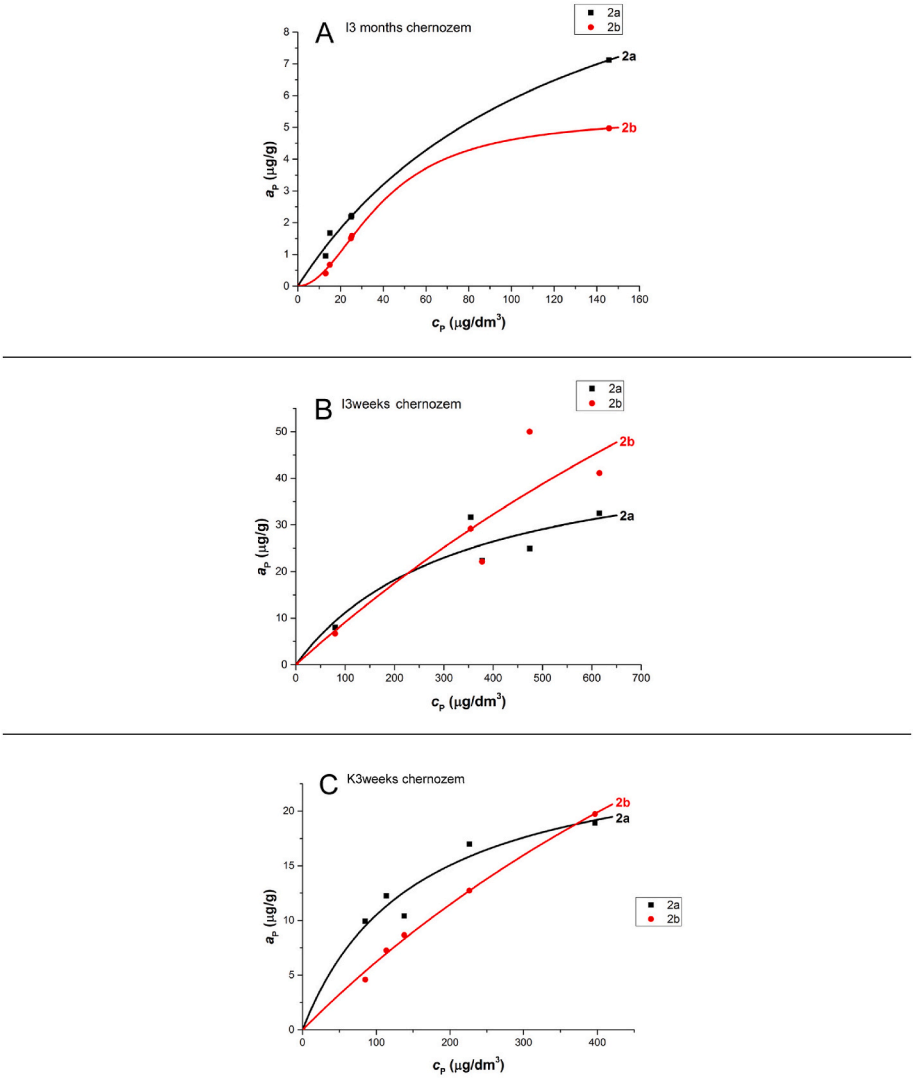

Fig. 2. Sorption isotherms of chernozem soil; A: I3months (Langmuir at 2a and S-shape at 2b), B: I3weeks (Langmuir at both 2a and 2b), C: K3weeks (Langmuir at both 2a and 2b) (a_P is the amount of weakly bonded phosphate at bonding site 2a or 2b in µgP/g soil, c_P is the equilibrium concentration of phosphate in the soil solution in µgP/dm^3 solution).

As for the desorption kinetics, first order, second order and mixed first and second order rate equations were tested as well, all the kinetic curves can be found in the Supplementary and the R^2 values in Appendix 2. Based on the R^2 values it can be stated that in the case of I3weeks, there is first order (1) at bonding site 2a (Fig. 3 A 2a curve, Table 4 column 2) and mixed first and second order (1–2) at 2b (Fig. 3 A 2b curve, Table 4 column 3). In the case of I3months, there is mixed first and second order (1–2) at bonding site 2a (Fig. 3 B 2a curve, Table 4 column 4) and first and second order (1) at 2b (Fig. 3 B 2b curve, Table 4 column 5), however, at 2b rate order has a high uncertainity because of the scattering of the data points. In the case of K3weeks, there is second order (2) at bonding site 2a (Fig. 3 C 2a curve, Table 4 column 6) and mixed first and second order (1–2) at 2b (Fig. 3 C 2b curve, Table 4 column 7). As for bonding site 2a in general it is clearly seen, that the slower desorption process takes part there, and the first order rate constants for the different series have similar values (0.0341 and 0.0145 min^{-1} for I3weeks and I3months, Table 4 row 4). The same is true for the second order rate constants (0.00399 and 0.00225 µg^{-1}min^{-1} for I3months and K3weeks, Table 4 row 6); as a conclusion, they probably belong to the same processes. However, the rate order shifts to second order as the incubation time increases. One possible explanation of this fact can be, that the phosphate ions are first sorbed at the outer surface of the soil particle, but later it penetrates deeper into the particle, and during the desorption it can get out from there by a second order diffusion process.

As for 2b, the faster desorption process takes part there, and both at shorter and at longer incubation times there are first and second order processes as well. The first order rate constants have similar values (0.474, 0.529 and 0.452 min^{-1} for I3weeks, I3months and K3weeks, Table 4 row 4), while the second order rate constants are increasing with incubation time (0.00775 µg^{-1}min^{-1} for I3weeks and 0.0303 for K3weeks). This indicates that the first order process is the same, while the characteristics of the second order process changes with time (probably according to similar transformations as mentioned in the case of bonding site 2a). Simillary to the isothermic behaviour, in the case of desorption kinetics it can also be noted that the uncertainty of the applied models is smaller at the K series than at the I series: in other words the scattering of data points decreases with increasing incubation time. The explanation also can be the same: if the surface has enough time to be recovered, it becomes more well-defined, and experimental uncertainties become smaller.

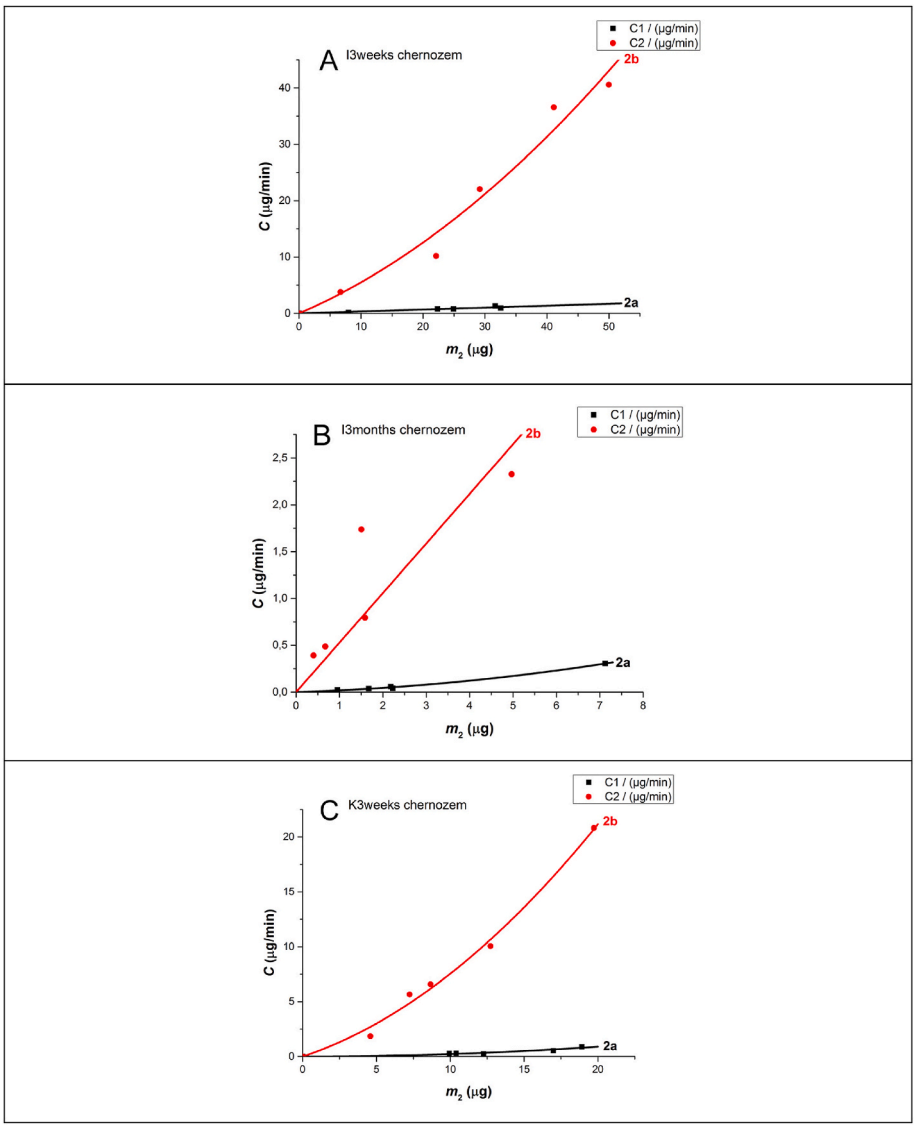

Fig. 3. Desorption kinetic curves of chernozem soil; A: I3weeks (1st order at 2a and 1-2nd order at 2b), B: I3months (1-2nd order at 2a and 1st order at 2b), C: K3weeks (2nd order at 2a and 1-2nd order at 2b) (C is the steady-state rate at bonding site 2a or 2b in µgP/min, m_2 is the amount of weakly bonded phosphate at bonding site 2a or 2b in µgP).

3.2. Marshy meadow soil

The fitted kinetic curves of the heterogeneous isotopic exchange for the series I1week, I3weeks, I3months, K1week, K3weeks and K3months can be seen in Fig. 4, the fitting parameters and their standard error can be found in Table 12 (Appendix2) and the results (m_1, m_{2a}, m_{2b}, C_1, C_2) in Table 5.

In the I3weeks, K1week and K3months series there are enough experiments with standard errors not higher than the magnitude of the parameters, so these series are judged to be suitable to obtain sorption isotherms (Fig. 5) and to examine the kinetics of desorption (Fig. 6). The parameters of the sorption isotherms are summarised in Table 6, and the rate orders and rate constants of desorption in Table 7.

It can be seen that in the K1week and K3months series the sorption process can be described at both bonding sites by the Langmuir isotherm (Eq. (5)) (Fig. 5 B and C). In the I3weeks series the 2a bonding site shows Langmuir characteristics (Fig. 5 A 2a curve), while the sorption at bonding site 2b can be described by the S-shape sorption isotherm (Eq. (6)) with $K_2 > K_1$ (Fig. 5 A 2b curve, Table 6 column 3). This would mean, that the sorption of phosphate ions at bonding site 2b shows positive cooperativity, but this can be stated only with high uncertainty because data points are missing both from the middle and from the saturation part of the curve. We cannot exclude cooperativity at 2b even in the series K1week and K3months because, as we can see in Fig. 5, all the data points are from the initial, linear part of the sorption isotherm. Nevertheless, the application of the Langmuir isotherm in the K1week series at bonding site 2a is reliable, because the distribution of data points is quite homogeneous, their scattering is relatively small, and they occur both in the initial, linear and in the middle, dynamic part of the curve.

As for the desorption kinetics, based on the R^2 values it is in almost all series at both types of bonding sites first order (1), except in the case of K1week at bonding site 2b where there is second order (2) (Fig. 6 B 2b curve). However, in the case of bonding site 2b rate order can be determined only with high uncertainty because of the scattering of the data points: it is especially true for I3weeks 2b (Fig. 6 A 2b curve) where the fitting parameters do not have reliable physical meaning. Simillary to chernozem soil, the slower desorption process takes part at bonding site 2a, and the values of the rate constants for the different series are very close to each other (0.0184, 0.0196 and 0.0190 min^{-1} for I3weeks, K1week and K3months, Table 7 row 4), which clearly indicates that they belong to the same process. The faster desorption process takes part at

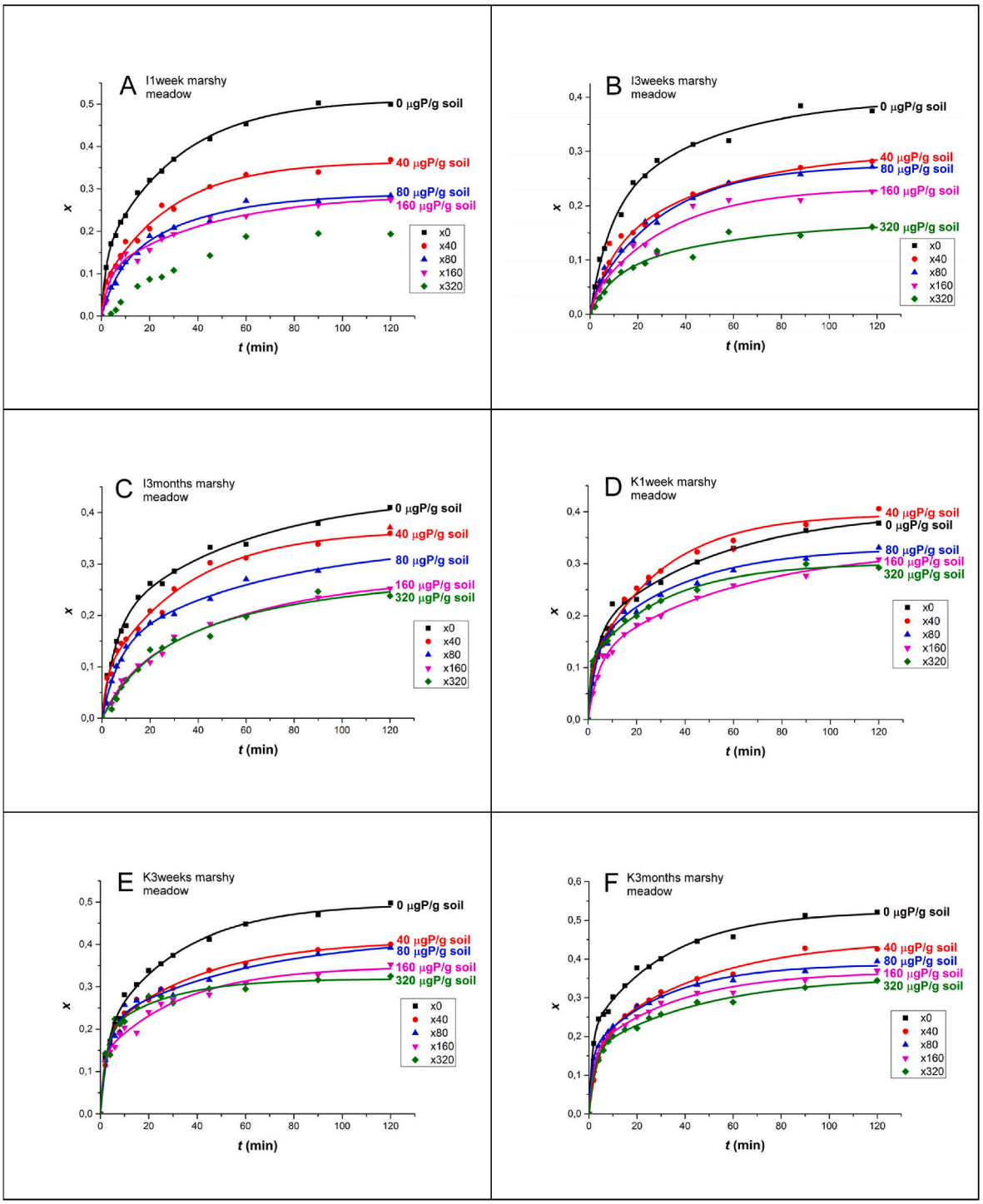

Fig. 4. Biexponential kinetic curves of heterogeneous isotopic exchange on marshy meadow soil; A: I1week, B: I3weeks, C: I3months, D: K1week, E: K3weeks, F: K3months (x is the relative radioactivity of soil, t is time).

bonding site 2b, and the values of rate constants here are also in the same magnitude (0.113, 0.641 and 0.421 min^{-1} for I3weeks, K1week and K3months, Table 7 row 4), so they probably also belong to the same process (the differences can be explained by the bigger scattering of data points compared to 2a).

3.3. Meadow soil

The fitted kinetic curves of the heterogeneous isotopic exchange for the series I1week, I3weeks, I3months, K1week, K3weeks and K3months can be seen in Fig. 7, the fitting parameters and their standard error can be found in Table 13 (Appendix2) and the results (m_1, m_{2a}, m_{2b}, C_1, C_2) in Table 8.

In the I1week, K1week, K3weeks and K3months series there are enough experiments with standard errors not higher than the magnitude of the parameters, so these series are judged to be suitable to obtain sorption isotherms (Fig. 8) and to examine the kinetics of desorption (Fig. 9). The parameters of the sorption isotherms are summarised in Table 9, and the rate orders and rate constants of desorption in Table 10.

It can be observed that in the K3week and K3months series the

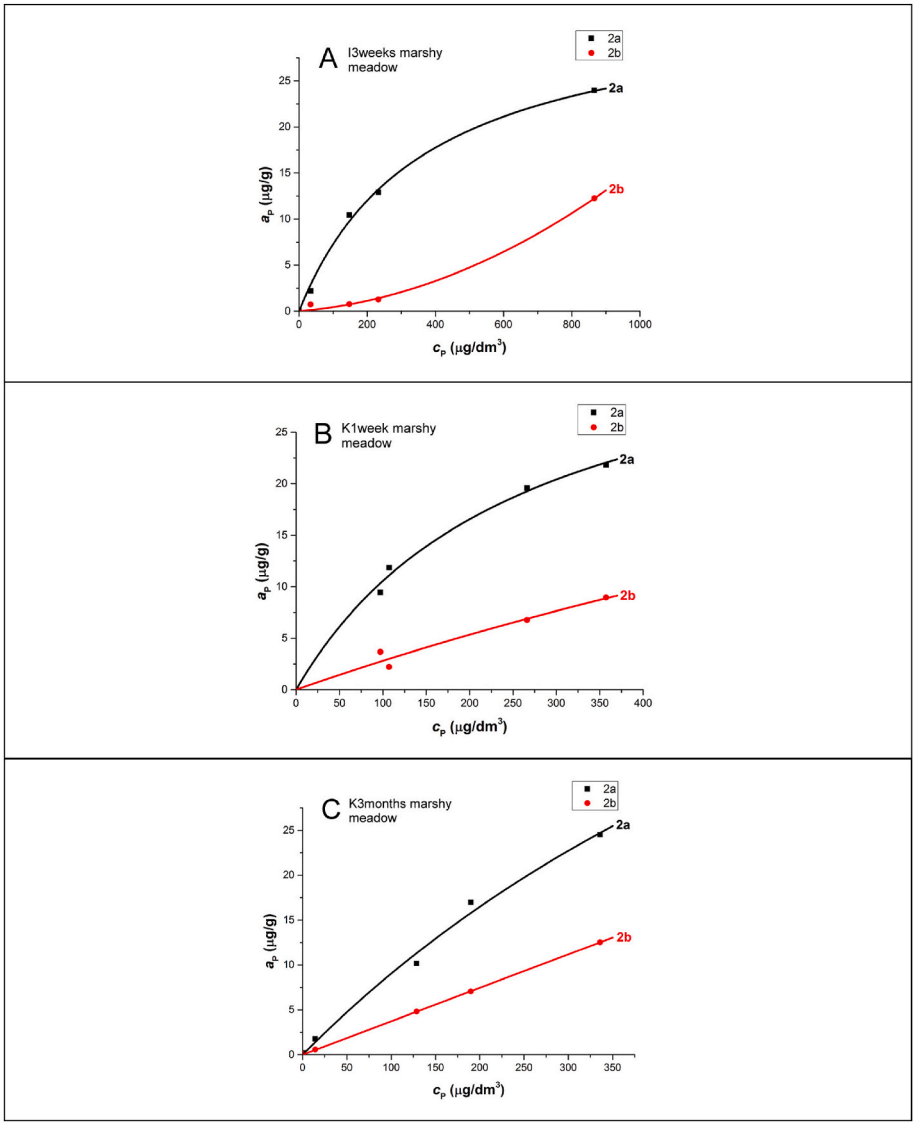

Fig. 5. Sorption isotherms of marshy meadow soil; A: I3weeks (Langmuir at 2a and S-shape at 2b), B: K1week (Langmuir at both 2a and 2b), C: K3months (Langmuir at both 2a and 2b) (a_P is the amount of weakly bonded phosphate at bonding site 2a or 2b in µgP/g soil, c_P is the equilibrium concentration of phosphate in the soil solution in µgP/dm^3 solution).

sorption process can be described at both bonding sites by the Langmuir isotherm (Eq. (5)) (Fig. 8 C and D), however in the case of K3months the sorption characteristics of bonding site 2b is uncertain because all the data points are from the initial, linear part of the sorption isotherm (Fig. 8 D). In the I1week and K1week series the 2a bonding site shows Langmuir characteristics (Fig. 8 A and B 2a curve), while the sorption at bonding site 2b can be described by the S-shape sorption isotherm (Eq. (6)) with positive cooperativity $K_2 > K_1$ (Fig. 8 A and B 2b curve, Table 9 columns 3 and 6). In the case of I1week and K3weeks, the data points are unevenly distributed. However, in the K1week series, both the distribution and the scattering of data points are optimal, that is why the application of both the Langmuir at 2a and the S-shape sorption isotherm at 2b can be considered reliable.

Based on the R^2 values, the desorption kinetics is in almost all series at both types of bonding sites first order (1) except in the case of K3months at bonding site 2a (Fig. 9 D), where second order (2) kinetics occurs, and at K1week 2b where there is mixed first second order (1-2) (Fig. 9 B). Simillary to chernozem and marshy meadow soils, the slower desorption process takes part at bonding site 2a, and the values of the rate constants for the different series are very close to each other (0.0226, 0.0219 and 0.0223 min^{-1} for I1week, K1week and K3weeks, Table 10 row 4), which clearly indicates that they belong to the same process. The faster desorption process takes part at bonding site 2b, and the values of rate constants here are also similar (0.910, 0.764, 0.675 and 1.009 min^{-1} for I1week, K1week, K3weeks and K3months, Table 10 row 4), so they probably also belong to the same process.

4. Discussion

The biexponential kinetic equation (Vörös et al., 2024) for the heterogeneous isotopic exchange of phosphate ions was tested on three types of humic soils. We can see that the equation fits the experimental data points well, which proves that in the case of these soils there are also two types of weakly bonded phosphates, which exchange with two different steady-state rates, just like we observed it earlier in the case of rendzina soil (Vörös et al., 2024). The slower and the faster exchange processes can be clearly separated. This is in accordance with the results of Lookman et al., 1995; Brown et al., 2020, who found that there are two types of desorbeable phosphate in soil: there is a fast and a slow desorption process. Nazarian et al. (2021) got similar results for the sorption of phosphate ions on lanthanum oxide. The biexponential equation makes it possible to examine the kinetics and thermodynamics

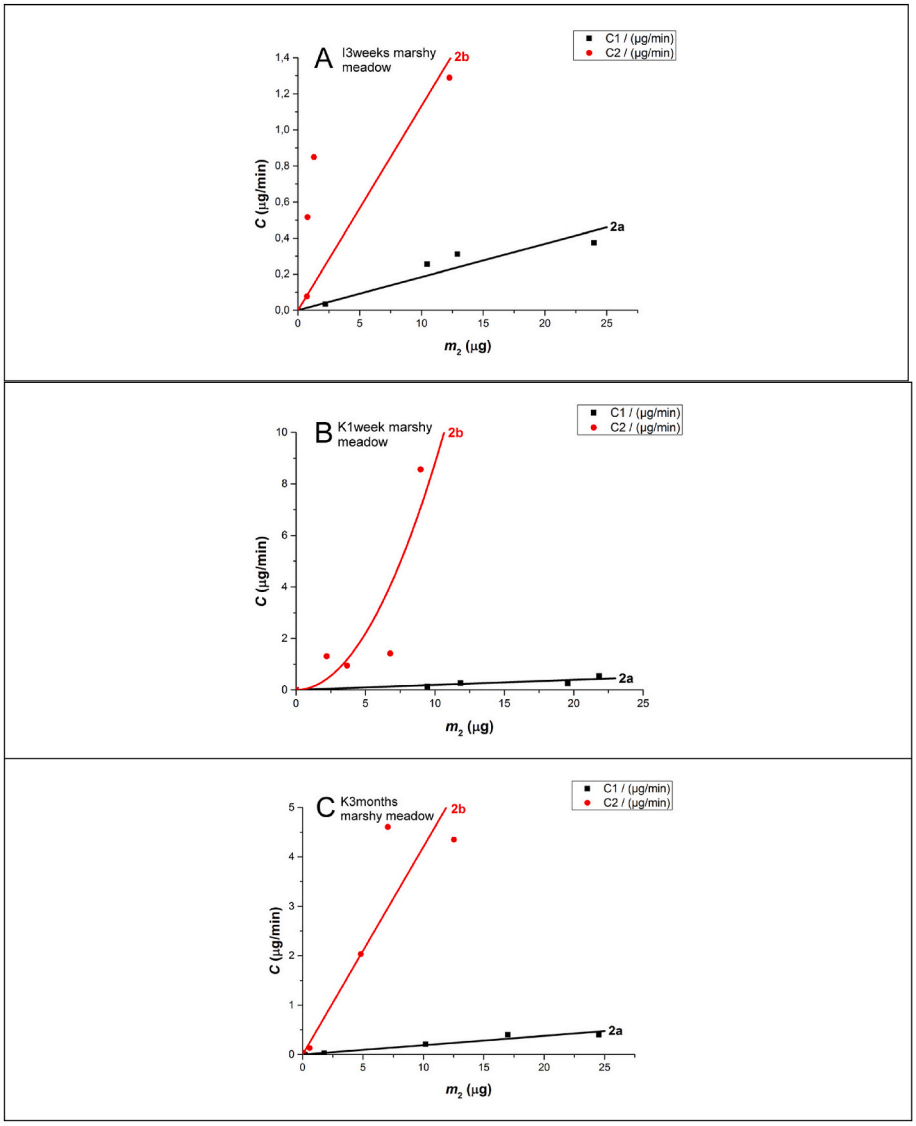

Fig. 6. Desorption kinetic curves of marshy meadow soil; A: I3weeks (1st order at both 2a and 2b), B: K1week (1st order at 2a and 2nd order at 2b), C: K3months (1st order at both 2a and 2b) (C is the steady-state rate at bonding site 2a or 2b in µgP/min, m_2 is the amount of weakly bonded phosphate at bonding site 2a or 2b in µgP).

of the sorption and desorption at the two different sites separately. Under the conditions of the experiments, in most cases the amount of sorbed phosphate at the slower bonding site (2a) is more than that of sorbed phosphate at the faster bonding site (2b), however, in the case of chernozem soil, they have about the same amounts. At the faster bonding site (2b) in some cases positive cooperativity can be observed during the sorption process, which can be explained in such way that a sorbed phosphate ion can help to fix the position of another one for example, via hydrogen bonds.

It is worth to mention that the results of the fitting of S-shape isotherm should be taken rather qualitatively than quantitatively: this means that we can decide in this way if there is some kind of cooperativity or not, but we cannot use for example the sorption constants for further thermodynamic investigations. This is so partly because of the relative high number of fitting parameters related to the number of data points (in the best case 6 data points including the 0; 0 point and 3 parameters); on the other hand, as we mentioned before, this sorption model is also a simplification. However, based on the results of this study we can draw up new experiments with more data points, where the S-shape isotherm could be used even quantitatively and the reliability of the Langmuir fittings would also increase. We should emphasize that the aim of this study was not to get proper isotherms in all cases: we simply wanted to examine how to get thermodynamic and kinetic data from the biexponential isotope exchange model. We also wanted to clarify what kind of problems can occur, and what causes that in some cases well fitting istotherms can be obtained while in other cases the fitting is pure or even unuseable.

It is interesting to see that the values of the first order rate constants are almost the same for each of the three types of soil: they are ca. in the range of 0.02–0.04 min^{-1} for 2a and 0.5–1.0 min^{-1} for 2b. This means that they do not depend on the type of soil, and they can have some relation to the general structure of soils. One possible explanation is, that 2b belongs to the outer surface of the soil while the 2a sites are inside the particle, and the rates are diffusion controlled. The diffusion is much more difficult from the inner sites that is why desorption rate at 2a is by about 2 magnitudes slower than at 2b. This is in accordance with the experiences of Shariatmadari et al. (2006), who found that the phosphate release from calcareous soils consists of two parallel diffusion controlled steps. However, Arroyave and Avena, 2020, examined the kinetics of phosphate desorption from goethite, and they concluded that it is reaction controlled with a rate constant $k_d = 1.66 \bullet 10^{-5}\ s^{-1}$ which is equal to 0.001 min^{-1}. This means that their rate constant for the

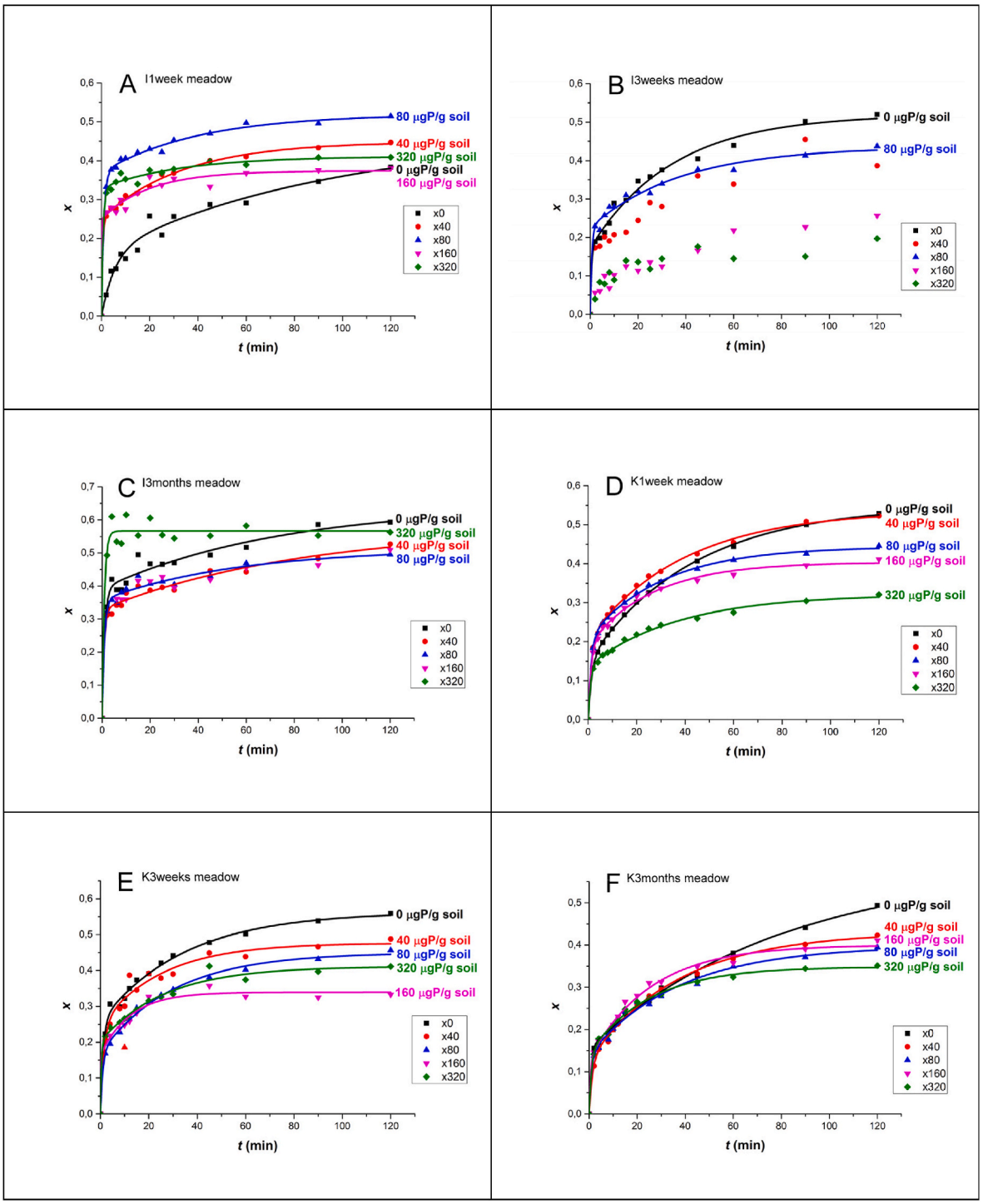

Fig. 7. Biexponential kinetic curves of heterogeneous isotopic exchange on meadow soil; A: I1week, B: I3weeks, C: I3months, D: K1week, E: K3weeks, F: K3months (x is the relative radioactivity of soil, t is time).

desorption of phosphate ions from goethite is about a magnitude smaller than the rate constants for the slower processes in our systems at bonding site 2a. Andrieux-Loyer and Aminot, 2023, obtained similar values for the rate constants of the desorption of phosphate ions from coastal sediments (0.001–0.002 min^{-1}). However, we should also consider that our systems are soils which are more complex than pure goethite and also contain organic matter. Xie et al. (2019), found that organic matter (in their study fulvic acid) can promote the desorption of phosphate ions. This is in accordance with the fact that the rate constants obtained for the soils examined in our study are a magnitude bigger than the desorption rate constants for the phosphate-goethite system. According to this, one possible explanation for the rate constants at bonding site 2a is that they belong to the desorption of phosphate ions from metal oxides or hydroxides which have interactions with the soil organic matter. However, Eichler-Löbermann et al., 2017, discovered that in the case of compost fertilizer the amount of mobile phosphate is bigger than in cases where manure was applied. This underlines that the role of organic matter in the fixation of soil phosphorus is very complex, and to clarify this role, further experiments should be done.

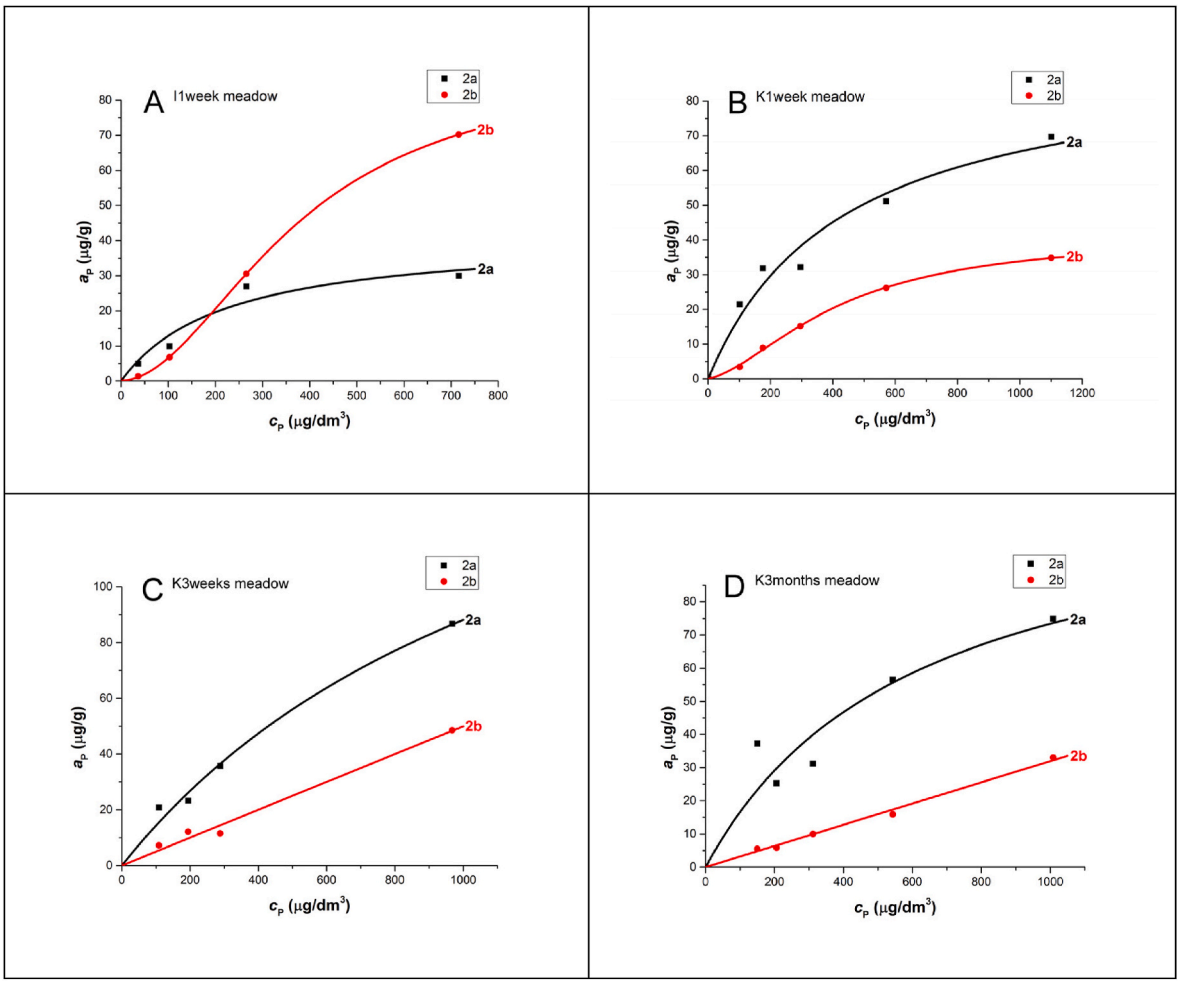

Fig. 8. Sorption isotherms of meadow soil; A: I1week (Langmuir at 2a and S-shape at 2b), B: K1week (Langmuir at 2a and S-shape at 2b), C: K3weeks (Langmuir at both 2a and 2b), D: K3months (Langmuir at both 2a and 2b) (a_P is the amount of weakly bonded phosphate at bonding site 2a or 2b in µgP/g soil, c_P is the equilibrium concentration of phosphate in the soil solution in µgP/dm^3 solution).

5. Summary and conclusion

The new biexponential kinetic equation established by Vörös et al. (2024) was tested on three types of humic soil (chernozem, marshy meadow and meadow), and it fits well experimental data points. From this, it can be concluded that in the case of these soils there are also at least two types of weakly bonded phosphate, just like we experienced earlier in the case of rendzina soil examined in our previous study (Vörös et al., 2024). The faster and slower exchange processes can be clearly separated, which makes it possible to determine the amounts of the two different types of weakly bonded phosphate and their steady-state rates. It is important to emphasize that the amounts of weakly bonded phosphate in this way are really in exchange with the phosphate ions in the soil solution, which also enables to establish equilibrium sorption isotherms. This is the main advantage of this method over the simple batch experiments, where the reversibly and irreversibly sorbed phosphate cannot be separated.

In most cases we were able to fit experimental data points obtained from the biexponential kinetic equation and photometry at both the slower and the faster exchange site by the Langmuir or the S-shape sorption isotherm. In some cases the Langmuir isotherm could be applied with relatively high reliability, while in other cases it was very uncertain because of the uneven distribution of data points or their high scattering. The S-shape sorption isotherm can be applied only for qualitative purposes – this means that we can decide with it if there occurs some kind of cooperativity between the sorption site sor not. It can also be observed that the longer is the incubation time, the smaller is the scattering of data points and the reliable is the parameter evaluation both at the isotherm fittings and during the examination of desorption kinetics. The reason for this can be that the treatment by KH_2PO_4 alters in some way the soil surface, but after a certain time it will be recovered or at least stabilized. From this we can also conclude that if we want to gain reliable sorption isotherms and desorption kinetic parameters we should choose longer incubation times (at least 3 months for example).

The characteristics of the soils examined in this study have both similarities and differences. In the case of chernozem, it can be concluded that the desorption at both bonding site 2a and 2b is complex, and can be divided into further processes with different rate orders. The first order rate constants do not change significantly, but the significance of the second order process, especially at the slower bonding site 2a increases with incubation time. In some cases, cooperativity can be observed according to the sorption isotherm, but there is no direct relationship between the characteristics of the sorption isotherm and the desorption kinetics. The sorption process on marshy meadow soil is more simple compared to chernozem, and the desorption at bonding sites 2a and 2b seem to be single processes, however, complex processes cannot be excluded, especially at 2b, because of the high uncertainty of the rate order. The presence of complex processes is also supported by the fact that in the I3weeks series at bonding site 2b cooperativity occurs. The sorption process on meadow soil is also complex, and cooperativity can occur at the faster bonding site 2b. The desorption shows in most of the cases first order kinetics, but with increasing incubation

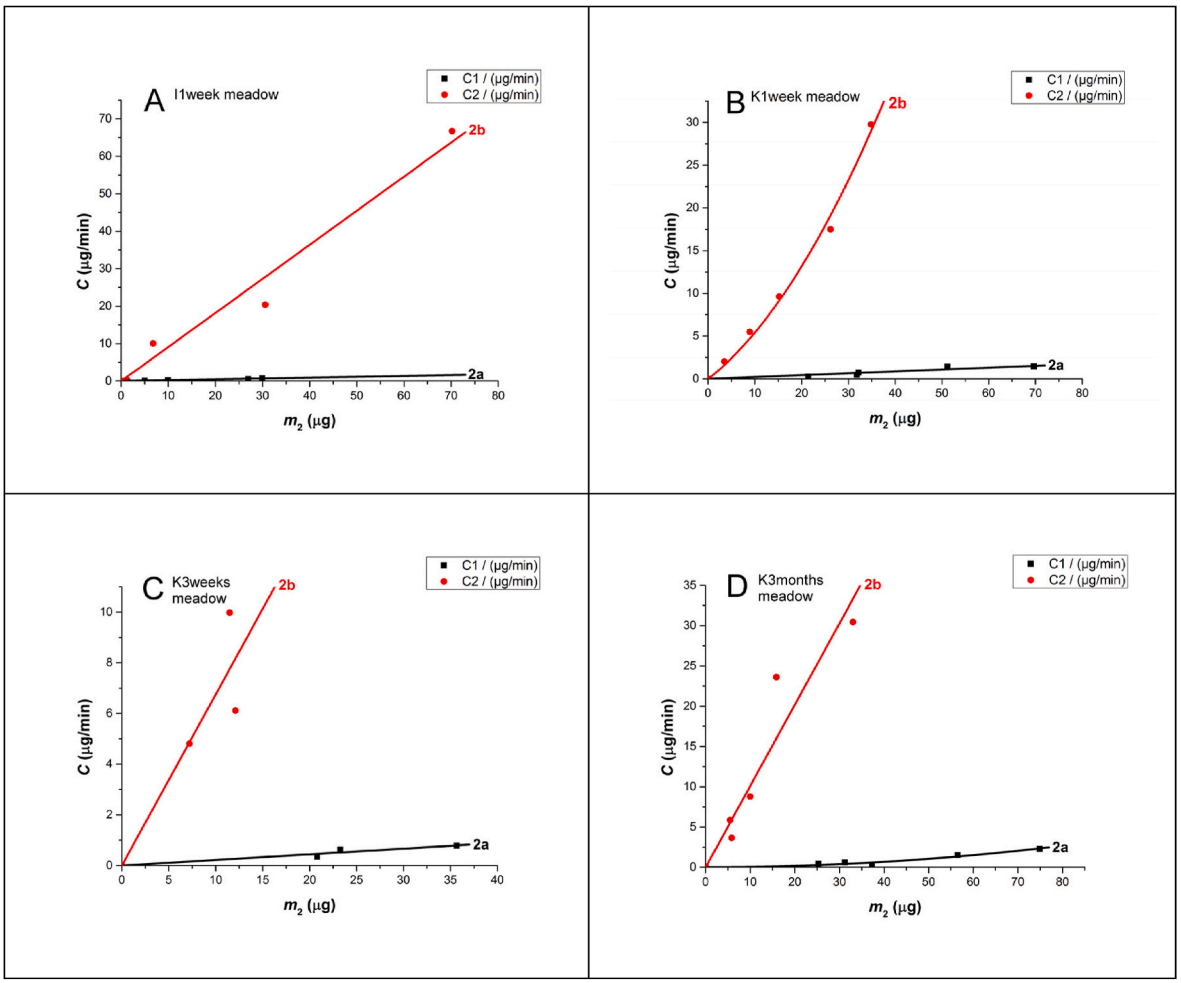

Fig. 9. Desorption kinetic curves of meadow soil; A: I1week (1st order at both 2a and 2b), B: K1week (1st order at 2a and 1-2nd order at 2b), C: K3weeks (1st order at both 2a and 2b), D: K3months (2nd order at 2a and 1st order at 2b) (*C* is the steady-state rate at bonding site 2a or 2b in µgP/min, m_2 is the amount of weakly bonded phosphate at bonding site 2a or 2b in µgP).

time, second order kinetics also can appear. The positive cooperativity occurring in the sorption process on the soils is probably due to hydrogen bonding between the sorbed hydrogenphosphate ions. The first order desorption kinetics underlines the simple Langmuir characteristics, while the second order desorption processes might be due to diffusion controlled desorption. To clarify the details of these processes, further theoretical and experimental investigations must be done.

Finally we can conclude that the new biexponential kinetic equation can be satisfactorily applied for the heterogeneous isotopic exchange of phosphate ions on humic soils, and the amounts of the two different types of weakly bonded phosphate and their steady-state rates can be calculated. These data can also be used for the examination of the kinetics of desorption, and real equilibrium sorption isotherms can be obtained as well. However, while fitting the isotherms, some technical problems can occur because of the uneven distribution of the data points or their high value of scattering. In order to mitigate these problems, longer incubation times and more experiments at several different phosphate concentrations are suggested.

CRediT authorship contribution statement

János Z. Vörös: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **József Kónya:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Noémi M. Nagy:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Data availability

All the data used in this article can be found in the main text of the manuscript and Appendix2 and in the Supplementary.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the Hungarian National Research, Development and Innovation Office [NKFIH K 120265].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apradiso.2024.111602.

References

Andrieux-Loyer, F., Aminot, A., 2023. Adsorption-desorption kinetics of phosphate between sediment and water in coastal areas. Estuar. Coast Shelf Sci. 292, 108453. https://doi.org/10.1016/j.ecss.2023.108453.

Arroyave, J.M., Avena, M., 2020. Determining rate coefficients for ion adsorption at the solid/water interface: better from desorption rate than from adsorption rate. Phys. Chem. Chem. Phys. 22 (20), 11695–11703. https://doi.org/10.1039/d0cp00993h.

Atkinson, R.J., Posner, A.M., Quirk, J.P., 1971. Kinetics of heterogeneous isotopic exchange reactions: derivation of an Elovich equation. Proc. Roy. Soc. Lond. A. 324, 247–256. https://doi.org/10.1098/rspa.1971.0138.

Barrow, N.J., 1991. Testing a mechanistic model. XI. The effects of time and of level of application on isotopically exchangeable phosphate. J. Soil Sci. 42, 277–288. https://doi.org/10.1111/j.1365-2389.1991.tb00409.x.

Brown, S., McLaren, T.I., Frossard, E., Tuyishime, J.R.M., Börjesson, G., Gustafsson, J.P., 2020. Phosphorus desorption and isotope exchange kinetics in agricultural soils. Soil Use Manag. 1–13. https://doi.org/10.1111/sum.12674, 00.

Buzetzky, D., Kónya, J., Kovács, E.M., Kovács Balla, A., Kremper, R., Kátai, J., Nagy, N. M., 2023. Analysis of phosphorus forms on different soil types using heterogeneous isotopic exchange reaction. Soil Tillage Res. 225, 105557. https://doi.org/10.1016/j.still.2022.105557.

Desiraju, G.R., Steiner, T., 2001. The Weak Hydrogen Bond in Structural Chemistry and Biology. Oxford University Press.

Eichler-Löbermann, D., Zicker, T., Wacker, K., Uptmoor, R., 2017. Phosphorus budgets and bioavailable phosphorus content in soil – results of a long-term field experiment. In: 25th International Symposium of the International Scientific Centre of Fertilizers „Significance of Sulphur in High-Input Cropping Systems. Groningen (The Netherlands), September 5-9, 2017.

Fardeau, J.C., 1996. Dynamics of phosphate in soils. An isotopic outlook. Fert. Res. 45, 91–100. https://doi.org/10.1007/bf00790658.

Gasser, S.A.A., Nielsen, K., Eichler-Löbermann, B., Armbruster, M., Merbach, I., Franko, U., 2023. Simulating the soil phosphorus dynamics of four long-term field experiments with a novel phosphorus model. Soil Use Manag. 39, 867–880. https://doi.org/10.1111/sum.12881.

IUSS Working Group WRB, 2014. World Reference Base for Soil Resources 2014. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps. World Soil Resourcesreports No. 106. FAO, Rome.

Kónya, J., Nagy, N.M., 2015. Determination of water-soluble phosphate content of soil using heterogeneous exchange reaction with ^{32}P radioactive tracer. Soil Tillage Res. 150, 171–179. https://doi.org/10.1016/j.still.2015.01.002.

Kosmulski, M., Jaroniec, M., Szczypa, J., 1983. Studies of isotope exchange kinetics at the electrolyte solution/solid interface. Mater. Chem. Phys. 9, 351–358. https://doi.org/10.1016/0254-0584(83)90010-X.

Liu, S., 2015. Cooperative adsorption on solid surfaces. J. Colloid Interface Sci. 450, 224–238. https://doi.org/10.1016/j.jcis.2015.03.013.

Lookman, R., Freese, D., Merckx, R., Vlassak, K., Riemsdijk, W.H., 1995. Long-Term kinetics of phosphate release from soil. Environ. Sci. Technol. 29, 1569–1575. https://doi.org/10.1021/es00006a020.

Mansell, R.S., Selim, H.M., Fiskell, J.G.A., 1977. Simulated transformations and transport of phosphorus in soil. Soil Sci. 124, 102–109. https://doi.org/10.1097/00010694-197708000-00007.

Misak, N.R., 1993. Langmuir isotherm and its application in ion exchange reactions. React. Polym. 21, 53–64. https://doi.org/10.1016/0923-1137(93)90054-J.

Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27, 31–36. https://doi.org/10.1016/S0003-2670(00)88444-5.

Nagy, N.M., Buzetzky, D., Kovács, E.M., Kovács Balla, A., Kátai, J., Vágó, I., Kónya, J., 2019. Study of phosphate species of chernozem and sand soils by heterogeneous isotope exchange with 32P radioactive tracer. Appl. Radiat. Isot. 152, 64–71. https://doi.org/10.1016/j.apradiso.2019.06.038.

Nagy, N.M., Kónya, J., 2018. Study of fast and slow consecutive processes by heterogeneous isotope exchange using P-32 radiotracer. J. Radioanal. Nucl. Chem. 318, 3. https://doi.org/10.1007/s10967-018-6231-4.

Nazarian, R., Desch, R.J., Thiel, S.W., 2021. Kinetics and equilibrium adsorption of phosphate on lanthanum oxide supported on activated carbon. Colloids Surf. A Physicochem. Eng. Asp. 624, 126813. https://doi.org/10.1016/j.colsurfa.2021.126813.

Probert, M.E., Larsen, S., 1972. The kinetics of heterogeneous isotopic exchange. J. Soil Sci. 23, 76–81. https://doi.org/10.1111/j.1365-2389.1972.tb01643.x.

Shariatmadari, H., Shirvani, M., Jafari, A., 2006. Phosphorus release kinetics and availability in calcareous soils of selected arid and semiarid toposequences. Geoderma 132, 261–272. https://doi.org/10.1016/j.geoderma.2005.05.011.

Vörös, J., Kónya, J., Nagy, N.M., 2024. Study of phosphate sorption on rendzina soil by heterogeneous isotopic exchange: a biexponential kinetic model. J. Radioanal. Nucl. Chem. 333, 1011–1028. https://doi.org/10.1007/s10967-023-09325-1.

Xie, F., Dai, Z., Zhu, Y., Li, G., Li, H., He, Z., Geng, S., Wu, F., 2019. Adsorption of phosphate by sediments in a eutrophic lake: isotherms, kinetics, thermodynamics and the influence of dissolved organic matter. Colloids Surf. A Physicochem. Eng. Asp. 562, 16–25. https://doi.org/10.1016/j.colsurfa.2018.11.009.