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Kinetics of the PO₄-P adsorption onto soils and sediments from the Mondego estuary (Portugal)



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ABSTRACT

In order to assess the status of a North Atlantic Ocean Ecoregion (Mondego system, Portugal) after the implementation of a management programme, a study on PO₄-P sorption was carried out. Considering that sorption velocity markedly determines the systems promptness to phosphorus external loading, the kinetics of the sorption of PO₄-P onto estuarine sediments and the upstream agricultural soils was studied. The pseudo-second order kinetic equation gave an appropriate description of PO₄-P sorption onto these soils and sediments, allowing for a quantitative comparison. For soils, the kinetic constants (k_2^* , $\mu\text{g}^{-1} \text{g h}^{-1}$) ranged between 0.007 and 0.017 $\mu\text{g}^{-1} \text{g h}^{-1}$ while, in the case of sediments these ranged between 0.008 and 0.012 $\mu\text{g}^{-1} \text{g h}^{-1}$. Results showed that the reduction of water residence time after the management action was relevant for the system status, affecting its reaction capacity to phosphorus loading.

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1. Introduction

Estuarine eutrophication is still a worrying problem all over the world. Although a causal link between anthropogenic nutrient sources and the occurrence of eutrophication symptoms is generally accepted (Smith, 2006), a straightforward relationship does not exist but the response to nutrient loading is system-specific (McQuatters-Gollop et al., 2009). Mostly, the nutrient status and budgets of estuaries depend on two main sources: (a) loading from diffuse and point sources; and (b) internal loading originating from the sediments (Zwolsman, 1994; Paludan and Morris, 1999; Coelho et al., 2004; Lillebø et al., 2004).

Regarding P, coastal systems may have a key role as buffer zones and may halt fluxes of P to coastal seas and to the oceans (López et al., 1996; Pratska et al., 1998; Coelho et al., 2004; Velasco et al., 2006; Wang and Li, 2010) but they may also act as P sources (Pratska et al., 1998; Wang et al., 2012). The role of estuaries as sources or sinks of P is regulated, to a higher or lesser extent, by sorption processes (Pratska et al., 1998) and the concentration and risks of P losses to overland and subsurface water flows is

dependent upon the ability of soils and/or sediments to sorb P (López et al., 1996; Kaňa and Kopáček, 2006). Furthermore, as external P sources become controlled, phosphorus release from sediments may become an important nutrient source (Lu et al., 2013). In any case, the study of the sorption of phosphorus onto sediments can give relevant information for understanding the P distribution in a system (López et al., 1996; Reddy et al., 1998; Zhou et al., 2005; Wang and Li, 2010; Zhang and Huang, 2011).

The Mondego estuary (Portugal), on the North Atlantic Ocean Ecoregion, is a relatively small system (3.4 km²) with a catchment area of 6670 km² (Flindt et al., 1997). This estuary (Fig. 1) receives intensely fertilized agricultural runoff from about 150 km² of local upstream cultivated land, mainly dominated by corn and rice fields (Lillebø et al., 2005) and the increase of eutrophication during the last decades of the 20th century is well-documented (Lillebø et al., 2005, 2012). In 1998, a management action was carried out and the estuarine hydrodynamics were altered aiming to reverse eutrophication in the most affected area of the system. Still, the estuary became polytrophic concerning the concentration of DIP (Lillebø et al., 2007) and the annual mean DIP concentration increased from 1.0 to 1.5 $\mu\text{mol P L}^{-1}$ between 1998 and 2008. The absence of a clear seasonal trend in the total amounts of exchangeable P or P speciation in the top layer of the sediment was pointed out by Coelho et al. (2004). These authors (Coelho et al., 2004) also highlighted that the annual net-export from the estuary (14 t P year⁻¹) was approximately 30 times lower than pools of exchangeable P,

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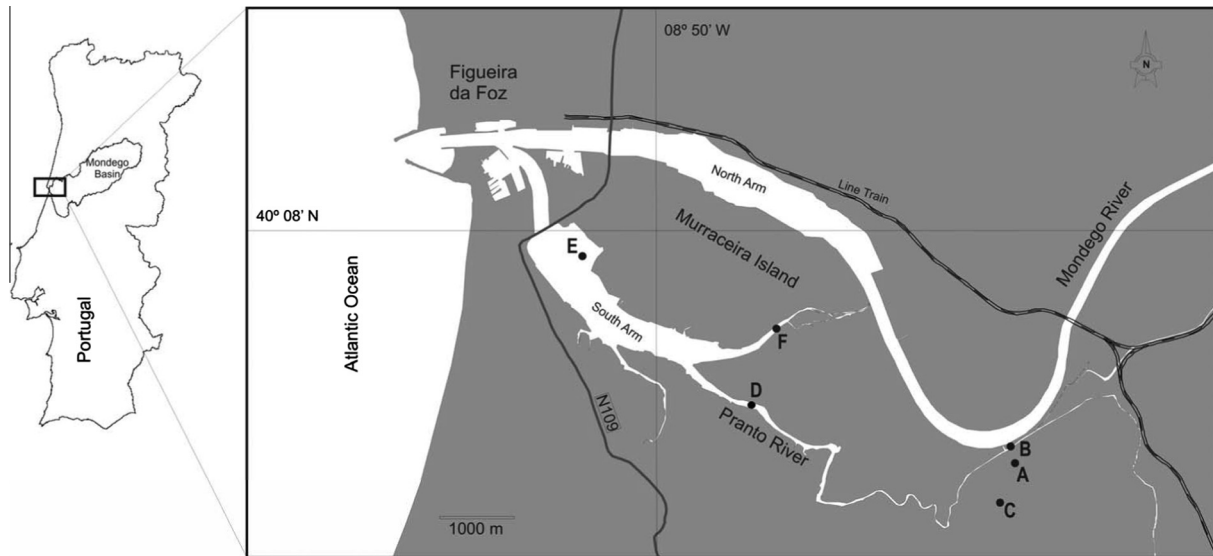


Fig. 1. Sampling sites at the Mondego estuary.

concluding that the annual P release from sediments was small compared to the pool-size. This background information led us to question if endogenous mineralization processes were still the main phosphate source to the water column, and/or if the increase in the concentration of DIP, namely during winter, could be linked with changes to the estuarine hydrology and to P adsorption processes.

In a previous work (Lillebø et al., 2012), a study on the adsorption equilibrium of phosphorus was carried out, showing that, in the Mondego estuary: (i) until 1998 (Fig. 2(a)), a nutrient-rich freshwater input from upstream cultivated lands entered the system through an area where sediments have a relative high $\text{PO}_4\text{-P}$ adsorption capacity and $\text{PO}_4\text{-P}$ availability in the water column was mostly dependent on the mineralization processes; (ii) after 1998 (Fig. 2(b)), freshwater was diverted to an area with a much lower $\text{PO}_4\text{-P}$ adsorption capacity and, consequently, sediments were not able to adsorb much of the $\text{PO}_4\text{-P}$, which led to a higher equilibrium concentration in the water column. In addition, in the first period the current velocity was low and dependent on the Pranto river sluice, whilst after 1998 became higher and not dependent on the Pranto river sluice (Lillebø et al., 2007). Previous studies have also shown that the Pranto river was the main source of nutrients (e.g. Martins et al., 2001; Lillebø et al., 2005, 2007; Leston et al., 2008).

Together with freshwater diversion, another change was induced in the hydrology of the Mondego estuary from 1998 on, which was the decrease of the water residence time in the estuary from moderate (weeks) to short (days) (Lillebø et al., 2007). Thus, in the present work, the sorption kinetics of $\text{PO}_4\text{-P}$ onto estuarine sediments and onto upstream agricultural soils was studied in order to assess its relative relevance regarding DIP concentration in the water column after changes to estuarine hydrology.

2. Materials and methods

2.1. Study area

The Mondego estuary is a warm-temperate system located on the Atlantic coast of Portugal (40°08' N, 8°50' W). (For a more detailed description, please see Flindt et al., 1997; Lillebø et al., 2005; Lillebø et al. 2012).

2.2. Sample collection and characterization

Three composite samples (each $N = 7$) from agricultural soils upstream (A, B and C) and three composite surface sediment samples (each $N = 7$) (D, E and F) were collected at the sites shown in Fig. 1. A detailed description on soils and sediments collection, transportation, laboratory procedures and characterization may be found elsewhere (Lillebø et al., 2012). Main properties of soils and sediments collected are shown in Table 1. Based on the soils and sediments properties, specifically moisture content, pH, total Fe and Fe oxides concentrations, and according to the similarities of their physicochemical properties, the sampled areas were divided into three groups: (1) sediment D, (2) soils B and C, and sediment E, and (3) soil A and sediment F.

2.3. Phosphorus sorption kinetics study

In the present work, a kinetic study was carried out to determine the affinity of the soils and sediments under study for phosphorus and the $\text{PO}_4\text{-P}$ sorption velocity onto them. In both cases, adsorption experiments were carried out using homogenised samples (particle diameter ≤ 1 mm) and the experimental design was based on the OECD Guideline (Dir 2001/59/EC, C18, 2001), for the Determination of Soil Adsorption/Desorption, using a Batch Equilibrium Method.

According with this OECD Guideline, a preliminary batch stirred sorption study was first carried out in order to: (1) determine an appropriate solid (soil or sediment) to solution ratio regarding the accuracy of the analytical methodology and the sorption capacity of the solids; (2) establish the time range for the kinetic study. It was found that 1 g of each solid and 20 mL of $\text{PO}_4\text{-P}$ solution ($2000 \mu\text{g L}^{-1}$) was an appropriate ratio for all the soils and sediments under study and that equilibrium time was around 48 h.

Taking into account the results from the preliminary study, and according with the OECD Guideline (Dir 2001/59/EC, C18, 2001), for each soil and sediment, and by triplicate, 1 g was placed in a glass flask together with 18 mL of CaCl_2 (0.01 M) and all flasks were stirred (150 r.p.m) overnight in a GFL 3017 Shaker at controlled room temperature (25 °C). Then, after equilibration, 2 mL of $\text{PO}_4\text{-P}$ stock solution ($20,000 \mu\text{g L}^{-1}$) to each flask and this was the starting point (time zero, $t = 0$) for the kinetic experiments.

Table 1Physicochemical properties (mean value \pm standard deviation) and Langmuir maximum adsorption capacities of A, B, C soils and D, E, F sediments Source: Lillebø et al. (2012).

Property (unit)	Soils			Sediments		
	A	B	C	D	E	F
Moisture (%)	47.7 \pm 9.4	15.2 \pm 1.1	21.7 \pm 0.8	44.2 \pm 3.3	33.6 \pm 3.1	48.5 \pm 3.0
LOI (%)	6.6 \pm 0.5	2.6 \pm 1.6	4.0 \pm 0.05	6.6 \pm 0.8	4.0 \pm 0.4	6.8 \pm 1.5
TOC (%)	2.12 \pm 0.10	1.05 \pm 0.25	1.49 \pm 0.61	1.63 \pm 0.20	1.25 \pm 0.14	2.27 \pm 0.44
Bulk density (kg L ⁻¹)	0.69 \pm 0.18	1.64 \pm 0.04	1.37 \pm 0.03	0.75 \pm 0.07	1.01 \pm 0.08	0.67 \pm 0.06
pH [H ₂ O]	5.7 \pm 0.1	7.5 \pm 0.1	7.4 \pm 0.0	7.1 \pm 0.0	7.1 \pm 0.1	6.8 \pm 0.0
pH [CaCl ₂]	5.3 \pm 0.1	6.9 \pm 0.0	7.1 \pm 0.1	7.0 \pm 0.0	6.9 \pm 0.1	6.7 \pm 0.1
Total P (mg g ⁻¹)	0.66 \pm 0.02	0.30 \pm 0.05	0.64 \pm 0.12	0.78 \pm 0.04	0.37 \pm 0.04	0.48 \pm 0.09
Total Fe (mg g ⁻¹)	34.77 \pm 0.79	17.36 \pm 0.22	11.00 \pm 0.43	39.65 \pm 0.39	22.03 \pm 0.99	30.23 \pm 0.45
Fe oxides (mg g ⁻¹)	3.39 \pm 0.16	0.67 \pm 0.04	0.80 \pm 0.04	3.64 \pm 0.04	1.47 \pm 0.05	2.14 \pm 0.04
Total Mn (mg g ⁻¹)	0.19 \pm 0.00	0.24 \pm 0.01	0.19 \pm 0.01	0.29 \pm 0.01	0.21 \pm 0.03	0.21 \pm 0.01
Mn oxides (mg g ⁻¹)	0.05 \pm 0.01	0.11 \pm 0.00	0.14 \pm 0.00	0.09 \pm 0.00	0.02 \pm 0.00	0.04 \pm 0.00
Q ($\mu\text{g g}^{-1}$ dwt)	902 \pm 27	554 \pm 34	672 \pm 20	1177 \pm 25	775 \pm 23	796 \pm 32

Table 2Parameters obtained from the linear regressions corresponding to the kinetic equations used to describe the phosphorus (PO₄-P) adsorption onto soils (A, B, C) and sediments (D, E, F) together with the corresponding coefficients of determination (R²) and standard errors (s).

Sample	Lagergren's			Pseudo-2 nd order				Elovich's				Power function			
	k ₁ (h ⁻¹)	R ²	s	k ₂ (μg^{-1} g h ⁻¹)	q _e ($\mu\text{g g}^{-1}$)	R ²	s	α (g μg^{-1})	a ($\mu\text{g g}^{-1}$ h ⁻¹)	R ²	s	ω (g μg^{-1})	σ ($\mu\text{g g}^{-1}$ h ^{-ω})	R ²	s
A	0.132	0.993	0.000	0.009	39.06	0.998	0.000	0.131	33.740	0.992	1.489	0.348	12.565	0.975	0.010
B	0.053	0.924	0.000	0.007	30.67	0.997	0.001	0.160	16.892	0.975	3.928	0.434	6.973	0.904	0.078
C	0.075	0.943	0.000	0.005	29.76	0.992	0.003	0.161	10.761	0.981	2.894	0.514	4.835	0.942	0.063
D	0.094	0.996	0.000	0.007	38.02	0.992	0.001	0.133	25.325	0.979	3.744	0.371	10.753	0.988	0.005
E	0.085	0.887	0.000	0.005	34.25	0.969	0.009	0.141	15.419	0.934	11.252	0.474	6.874	0.923	0.059
F	0.088	0.967	0.000	0.006	39.68	0.994	0.002	0.129	25.509	0.963	9.017	0.407	10.232	0.933	0.048

The stock solution, which was obtained by dissolving the salt KH₂PO₄ (p.a, Sigma–Aldrich) in water (conductivity < 5 $\mu\text{S/cm}$), was prepared within the 24 h before use and kept closed in the dark at 4 °C until use. From the time zero on, stirring was maintained and flasks were removed from the shaker after the following time intervals (*t*): 1, 2, 4, 8, 12, 18, 24, 36, 48, and 60 h. For each soil and sediment, as many flasks as time intervals were prepared in triplicate, all containing the same solid to solution ratio as for the application of a parallel method (Dir 2001/59/EC, C18, 2001). Furthermore, for each *t*, one blank (1 g of sediment/soil and 20 mL of 0.01 M CaCl₂) and one control (2 mL of PO₄-P (20,000 $\mu\text{g L}^{-1}$) in 18 mL of 0.01 M CaCl₂ without solid) were also run in triplicate. After each agitation time considered (1, 2, 4, 8, 12, 18, 24, 36, 48, and 60 h), the corresponding flasks (experiments, blanks and controls) were removed from the shaker. The PO₄-P remaining in solution at each time was determined for each flask removed from the shaker: the supernatant was taken from each flask, centrifuged, filtered (1.2 μm) and analysed for reactive phosphorus (PO₄-P) using the ascorbic acid method, following the Limnologisk Metodik (1992) methodology. The detection limit was 0.2 $\mu\text{g L}^{-1}$ ($y = y_{\text{blank}} + 3 \text{ std}_{\text{blank}}$ (Miller and Miller, 1984)) and the accurate quantification limit 1 $\mu\text{g L}^{-1}$ ($y = y_{\text{blank}} + 10 \text{ std}_{\text{blank}}$ (Miller and Miller, 1984)).

The amount of PO₄-P adsorbed onto the different soils and/or sediments at each time, q_t ($\mu\text{g g}^{-1}$), was calculated by a mass balance relationship (Eq. (1)):

$$q_t = (C_0 - C_t) \frac{V}{W} \quad (1)$$

where C_0 ($\mu\text{g L}^{-1}$) is the initial liquid-phase PO₄-P concentration, C_t ($\mu\text{g L}^{-1}$) is the blank corrected concentration of PO₄-P at the time *t*, *V* (L) is the volume of the solution and *W* (g) is the mass of dried soil/sediment.

From a practical point of view and for comparison purposes, it is very useful to describe experimental results by simple equations that may be used for prediction purposes and may be easily

applied. In this study four different equations, namely the Lagergren's, the pseudo-second order, the Elovich's and the power function, which description is given as [Supplementary material](#), have been used trying to find if any was appropriate for the description of experimental results.

3. Results and discussion

Fig. 3 shows the experimental results corresponding to the sorption of PO₄-P onto the soils and sediments under study (q_t versus *t*) together with fittings to the kinetic equations here considered. As it may be seen in these figures, the sorption of PO₄-P from solution onto the soils and the sediments was relatively rapid in the first few hours and progressively diminished until approaching an apparent equilibrium, which agrees with early published results on P sorption from solution (Van der Zee and Van Riemsdijk, 1986; López et al., 1996). The gradual reduction in PO₄-P sorption rate with time may be a result of occupation of the active sorption sites on the soils and sediments particles. For these soils and sediments, most of PO₄-P is adsorbed during the first 8 h. Moreover, at any rate, sorption equilibrium is reached within 48 h for all soils and sediments. Zhou et al. (2005) obtained similar results for the adsorption kinetics of PO₄-P sorption onto sediments from Chinese Taihu Lake, considering that equilibrium conditions were attained within 48 h.

The rate constants and parameters derived from the linear regression obtained for each of the considered equations are shown in Table 2 together with the respective uncertainties. Fittings in Fig. 3 show that the Lagergren's first-order fits the experimental points once the equilibrium is attained but fails to explain the first stage of PO₄-P sorption onto the soils and sediments under study. The simplified Elovich's equation and the power function describe the first and faster sorption stage but overestimate the PO₄-P sorption at longer times. Relatively good fittings were obtained for the pseudo-second-order equation for all the soils and sediments under study. The appropriateness of this

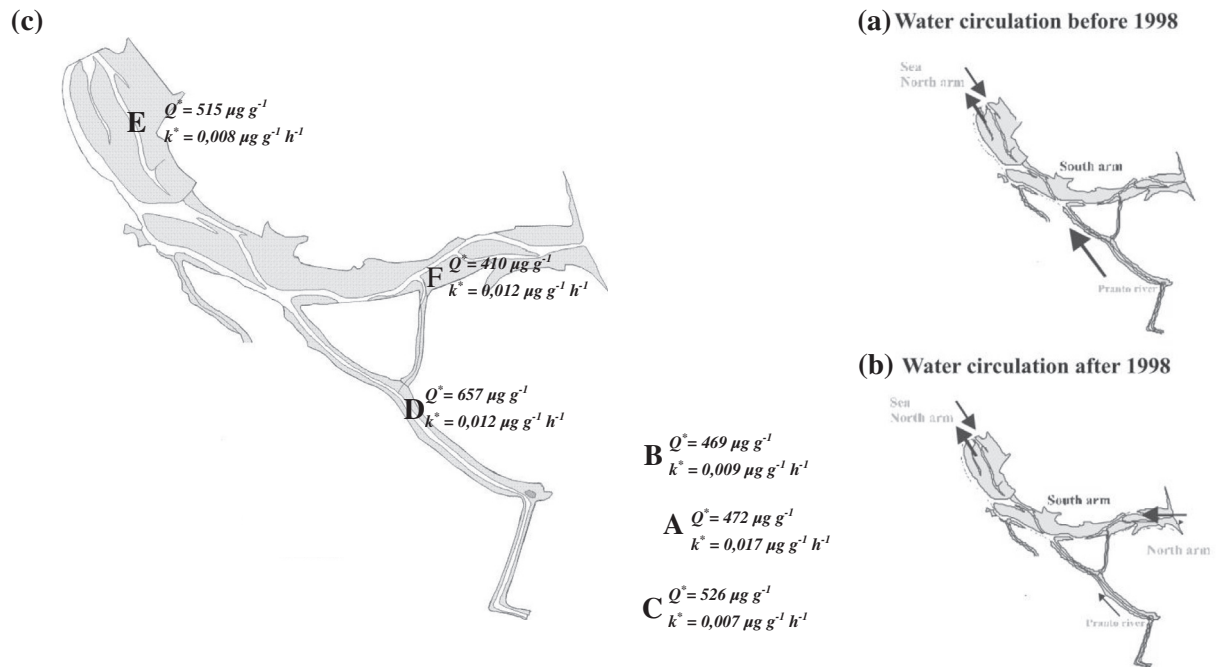


Fig. 2. (a and b) Changes on the system main freshwater sources related to the implementation of the management program. (c) Schematic representation of the south arm of the Mondego estuary with the approximate location of each soil (A–C) and sediment (D–F) together with the corresponding pseudo-second order kinetic parameters corrected for moisture (k_2^*) (this work) and the Langmuir maximum adsorption capacity corrected for moisture (Q^*) (Lillebø et al., 2012), determined for the sorption of $PO_4\text{-P}$.

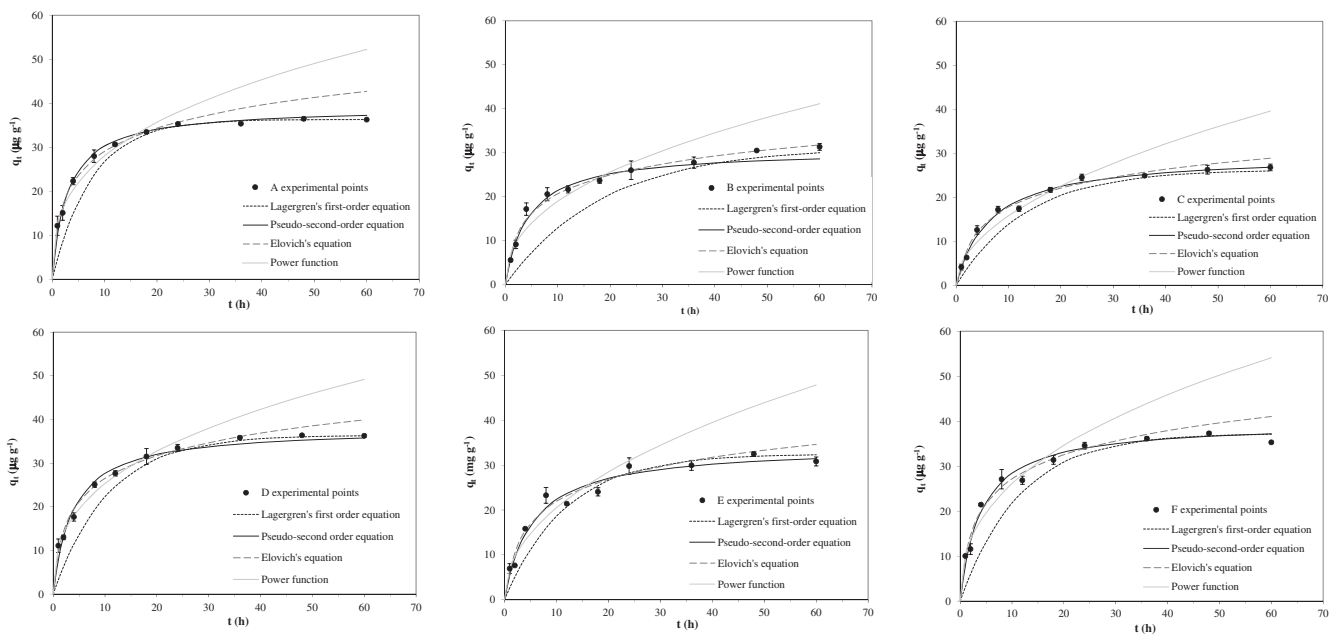


Fig. 3. Experimental kinetic curves (q_t versus t) and fittings corresponding to the different kinetic equations for the sorption of $PO_4\text{-P}$ onto the soils (A–C) and sediments (D–F).

model is coincident with results obtained by Eljamaal et al. (2013) on the kinetics of phosphorus sorption onto natural materials. Consequently, in this work, it may be said that the pseudo-second-order equation can be used for the prediction and comparison of the $PO_4\text{-P}$ sorption kinetics onto the studied solids and assumed that the $PO_4\text{-P}$ sorption rate onto them depend on the number of available sorption sites, which is the driving force.

The previously determined (Lillebø et al., 2012) Langmuir maximum capacities (Q , $\mu\text{gP g}^{-1}$ dwt) for the soils and sediments here

used are shown in Table 1. As it may be seen, the highest Q ($\mu\text{gP g}^{-1}$ dwt) values were those corresponding to A, and D. Coincidentally, in the case of soils, A, from land used for rice cultivation, was the soil displaying the largest kinetic constant k_2 (Table 2). Regarding sediments, they displayed closer $PO_4\text{-P}$ adsorption kinetic constants than soils, and k_2 values were: $D > F > E$. Comparing the kinetic constants obtained for soils and sediments with the physico-chemical characterization, given in Table 1, it must be highlighted that A, D and F are those solids having larger values

of loss on ignition (LOI), total organic carbon (TOC), total Fe and Fe oxides content and lower bulk density. Adsorption velocity was then favoured by the organic matter content of the samples, which is related to LOI (Howard and Howard, 1990). Furthermore, soils and sediments with lower bulk density, which are likely to have higher organic matter levels, displayed higher PO₄-P adsorption velocity. However, total Fe and, specifically, Fe oxides content are the most determining properties regarding PO₄-P adsorption by soils and sediments under study. As it may be seen, A and D, which had the highest total Fe and Fe oxides content among soils and sediments under study displayed, not only the largest k_2 (Table 2) but also the largest Q (Table 1). Thus, total Fe and Fe oxides favoured both the velocity and capacity of PO₄-P adsorption, which is agreement with the literature (McGeacham, 2002; Pant and Reddy, 2001; Zhou et al., 2005). With respect to pH, measured either in H₂O or in CaCl₂, it seems that, in the range of the values found for the solids here used, PO₄-P adsorption capacity is enhanced by relatively low pH values, which has already been observed for sediments (Zhou et al., 2005). Thus, A had the highest Q and k_2 among soils and, as it may be seen in Table 1, it is the soil having the highest Fe oxides content, having a slightly acidic pH, either in H₂O or in CaCl₂. In the case of sediments, as it has already been highlighted, kinetic constants were more alike than for soils. Anyway D and F displayed larger k_2 than E, which must be related to the Fe oxides content. Although in freshwater phosphorus is transported mainly adsorbed to Fe and Al oxides (Lebo, 1991; Zwolsman, 1994), in areas with a higher marine influence, the increase in pH with salinity may prevent phosphate adsorption onto Fe oxides, by shifting the speciation of phosphate from H₂PO₄⁻ to HPO₄²⁻, and by changing the surface charge of the Fe oxides (Lebo, 1991; Zwolsman, 1994).

The k_2 rates obtained in this work indicate that PO₄-P sorption occurs relatively rapidly onto the studied soils and sediments when compared with other adsorbents with higher sorption capacity (Namasivayam and Sangeetha, 2004; Karaca et al., 2004).

All of the above results were obtained and expressed for dry soils and sediments, as required by the corresponding OECD Guideline (Dir 2001/59/EC, C18, 2001). However, as it may be seen in Table 1, soils and sediments have different physicochemical properties, namely concerning moisture content. Thus, to assess the response of the Mondego estuary to the induced changes in the hydrology to control eutrophication, results were corrected for moisture content. The corrected for moisture parameters k_2^* ($\mu\text{g}^{-1} \text{g h}^{-1}$) from the fittings to the pseudo-second order equation together with the corrected for moisture Langmuir capacities (Q^* , $\mu\text{g P g}^{-1}$ ww) are represented in Fig. 2c. As already mentioned for k_2 (from the fittings to the pseudo-second-order equation) the variability of k_2^* ($\mu\text{g}^{-1} \text{g h}^{-1}$) of the soils is relatively high (k_2^* ranged between 0.007 and 0.017 $\mu\text{g}^{-1} \text{g h}^{-1}$) when compared to sediments (k_2^* ranged between 0.008 and 0.012 $\mu\text{g}^{-1} \text{g h}^{-1}$).

In the present study, among all solids, A: from land used for rice cultivation presented the highest k_2^* (0.017, $\mu\text{g}^{-1} \text{g h}^{-1}$). On the other hand, B: from uncultivated land; and C: from land used for maize cultivation showed the lowest sorption kinetics (respectively, $k_2^* = 0.009$ and 0.007, $\mu\text{g}^{-1} \text{g h}^{-1}$). Regarding Langmuir sorption maxima, soils A and B showed quite similar values ($Q^* = 472$ and 469, respectively) while C had a larger sorption maximum ($Q^* = 526 \mu\text{gP g}^{-1}$). Thus, although A has a lower Q^* capacity than C, it is able to faster adsorb P-PO₄. In any case, it may be seen that, even when these soils (A and C) are submitted to strong cultivation and fertilization, they have a higher adsorption rate and/or a higher adsorption capacity than the uncultivated soil (B).

With respect to sediments, those from the Pranto river sluice (D) and from the Southern arm (F) showed equivalent sorption kinetic constants corrected for moisture ($k_2^* = 0.012 \mu\text{g}^{-1} \text{g h}^{-1}$) while sediments from the Gala bridge (E) displayed slower PO₄-P

adsorption kinetics ($k_2^* = 0.008 \mu\text{g}^{-1} \text{g h}^{-1}$). Regarding Langmuir sorption maxima, D had the largest Q^* (657 $\mu\text{gP g}^{-1}$) among all solids under study, and, specifically, a larger Q^* than F ($Q^* = 410 \mu\text{gP g}^{-1}$) and E ($Q^* = 515 \mu\text{gP g}^{-1}$). As stated before, in the Mondego estuary, after 1998, coinciding with freshwater diversion to an area with a much lower PO₄-P adsorption capacity (F, $Q^* = 410 \mu\text{g g}^{-1}$ ww), the water residence time diminished from moderate to short. Taking into account that PO₄-P adsorption velocities at D and at F are equal, from the kinetic point of view, the shorter residence time, but not the hydrology diversion, may have affected the system response promptness to phosphorus (PO₄-P) external loadings. Diversion of water to an area with a much lower PO₄-P adsorption capacity caused a decreased of the system adsorption capacity (Lillebø et al., 2012). However, considering that the water residence time decreased from moderate (weeks) to short (days), sedimentary PO₄-P adsorption kinetics may have not being fast enough for attaining equilibrium, so contributing to the DIP increase in the water column after the hydrological management action.

4. Conclusion

The induced hydrological change implemented in the Mondego estuary constitutes a case study of a North Atlantic Ocean Ecoregion. In this work, it has been shown that the study of the PO₄-P sorption kinetics is a valuable tool for the evaluation of the system response to phosphorus (PO₄-P) external loadings. The pseudo-second order kinetic model gave an appropriate description of PO₄-P sorption onto estuarine sediments and onto the upstream agricultural soils. The study of the sedimentary adsorptive response to the management program implemented in the Mondego system indicated that: (i) hydrology diversion caused a decrease of the PO₄-P retention capacity of the system due to water circulation through an area with lower adsorption capacity; and (ii) a shorter water residence time, but not the adsorption velocity, has reduced the response time of the system, also conditioning the phosphorus status. Since the Mondego system still receives agricultural runoff from upstream cultivated land, conservation measures should be taken to control agricultural runoff. Additional work on the comparison of PO₄-P adsorption and desorption is to be carried out to further elucidate the response of the system. In any case, results obtained in the present work strengthen arguments in favour of management at the system level, which should be accomplished by reducing phosphorus loads, namely by improving agriculture practices in the Mondego river valley and by implementing long term environmentally friendly solutions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.marpolbul.2013.08.039>.

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