

## Assessing exchangeable phosphate and related data in coastal sediments: Theoretical and practical considerations

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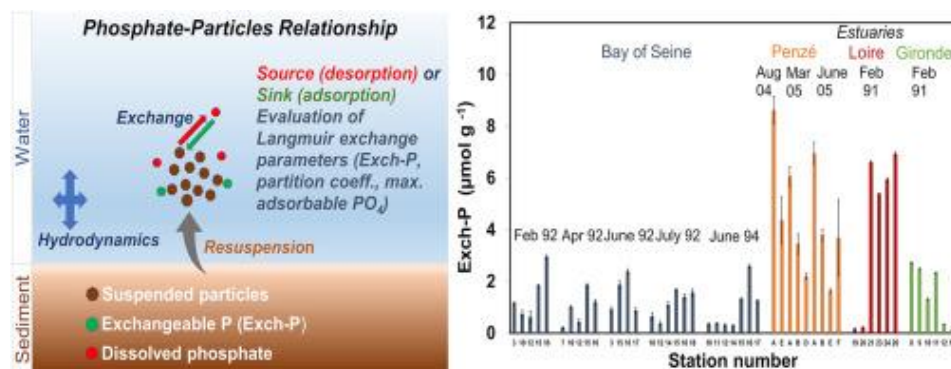
### Abstract :

This article deals with the adsorption-desorption processes of phosphate on sediments according to the Langmuir theory. The theoretical developments are described and applied to the experiments which enable the determination of phosphate that is exchangeable with surrounding water (exch-P). Langmuir equation parameters such as the partition coefficient and the maximum adsorption capacity for exchange of phosphate between solid and water are assessed and discussed. The dataset consisted of contrasting sediments gathered over fifteen years from a large number of coastal and estuarine areas.

The determination of exch-P was carried out with linear and asymptotic computations. The values, ranging from a few tenths of  $\mu\text{mol g}^{-1}$  in sandy sediments up to approximately  $9 \mu\text{mol g}^{-1}$  in muddy sediments, are slightly more precise by using the linear computation. Partition coefficients ( $K_p$ :  $0.03\text{--}3.8 \text{ L g}^{-1}$ ), increasing with the proportion of fine particles, are likely related to the Fe content. It is proposed to use  $K_p$  as a criterion for the examination of the potential exchange of phosphate with the surrounding water.

The maximum phosphate adsorption capacity of sediments ( $Q_0$ ) derived from the Langmuir equations exhibits large confidence interval. So, it is not found significantly higher than the exchangeable phosphate, as expected from published sediment saturation experiments.

### Graphical abstract



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## Highlights

► Langmuir theory and its constants for exchangeable phosphate in coastal sediments. ► A simple linear model to obtain exchangeable-P from the Infinite Dilution Experiment. ► Partition coefficient, a criterion for sediment-water phosphate exchange. ► Is the determination of the maximum adsorption capacity reliable ?

**Keywords** : Exchangeable phosphate, sediment, Langmuir, adsorption, desorption

## 72 1. INTRODUCTION

73

74 In shallow transient zones such as estuarine and coastal areas, eutrophication induced by nutrient  
75 enrichment from anthropic activities has been well documented (Boesch, 2002; Seitzinger et al., 2005). However,  
76 beyond direct riverine inputs, various mechanisms influence nutrient concentrations in these areas, such as  
77 remineralization or interactions with particulate matter. In contrast with inorganic nitrogen, phosphate exhibits  
78 various types of interactions with solids such as exchanges at the solid-liquid interface and precipitation/dissolution  
79 reactions involving iron, calcium and aluminium present in the solid (Sundby et al., 1992; Ruttenberg and Berner,  
80 1993; Slomp et al., 1996). The resulting differential changes in N and P availability in the water column may  
81 induce shifts in nutrient limitations for planktonic species, with possible growth of toxic algae (Ding et al., 2018;  
82 Ratmaya et al., 2019).

83 The most labile form of solid phosphate is that adsorbed at the solid surface. It is named exchangeable  
84 phosphate (exch-P) and is defined as “*the amount of phosphate that could be released from a solid into an oxic*  
85 *water body of infinite volume, totally depleted in phosphate*” (Froelich, 1988). According to the law of mass action,  
86 when suspended particles from a river are transported into the estuary then into coastal waters, phosphate sorbed  
87 onto these particles may be released into the water column, to counterbalance the decrease in phosphate  
88 concentrations along the salinity gradient (Conley, 1995; Deborde et al., 2007). In rivers and estuaries these  
89 reactions are considered to regulate dissolved phosphate concentrations, a phenomenon called the buffering  
90 mechanism of P (Froelich 1988). Consequently, the solid phase is a potential phosphate reservoir when there is a  
91 high demand during intense primary producer growth (Van Raaphorst et al., 1994; Smil, 2000). In oxic coastal  
92 and estuarine areas, the adsorption-desorption mechanism of exchangeable phosphate may thus become the main  
93 phosphate source as compared to other processes which require more complex chemical and redox mechanisms,  
94 and significantly contributes to the final trophic level of water bodies (Jarvies et al., 2002; Zhang et al., 2012).

95 Phosphorus forms in marine sediments have been studied through the use of sequential extractions  
96 (Ruttenberg, 1992; Raimonet et al., 2013; Samadi-Maybodi et al., 2013; Ait Ballagh et al., 2020), in order to  
97 identify the essential P compartments for diagenetic models of P burial (Defforey and Paytan, 2018). In these  
98 methods, exchangeable phosphate (also called loosely bound -P, labile-P or adsorbed-P) is extracted either together  
99 with the strongly linked iron-bound P or using a one-step extraction procedure which does not meet the requirement  
100 of the above-mentioned Froelich’s definition (Aminot and Andrieux, 1996). In the diagenetic models, adsorbed  
101 phosphate generally plays a minor role and is often included in the iron-bound P fraction (Cha et al., 2005; Ait

102 Ballagh et al., 2020). In contrast, in coastal waters where eutrophication events are expected, the contribution of  
 103 exchangeable phosphate is of primary importance upon forms strongly linked to the sediment (Baretta et al, 1995;  
 104 Couceiro et al., 2013). Its determination affords accurate modeling of phosphate behavior and provides  
 105 environmental modelers with tools to assess the potentials risks of excessive or toxic algal growth. Therefore, we  
 106 propose in this article to re-examine the determination of *exch-P* by the Infinite Dilution Extrapolation (IDE)  
 107 method (Aminot and Andrieux, 1996). In brief, this method is based on the Langmuir's theory because of its  
 108 simplicity and applicability, and will be detailed further. In addition to *exch-P*, it enables us the evaluation of both  
 109 the water-sediment partition coefficient of *exch-P* as well as the theoretical maximum amount of phosphate which  
 110 might be adsorbed onto a sediment.

111 The method has been validated using a large compilation of datasets collected over many years from various  
 112 French coastal and estuarine areas which exhibit contrasted types of sediments (Bay of Seine and Penzé estuary,  
 113 northern coast of France; Loire and Gironde estuaries, western coast of France). The reliability of the results  
 114 obtained with the method is discussed as well as certain aspects of their field behavior.

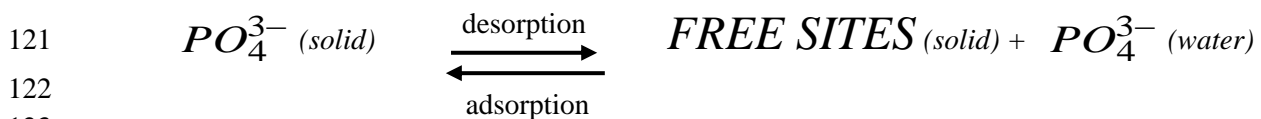
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## 116 2. THEORETICAL CONSIDERATIONS

### 117 2.1. Theoretical basis for adsorption-desorption processes

118 A solid in contact with water will exchange phosphate with that water until a dynamic equilibrium is  
 119 reached. The process can be schematically described by the equation:

120



122

123  
 124 The basic description of this process, which will be used hereafter, is derived from Langmuir. Initially  
 125 developed for gas solid exchanges, Langmuir's approach was later extended to solid-solution interactions (see  
 126 Voice and Weber, 1983). The assumptions upon which the model is based state that adsorption, on a single layer,  
 127 is a reversible process with no interaction between adsorbed ions nor a difference between adsorption sites. The  
 128 nature of the solid largely determines desorption and adsorption rates and resulting equilibrium conditions  
 129 (O'Connor and Connely, 1980). Adsorption-desorption and precipitation-dissolution may be involved; however,  
 130 on the short-term timescale considered in most studies dealing with exchangeable phosphate, only the first type of  
 131 process is involved. Therefore, from a macroscopic point of view, the solid can be assumed to have a single type

132 of exchange surface in contact with the surrounding water mass. While double-layer adsorption models have been  
 133 developed for phosphate adsorption onto metal oxides (Brinkman, 1993), phosphate concentrations are usually not  
 134 able to saturate the solid surface in the water column, justifying the application of the Langmuir's monolayer  
 135 adsorption principle. When ecological models include physical, biological and sedimentary processes, Langmuir's  
 136 theory should be the first consideration if solid-water exchange processes have to be taken into account.

137 According to Voice and Weber (1983), the solid-water exchange is characterized by the adsorption and  
 138 desorption rates which are treated as first order processes for each reaction component, i.e. governed by  
 139 concentrations on either side of the equation. In a eutrophication context, the phosphate concentration of water is  
 140 the main parameter, therefore, desorption is treated as an increase (positive rate), and adsorption as a decrease  
 141 (negative rate) in the concentration of phosphorus. Additionally, in a given water mass, the active phosphate  
 142 concentration of the solid phase is the product of phosphate on solid ( $\mu\text{mol g}^{-1}$ ) and solid in water ( $\text{g L}^{-1}$ ). So:

143 Desorption rate:  $V_d = \{d([PO_4]_{water})/dt\}_d = k_d[PO_4]_{solid}[solid]_{water}$  (1)

144 Adsorption rate:  $V_a = -\{d([PO_4]_{water})/dt\}_a = k_a[PO_4]_{water}[free\ sites]_{solid}[solid]_{water}$  (2)

145 In equations (1) and (2), the rate constants for desorption and adsorption are respectively  $k_d$  and  $k_a$ . For  
 146 consistency, the Langmuir nomenclature was used (as previously described in Aminot and Andrieux, 1996). It is  
 147 summarized in Table 1. Phosphate concentrations are symbolized in water by  $C$  ( $\mu\text{mol L}^{-1}$ ) and on solid by  $q$   
 148 ( $\mu\text{mol g}^{-1}$ ).

149 **Table 1** Nomenclature used herein.

Variable	symbol	unit
Desorption rate	$V_d$	$\mu\text{mol L}^{-1} \text{h}^{-1}$
Adsorption rate	$V_a$	$\mu\text{mol L}^{-1} \text{h}^{-1}$
Desorption constant	$k_d$	$\text{h}^{-1}$
Adsorption constant	$k_a$	$\text{L } \mu\text{mol}^{-1} \text{h}^{-1}$
Partition coefficient	$K_p = q_e/C_e$	$\text{L g}^{-1}$
Maximal adsorption capacity	$Q^o$	$\mu\text{mol g}^{-1}$
Langmuir coefficient	$b = k_a/k_d$	$\text{L } \mu\text{mol}^{-1}$
IN BATCH		
Solution volume	$V$	$\text{L}$
Solid mass	$m$	$\text{g}$
Solid concentration	$S = m/V$	$\text{g L}^{-1}$
Initial $PO_4$ conc. in liquid phase	$C_i$	$\mu\text{mol L}^{-1}$
Initial $PO_4$ conc. on solid (= exchangeable phosphate 'exch-P')	$q_i$	$\mu\text{mol g}^{-1}$
$PO_4$ conc. in liquid phase at time 't'	$C_t$	$\mu\text{mol L}^{-1}$
$PO_4$ conc. on solid at time 't'	$q_t$	$\mu\text{mol g}^{-1}$
$PO_4$ conc. released from solid at time 't'	$q_{Rt} (= q_i - q_t)$	$\mu\text{mol g}^{-1}$
$PO_4$ conc. in liquid phase at equilibrium	$C_e$	$\mu\text{mol L}^{-1}$
$PO_4$ conc. on solid at equilibrium	$q_e$	$\mu\text{mol g}^{-1}$
$PO_4$ conc. released from solid at equilibrium	$q_{Re} (= q_i - q_e)$	$\mu\text{mol g}^{-1}$

150

151 According to the nomenclature, the above rates are written:

$$152 \quad V_d = \{dC_t/dt\}_d = k_d q_t S \quad (3)$$

$$153 \quad V_a = -\{dC_t/dt\}_a = -k_a C_t (Q^o - q_t) S \quad (4)$$

154

155 The total rate (equation (3) + (4)) is:  $V_T = V_d + V_a$

156

157 Solid and water concentrations are stable when the equilibrium is reached, i.e. when  $V_T = 0$ , hence:

$$158 \quad k_d q_e S = k_a C_e (Q^o - q_e) S \quad (5)$$

159

160 When water phosphate concentrations are depleted after algal blooms, the solid has also released part of its  
 161 adsorbed amount. In such conditions, which are the most critical for algal growth modeling, the assumption that  
 162  $Q^o$  (the maximum amount of solute sorbed per unit mass of solid) is much greater than the equilibrium  
 163 concentration is justified ( $Q^o \gg q_e$ ) and consequently from equation (5), the partition coefficient at equilibrium  
 164 is a constant:

$$165 \quad K_p = q_e / C_e = b(Q^o - q_e) \approx bQ^o \quad (6)$$

166

167 In addition, when the above assumption ( $Q^o \gg q_e$ ) is valid, the adsorption rate (equation (4)) can thus be expressed  
 168 as:

$$169 \quad V_a \approx k_a C_e Q^o S \quad (7)$$

170 In summary, the essential data needed to incorporate phosphate adsorption into ecological models are the  
 171 following: exchangeable phosphate (exch-P, here symbolized as  $q_i$ ), partition coefficient ( $K_p$ ), maximal adsorption  
 172 capacity ( $Q^o$ ) and rate constants for desorption ( $k_d$ ) and adsorption ( $k_a$ ). To obtain these data, two types of batch  
 173 experiments are required, both relying on desorption of phosphate according to the Infinite Dilution Extrapolation  
 174 (IDE) experiment previously developed (Aminot and Andrieux, 1996). One is a determination of phosphate  
 175 concentration at quasi-equilibrium for various solid concentrations in water (it provides  $q_i$ ,  $K_p$ , and potentially  $Q^o$   
 and  $b$ ). The other is a kinetics determination of phosphate release in solution (it provides  $k_d$  then  $k_a$  and  $k_a Q^o$ ).

176 In this paper we focus on exchangeable phosphate and its static Langmuir parameters (partition constant  
 177 and maximum adsorption capacity). Dynamics of exchanges and kinetic constants will be treated in forthcoming  
 178 article.

179

180

## 181 2.2. Application to batch experiments

182 In the literature, solid-liquid exchanges in laboratory batch experiments are performed by adding known  
 183 masses of sediment to fixed volumes of water of known phosphate concentrations. At regular time intervals, the  
 184 concentrations of phosphate in the liquid phase are measured. However, a major shortcoming of these studies is  
 185 that they have often been conducted using solutions of KCl or NaCl in distilled or deionized water without pH  
 186 control. Considering the importance of pH in phosphate exchange (Aminot and Andrieux, 1996; Zhou et al., 2005;  
 187 Peng et al., 2007), it is essential to operate as close as possible to natural conditions prevailing in the studied area.

188 In this study, focused on phosphate adsorbed on coastal sediments, natural seawater devoid of phosphate  
 189 (Phosphate-Free Seawater (PFS)) was used for all desorption experiments. The low sediment concentrations used  
 190 in our experiments did not alter the naturally buffered seawater pH. Before proceeding to equilibrium batch  
 191 experiments, the time for equilibrium to be reached has to be determined by preliminary kinetic experiments (see  
 192 3.2). At the beginning of the experiment (time 0), the initial phosphate concentrations on the solid and in the liquid  
 193 phases are respectively  $q_i$  and  $C_i$ . At equilibrium, released phosphate from the solid is  $q_{Re}$  and the concentrations  
 194 are  $q_e$  and  $C_e$ . In batch experiments, the total number of phosphate ions is constant:

$$195 \quad q_{Re} = (q_i - q_e) = (C_i - C_e)/S \quad (8)$$

196 In the case of seawater devoid of phosphate,  $C_i = 0$ , equation (8) becomes (where concentrations are counted  
 197 positively):

$$197 \quad q_{Re} = (q_i - q_e) = (C_e)/S \quad (9)$$

198 In a single batch, where  $C_e$  is measured and  $S$  is known, the exchangeable phosphate  $q_i$  could be obtained  
 199 for  $q_e = 0$ . This means that all adsorbed phosphate would be desorbed, implying an infinite dilution of the solid.  
 200 As this is not experimentally feasible, the Infinite Dilution Experiment (IDE) method was proposed (Aminot and  
 201 Andrieux, 1996). Several batches with a range of solid concentrations in phosphate-free water have to be prepared  
 202 so that  $C_e$  and  $S$  can be mathematically fitted in order to calculate the theoretical value of exchangeable phosphate  
 203 obtained at infinite dilution. The partition coefficient  $K_p = q_e/C_e$  is introduced in the released phosphate formula:

$$204 \quad q_{Re} = (q_i - q_e) = q_i - K_p C_e \quad (10)$$

$$205 \quad \text{then, from equation (9)} \quad (q_i - q_e) = q_i - K_p S (q_i - q_e) \quad (11)$$

$$206 \quad \text{recombining} \quad (q_i - q_e)(1 + K_p S) = q_i \quad (12)$$

$$207 \quad \text{to give the asymptotic equation} \quad q_{Re} = (q_i - q_e) = q_i / (1 + K_p S) \quad (13)$$

$$208 \quad \text{which is linearized as} \quad S/C_e = (1 + K_p S)/q_i \quad (14)$$

209 Finally, we obtain the main linear equation used for the treatment of the batch data:

$$210 \quad 1/C_e = (1/S)(1/q_i) + K_p/q_i \quad (15)$$

211 **Determination of exchangeable phosphate ( $q_i$ ).** The above linear equation (15) is applied as  $y = mx + n$ ,  
 212 by plotting the inverse of the equilibrium water concentration ( $y = 1/C_e$ ) versus the solid dilution ( $x = 1/S$ ): the  
 213 slope provides the inverse of  $q_i$ . Previously (Aminot and Andrieux, 1996), we used the asymptotic equation (13),  
 214 plotting released phosphate ( $q_{Re}$ ) versus solid dilution ( $1/S$ ) which provides a better graphical display of the infinite  
 215 dilution process. A comparison of the two computation methods is given in the Results section.

216 **Determination of the partition coefficient ( $K_p$ ).**  $K_p$  is obtained according to equation (15) in the form  
 217  $y = mx + n$  as above, hence  $K_p$  is the ratio of the intercept by the slope (since  $n = K_p/q_i$  and  $q_i = 1/m$  then  $K_p = n/m$ ).

218 **Determination of the maximal adsorption capacity ( $Q^o$ ).** At equilibrium, adsorption and desorption rates  
 219 are equal and equation (5) can be re-written as:

$$220 \quad k_d/k_a = C_e(Q^o - q_e)/q_e \quad (16)$$

221  
 222 According to Voice and Weber (1983), equation (16) (using  $b = k_a/k_d$ ) may be linearized under two forms:

$$223 \quad \text{either} \quad 1/q_e = (1/bQ^o)(1/C_e) + 1/Q^o \quad (17)$$

$$224 \quad \text{or} \quad 1/C_e = bQ^o(1/q_e) - b \quad (18)$$

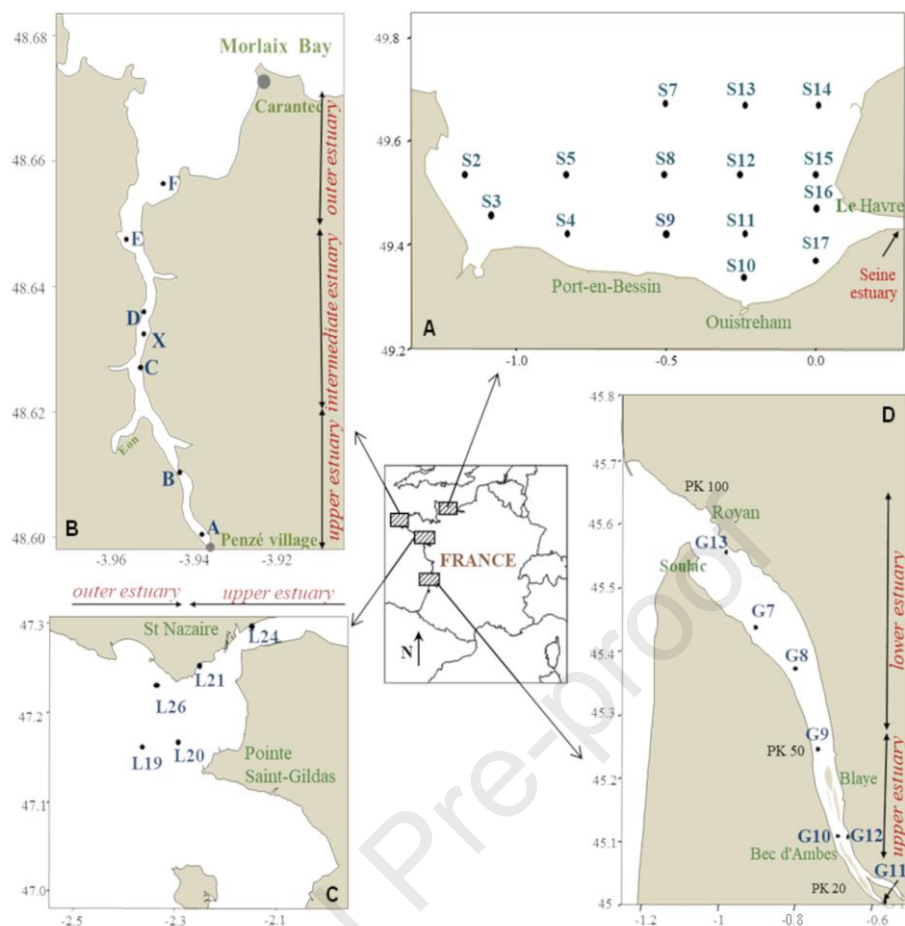
225 Either equations (17) or (18) may be fit with the same sets of data obtained from the IDE desorption  
 226 experiment to determine  $Q^o$ . It may be noted that these two equations also provide the Langmuir constant  $b$  (not  
 227 used here).

### 228 3. MATERIAL AND METHODS

#### 229 3.1. Sampling and storage

230 Localities with varying types of sediments were studied (Fig. 1). Sampling was undertaken in the Bay of  
 231 Seine in February, April, June and July 1992, then in June 1994; sediments were collected in 8 to 11 sampling  
 232 stations during these cruises (Andrieux and Aminot, 1997). In the Penzé estuary 7 stations were collected from the  
 233 upper to outer estuary in August 2004, March and June 2005. In the Loire and Gironde estuaries 7 and 4 stations  
 234 were sampled, respectively, in February 1991. The main sediment characteristics and relationships with phosphate  
 235 forms for each locality were previously described in Andrieux-Loyer and Aminot, (2001), Andrieux-Loyer et al.  
 236 (2008) and are presented Table S1 (Supplementary data).





237  
 238 **Fig. 1.** Map of surveyed areas and location of sampling stations. A: The Bay of Seine; B: The Penzé estuary; C: The  
 239 Loire estuary; D: The Gironde estuary.

241 The superficial 2 cm layer of the sediments was collected using a Shipek grab. This layer was usually well  
 242 oxygenated. Whenever it was possible, experiments were performed on board as follows using the freshly collected  
 243 sediments. The sediment was added to flasks containing Phosphate-Free Seawater (PFS) using 0.5 to 5 ml  
 244 measuring spoons in order to obtain a range of low concentrations of the solid in suspension, typically from 50 to  
 245 2000 mg l<sup>-1</sup> as described in section 3.2.2. At the end of the experiment, supernatants were collected by  
 246 centrifugation, then frozen for further phosphate analysis in the laboratory. Sediment remaining after collection of  
 247 the supernatant was kept for mass determination as described in section 3.2.2.

248 When on-board operations were not possible, samples were immediately placed in polycarbonate vials and  
 249 stored frozen (-20 °C). Within a few months they were then freeze-dried in the shore laboratory and sieved at  
 250 500 µm before use. A comparison of exch-P results using fresh, freeze-thawed and lyophilized samples was  
 251 undertaken using sediments from stations 10 and 16 ranging from 0.3 to 8 µmol g<sup>-1</sup>. These results from lyophilized

252 vs fresh sediments, exhibited a linear relationship with a slope of  $0.97 \pm 0.05$  and  $R^2 = 0.99$ . This shows that  
253 potential low oxygen contents of fresh sediments and oxygen saturated lyophilized sediments exhibit the same  
254 behavior in desorption experiments. Freeze-thawed samples were not used since they exhibited a poorer correlation  
255 with fresh samples, attributed to the more difficult handling of these samples. In addition, in the Bay of Seine, the  
256 water column was sampled at 1 meter above the bottom using 8 L Niskin bottles for phosphate measurement.

## 257 **3.2. Laboratory experimental procedures**

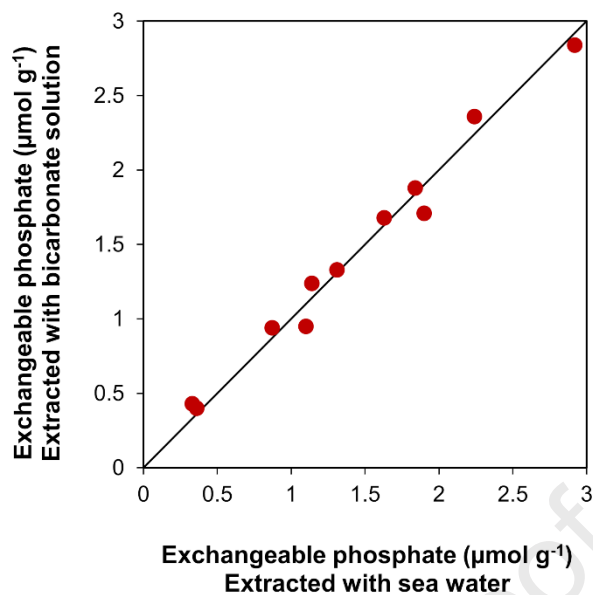
### 258 **3.2.1. Analytical conditions**

259 The concentration of phosphate was determined using Segmented Flow Analysis (SFA; Aminot et al., 2009)  
260 with conditions close to those of Murphy and Riley (1962). Precision within series is about  $0.005 \mu\text{mol L}^{-1}$ .

261 Experiments used Phosphate-Free Seawater (PFS) which can be obtained as follows (Aminot et al., 2009).  
262 A bulk volume of clean coastal seawater is collected when nutrient concentrations have been lowered by  
263 phytoplankton growth, generally at the end of spring. Once roughly filtered at about 20-50  $\mu\text{m}$  to remove most  
264 zooplankton species, the water is stored in a non-opaque carboy at ambient light and temperature in the laboratory.  
265 Phosphate is naturally removed by the remaining phytoplankton to very low concentrations within about 2 months  
266 and maintained at this level, as long as the water is not filtered. The water is then filtered just before experiments  
267 using Whatman GF/F glass fiber filters ( $\sim 0.7 \mu\text{m}$  pore size) to remove phytoplankton and most other micro-  
268 organisms.

269 The main importance of pH over any other dissolved compound was checked by comparing data obtained  
270 with PFS and a bicarbonate solution at the same concentration as that of seawater ( $2.5 \text{ mmol L}^{-1}$ ). Fig. 2 shows  
271 that both media lead to comparable results. We conclude that, where PFS cannot be obtained, bicarbonate solution  
272 in ultrapure water may be used. However, all our experiments were realized with PFS to remain as close as possible  
273 to natural conditions.

274



275

276 **Fig. 2.** Comparison of exchangeable phosphate concentrations obtained by the Infinite Dilution Extrapolation  
 277 (IDE) method, using Phosphate-Free Seawater (PFS) and bicarbonate solution ( $2.5 \text{ mmol l}^{-1}$ ) for various sediments  
 278 from the Bay of Seine. Sediments were sampled at different periods of the year (size fraction  $<63\mu\text{m}$ ,  $<0.1\text{-}3 \%$ ;  
 279 loss at  $500^\circ\text{C}$ ,  $1\text{-}2 \%$ ).

### 280 **3.2.2. Equilibrium experiments**

281 To determine exchangeable phosphate according to the IDE experiment (Section 2.2), a range of solid  
 282 concentrations were introduced in phosphate-free seawater, typically from  $50$  to  $2000 \text{ mg L}^{-1}$ . The water was  
 283 poisoned with  $40 \text{ mg L}^{-1}$  of mercuric chloride to prevent alteration of phosphate concentrations due to bacterial  
 284 activity (this does not alter the pH of the medium). Experiments were performed at  $20^\circ\text{C}$  and the flasks were  
 285 placed on a shaking table. The contact time to reach equilibrium at  $20^\circ\text{C}$  (established from preliminary kinetics  
 286 experiments, Fig. 3) is 25-30 hours. Then, after centrifugation ( $3,000 \text{ g}$  for ten minutes), water phosphate  
 287 concentrations were measured.

288 For experiments performed with fresh sediment, the solids were collected after the experiment by filtration  
 289 through pre-weight GF/F Whatman glass fiber filters. The filters with sediments were rinsed with deionized  
 290 MilliQ- water to remove salt residues and dried overnight at  $100^\circ\text{C}$  in glass petri dishes. The filters were stored  
 291 in a dessicator until they reach ambient temperature before weighing.

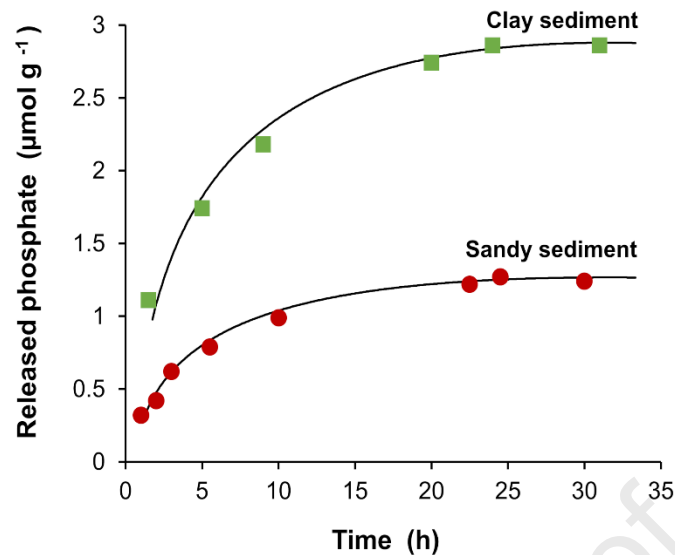


Fig. 3. Kinetic experiments performed at 20 °C for two typical coastal sediments.

### 3.3. Surveyed areas characteristics

In the Bay of Seine, a pattern of decreasing grain-size is observed from offshore to the coast (Méar, 2006). Superficial sediments in the mouth of the Seine River are composed of muddy fine sand and silt with varying amounts of mud deposits (Avoine, 1986; Lesourd et al., 2003; Lesourd et al., 2016). Sediments have a terrigenous siliceous fraction and a marine carbonate fraction, decreasing from west (50-70 %) to east (< 40 %) along with enrichment in fine particles.

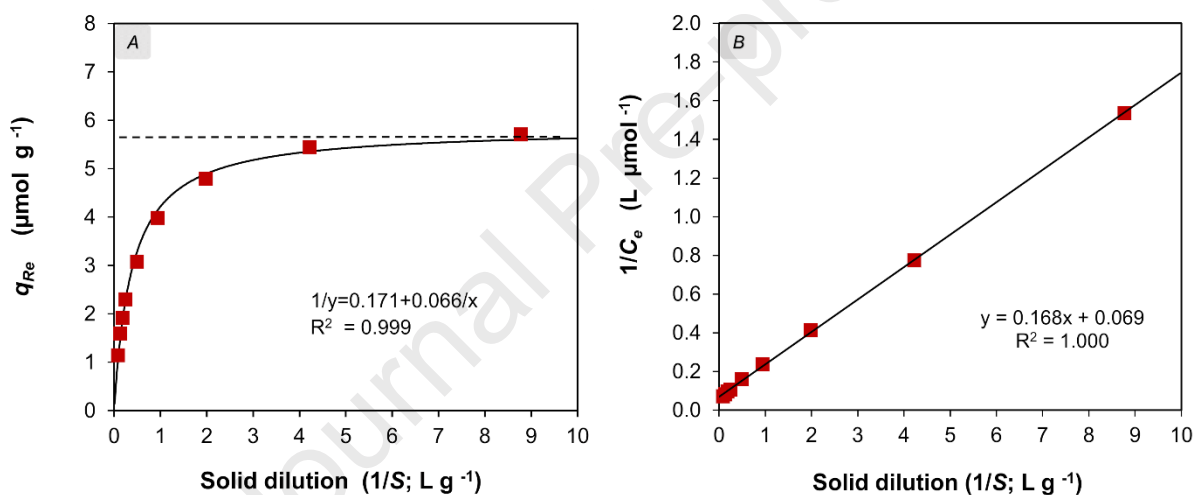
In the Penzé estuary, the axis of the channel, mainly consisting of sandy sediments is situated between two muddy banks. According to the sedimentary characterization of Larsonneur (1971), the sediments collected for this study (Andrieux-Loyer et al., 2008) were all silty sands, the inner station always presenting the highest percentage of lutites (about 60 %).

In the Loire estuary, according to the C.S.E.E.L (1984), mud is found in the North channel and muddy-sand to sandy-mud in the other areas of the outer estuary. The fine fraction (< 40 μm) is composed of silts (35 %), carbonates (17 %), clay minerals and some organic matter (Migniot and Le Hir, 1996).

In the Gironde, the estuarine sediments consist of silt and clay in the channels, where samples were collected. According to Jouanneau and Latouche (1981), most of these sediments are characterized by a predominance of the small fraction, notably silts (< 2 μm: 35 %; 2-60 μm: 56 %; > 60 μm: 9 %). Sediments are mainly composed of carbonates (5-10 %), quartz and feldspars (20-40 %) and clays (30-60 %).

313 **4. RESULTS**314 **4.1. Exchangeable phosphate (exch-P)**

315 Results of exch-P from the desorption equilibrium experiments may be mathematically treated either by an  
 316 asymptotic (13) or by a linear function (15) as described in Section 2.2. In the two treatments, the calculation  
 317 provides the reciprocal of exch-P with its standard error. Fig. 4 shows an example of the plots using the two  
 318 functions for treating the data of a particular desorption experiment. Regardless of the grain-size, the values of  
 319 exch-P obtained by the two treatments are comparable and within a  $1.9\% \pm 4.4\%$  difference over the range of  
 320  $0.15$  to  $8.6 \mu\text{mol g}^{-1}$ . It appears that the linear fitting provides a smaller standard error for exch-P by a factor of  
 321 about 1.5-2. On the 48 IDE experiments, the average standard error with the linear treatment is  $2.3\%$  ( $\pm 1.4\%$ ),  
 322 so it is recommended instead of the asymptotic fitting.



323 **Fig. 4.** Application of the IDE experiment to the determination of exchangeable phosphate of a coastal sediment  
 324 from the Loire estuary; size fraction  $< 63 \mu\text{m}$ , 93 %. Exchangeable phosphate is mathematically treated by A: an  
 325 asymptotic function (equation (13)), B: a linear function (equation (15)).  
 326

327  
 328 All measured exch-P values in the studied areas (Table 2) lie between  $0.15$  and  $8.6 \mu\text{mol g}^{-1}$ . Map  
 329 distributions (Andrieux and Aminot, 1997; Andrieux-Loyer and Aminot 2001; Andrieux-Loyer et al. 2008), will  
 330 not be discussed further here. A complementary graphical comparison of exch-P in the studied sites is provided in  
 331 supplementary material. Sandy sediments (Bay of Seine) have systematically lower exchangeable phosphate  
 332 concentrations than muddy sediments (mainly Penzé and Loire estuaries). In the Bay of Seine itself, the highest  
 333 concentrations of exch-P (up to  $\approx 3 \mu\text{mol g}^{-1}$ ) occur at stations 15, 16 and 17, close to the Seine estuary where the  
 334 fine particles are the most abundant (1-3 % of particles  $< 63 \mu\text{m}$ ). The overall highest concentrations are found in

335 the muddy sediments of the Penzé estuary (> 50 % of particles < 63  $\mu\text{m}$ ) with almost  $\approx 9 \mu\text{mol g}^{-1}$  exch-P. In this  
336 estuary, dissolved interstitial phosphate concentrations represent less than 2 % of exch-P although these  
337 concentrations of 4-15  $\text{mol l}^{-1}$  are among the highest reported in the literature which mostly lie below 5-6  $\text{mol l}^{-1}$   
338 in surface sediments (Corbett, 2010; Ait Ballagh et al., 2020, 2021; Anschutz et al, 2007; Sundby et al., 1992;  
339 Luhauka-Matuszewska and Burska, 2011; Sasaki et al., 2001). Therefore, with concentrations 10-100 times higher  
340 than those measured in the corresponding surface interstitial waters, the high amounts of quickly available  
341 exchangeable phosphate constitute a significant reservoir for potential enrichment of the coastal zone.

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363 **Table 2.** Exchangeable phosphate (exch-P) and partition coefficients ( $K_p$ ) in surface sediments of the studied  
 364 French coastal and estuarine areas.

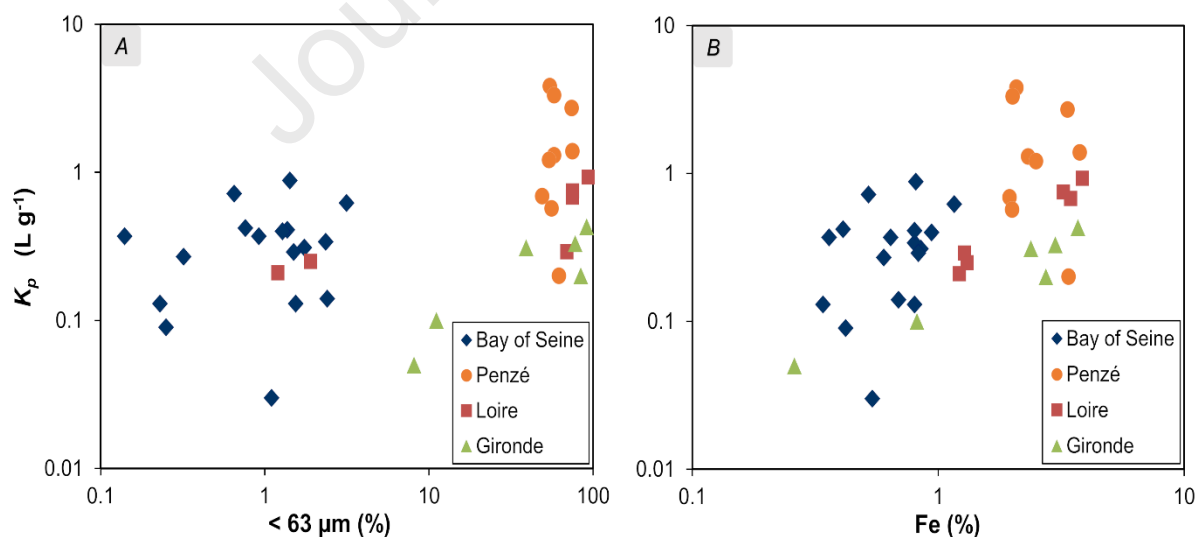
Sampling site	Date	Station	Exchangeable phosphate			Partition coefficient		
			Exch-P $\mu\text{mol g}^{-1}$	s $\mu\text{mol g}^{-1}$	CV %	$K_p$ $\text{L g}^{-1}$	s $\text{L g}^{-1}$	CV %
<b>Bay of Seine</b>	February 92	3	1.16	0.02	1.6	0.21	0.06	28
		10	0.74	0.03	4.3	0.37	0.15	40
		12	0.61	0.04	6.6	0.68	0.25	36
		15	1.85	0.03	1.8	0.15	0.04	24
		16	2.95	0.06	2.0	0.34	0.07	21
	April 92	7	0.21	0.00	1.1	0.16	0.03	17
		10	1.01	0.01	1.3	0.31	0.04	14
		12	0.42	0.01	2.9	0.37	0.12	32
		15	1.86	0.03	1.4	0.18	0.05	26
		16	1.20	0.03	2.6	0.24	0.10	42
	June 92	3	0.92	0.03	3.2	0.27	0.10	39
		15	1.87	0.09	4.8	0.61	0.16	26
		16	2.39	0.07	3.1	0.43	0.10	24
		17	0.87	0.02	2.7	0.63	0.09	15
	July 92	10	0.65	0.03	3.9	0.37	0.13	36
		12	0.38	0.01	2.9	0.28	0.08	28
		14	1.09	0.04	3.6	0.62	0.13	21
		15	1.69	0.02	1.3	0.24	0.04	15
		16	1.39	0.04	2.9	0.41	0.12	28
		18	1.57	0.06	4.0	0.40	0.14	34
	June 94	10	0.37	0.00	0.4	0.03	0.01	39
		11	0.38	0.00	1.0	0.09	0.03	29
		12	0.33	0.00	1.3	0.16	0.04	23
		14	0.30	0.00	1.1	0.02	0.02	85
		15	1.33	0.01	0.7	0.07	0.02	26
		16	2.58	0.11	4.1	0.20	0.07	34
		17	1.27	0.02	1.4	0.15	0.03	21
	<b>Penzé</b>	August 04	A1	8.61	0.21	2.4	1.39	0.52
E1			4.37	0.22	4.9	3.81	0.91	24
March 05		A1	6.06	0.14	2.3	1.61	0.38	24
		B1	3.45	0.06	1.7	1.30	0.39	30
June 05		D1	2.20	0.01	0.6	0.69	0.12	18
		A1	6.95	0.19	2.8	2.71	0.43	16
		B1	3.79	0.06	1.6	1.21	0.23	19
		E1	1.64	0.01	0.9	0.45	0.07	16
F1	3.68	0.19	5.2	3.32	1.46	44		
<b>Loire</b>	February 91	19	0.17	0.002	1.5	0.17	0.02	14
		20	0.23	0.005	2.2	0.21	0.02	9
		21	6.60	0.117	1.8	0.75	0.04	6
		23	5.39	0.060	1.1	0.31	0.02	8
		24	5.93	0.151	2.5	0.70	0.09	12
		26	6.92	0.250	3.6	1.07	0.07	7
		<b>Gironde</b>	February 91	8	2.73	0.04	1.3	0.43
9	2.47			0.03	1.4	0.36	0.05	13
10	1.30			0.01	1.0	0.31	0.03	11
11	2.33			0.02	0.9	0.32	0.03	8
12	0.35			0.00	0.7	0.10	0.01	10
13	0.15			0.001	0.5	0.09	0.01	7

365 **4. 2. Partition coefficient ( $K_p$ )**

366  $K_p$  is computed as the ratio of the intercept by the slope from the linear treatment of the IDE equilibrium  
 367 batch experiments data according to equation (15). The  $K_p$  values of the 4 study areas, with their standard errors,  
 368 are listed in Table 2 and graphically compared in Fig. S1 of supplementary material. The values cover a wide range  
 369 from 0.03 to 3.8 L g<sup>-1</sup>, but all the highest  $K_p$  values are measured in the Penzé estuary, while 40 out of the 48 values  
 370 are lower than 1 L g<sup>-1</sup>. The lowest values found here are comparable with those reported from the Wadden sea by  
 371 Van Raaphorst and Kloosterhuis (1994) for sandy sediments (about 0.2 L g<sup>-1</sup>; less than 6 % < 63  $\mu$ m). Standard  
 372 errors of  $K_p$  were computed from the standard errors of the slope and intercept of the IDE linear treatment based  
 373 on the propagation of uncertainties. The average RSD of  $K_p$  for the 48 sediments is 24 %, with values around 10  
 374 % for the Loire and Gironde estuaries and around 25-30 % in the Penzé estuary and the Bay of Seine.

375 Relationships between  $K_p$  and fine particles and Fe content (see Table S1 in Supplementary data section)  
 376 were examined in Fig. 5. Although exchangeable phosphate binds to surface Fe, total Fe, which was available,  
 377 was tentatively used instead of surface Fe since total and surface Fe are generally correlated (Rutten and de Lange,  
 378 2003). Total Fe was determined using fusion with LiBO<sub>2</sub> and HNO<sub>3</sub>, followed by measurement by ICP-emission  
 379 (Centre de Recherches Petrographique et Chimique du Centre National de la Recherche Scientifique  
 380 (CRPG/CNRS)).

381



382

383 **Fig. 5.** Partition coefficient ( $K_p$ ) as a function of A: the < 63  $\mu$ m sediment fraction and B: the Fe content in the  
 384 studied French coastal and estuarine areas.

385



386 The correlation parameters (Table 3) show an overall significant trend (CL 95 %) for  $K_p$  which increases  
 387 as the fine particles and iron contents increase (p-values: 0.01 and 0.02 respectively), despite a wide dispersion of  
 388 its values. In individual sites, significant correlations are observed only in the Loire and Gironde estuaries. Within  
 389 the exception of the Penzé results, all  $K_p$  lies within  $0.33 \pm 0.22 \text{ L g}^{-1}$  (mean  $\pm$  SD).

390

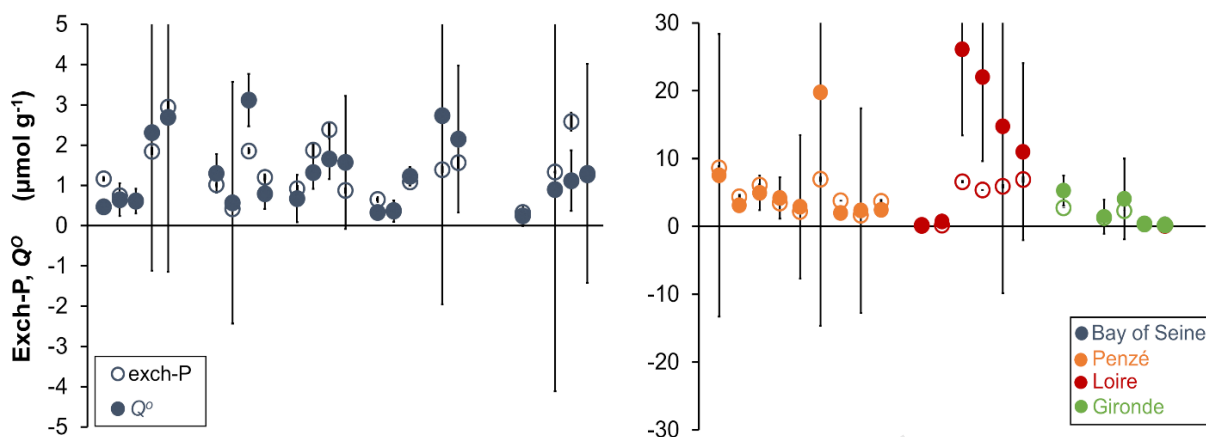
391 **Table 3.** Relationship parameters of  $K_p$  vs percent of  $< 63 \mu\text{m}$  particles and total Fe-content of studied site  
 392 sediments

Site	$K_p$ vs % $< 63 \mu\text{m}$		$K_p$ vs total Fe	
	R <sup>2</sup>	p-value	R <sup>2</sup>	p-value
<b>Bay of Seine</b>	0.04	0.47	0.12	0.18
<b>Penzé estuary</b>	0.01	0.76	0.03	0.64
<b>Loire estuary</b>	0.69	0.04	0.97	0.0005
<b>Gironde estuary</b>	0.63	0.06	0.88	0.006
<b>All together</b>	0.16	0.01	0.14	0.02

393

### 394 4. 3. Maximal Adsorption Capacity ( $Q^o$ )

395 By application of the Langmuir theory, the determination of  $Q^o$  was tentatively done using both equations  
 396 (17) and (18) (as described in Section 2.2) applied to the data from our batch IDE experiments (48 sediments of  
 397 the 4 main sampling areas). Since these equations led to an erratic dispersion of the points at low sediment  
 398 concentrations, the latter were omitted in most samples for  $Q^o$  determination. Equation (17) yielded  $Q^o$  values on  
 399 average 20 % larger than equation (18), but also standard errors about twice greater. As a result, only  $Q^o$  values  
 400 obtained from equation (18) were retained, even if for five sediments negative  $Q^o$  were determined, 4 of which had  
 401 the lowest exch-P. The results point out the high standard error of  $Q^o$  which lie between 5 and 140 % (mean: 45 %),  
 402 after removal of 5 values up to 320 %.



403

404 **Fig. 6.** Comparison of exch-P and  $Q^o$  with 95 % confidence levels intervals. Confidence intervals of exch-P are generally within the corresponding open symbol

406

407 A graphical comparison of  $Q^o$  and exch-P with their 95 % confidence intervals is provided in Fig. 6. Given  
 408 its poor precision, it is not possible to conclude that  $Q^o$  is statistically greater than exch-P (with a few exceptions)  
 409 which should normally be expected. In addition, the hypothesis of  $Q^o/\text{exch-P} > 1$  was assessed by a Student-t test  
 410 which indicates significance at the 95 % CL on the whole dataset (42 samples; p-value = 0.007), but is insignificant  
 411 when removing the highest Loire samples (36 samples; p-value = 0.10). Consequently, due to the uncertainty of  
 412 the  $Q^o$  results, their values were not presented in Table 2.

413

## 414 5. DISCUSSION

### 415 5.1. Exchangeable phosphate

416 Although a large number of processes are considered for sound environmental management, sediment-  
 417 water phosphate exchange due to adsorption–desorption is often omitted because of its complexity (Baretta et al.,  
 418 1995). Wei et al (2022) recently developed a thorough model to study nutrient transport and transformation in  
 419 macrotidal estuaries, but pointed out that it “does not yet include an explicit benthic compartment” and that “P  
 420 adsorption and desorption to particulate material to form an iron-bound complex, is not accounted for”. Ecosystem  
 421 models of nutrient cycles also require more parameter determination in order to integrate phosphate adsorption  
 422 process (Reigner et al., 2013; Defforey and Paytan, 2018).

423 For many years, diagenetic models have been applied to marine and coastal sediments and they improved  
424 the knowledge of P burial (Defforey and Paytan, 2018). Thanks to the measurement of phosphorus forms using  
425 sequential extractions (Ruttenberg, 1992; Samadi-Maybodi et al., 2013; Yang et al, 2019), exchangeable phosphate  
426 is obtained by a one-step extraction using varying solutions and solid concentrations (Leote et al., 2014; Kang et  
427 al., 2017; Yang et al., 2021). Subsequent results, although they tend to underestimate *exch-P*, remain valid for  
428 sediment diagenetic models which generally treat iron-bound P as a whole including a minor part of *exch-P* (Cha  
429 et al., 2005; Küster-Heins et al., 2010; Raimonet et al., 2013; Ait Ballagh et al., 2020). However, these *exch-P*  
430 results do not satisfy ecological management models in which the contribution of phosphate adsorbed on  
431 suspended particles is a major factor. Decades ago, such discrepancy was already pointed out by Froelich (1982)  
432 who mentioned that uncertainties of these data were assumed to be an important limitation in the estimation of  
433 phosphate fluxes from rivers to the ocean. For that reason, the present re-examination of the Infinite Dilution  
434 Extrapolation method (IDE) highlights the complete basis of the method and expands on the associated parameters  
435 ( $K_p$ ,  $Q^o$ ) that might be of interest in coastal modeling of dissolved phosphate, especially where eutrophication  
436 management is concerned.

437 We show that our *exch-P* method, which was tested over a large number of sediments with contrasted grain  
438 size characteristics, provides results with a precision of a few percent overall. The measured concentrations reach  
439 up to  $\approx 9 \mu\text{mol g}^{-1}$  *exch-P*, especially in the muddy sediments (Loire, Gironde and Penzé estuaries), which shows  
440 that exchangeable phosphate may represent a pool of phosphorus liable to enrich the water column. These values  
441 are generally higher than those reported in other coastal environments (below  $1.5 \mu\text{mol g}^{-1}$ ; i.e, Samadi-Maybodi  
442 et al., 2013; Yang et al., 2019; Yang et al., 2021) as expected from the difference in extraction procedures  
443 respectively used and above mentioned.

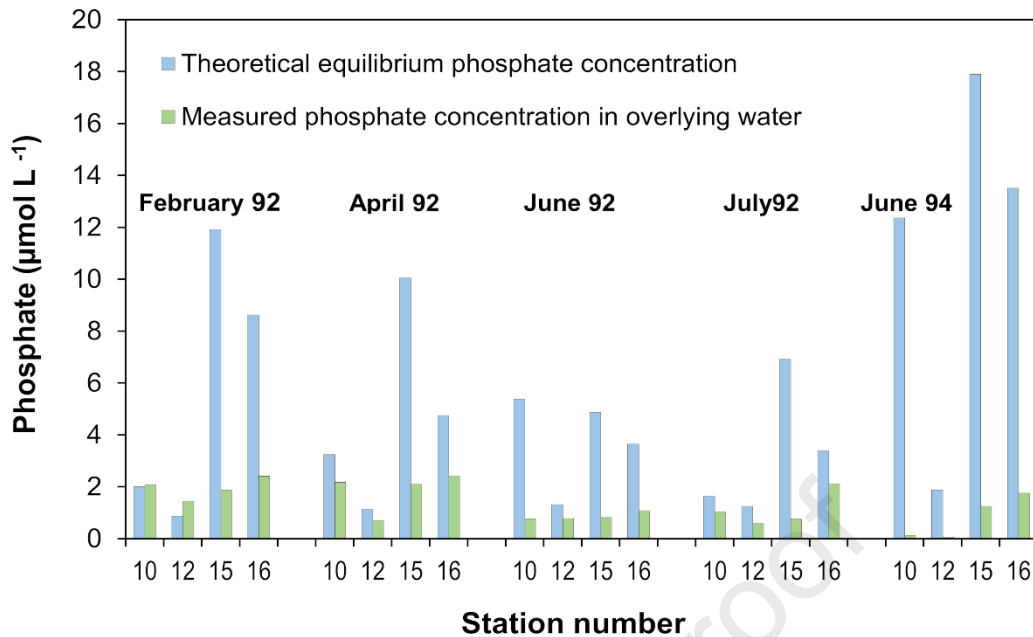
444 Reliable determination of *exch-P* is essential in oxic coastal environments where most other P-forms are  
445 unreactive (Kamp-Nielsen, 1975) and where highly dynamic conditions lead to intense resuspension events  
446 (Corbett, 2010; Tammeorg et al., 2013). Couceiro et al. (2013) showed that the only use of diffusive fluxes of  
447 interstitial nutrient concentrations, by omitting the resuspension in a North Sea biochemical model (Baretta et al.,  
448 1995) led to a large underestimation of nutrients concentrations in the water column and more particularly those  
449 of phosphate (from the adsorbed fraction (Sondergaard et al., 1992)). Moreover, with increasing storm frequency  
450 (Garnier et al., 2018), intensity and duration (Stockwell et al., 2019), resuspensions events (along with  
451 exchangeable phosphate release) are expected to increase (Tammeorg et al., 2013).

## 452 **5.2. Partition coefficient ( $K_p$ )**

453 The partition coefficient is a characteristic of the solid driving the amount of phosphate that can be adsorbed  
454 for a given water concentration of phosphate. As observed, a general relationship of  $K_p$  with the two main  
455 characteristics of the sediments, fine fraction and Fe contents, could be expected. Here, we find a concomitant  
456 increase of  $K_p$  with both Fe and fine particle contents, in agreement with the fact that iron oxides are essentially  
457 associated to fine particles (Andrieux-Loyer and Aminot, 2001). In the muddy sites a correlation between surface  
458 and total Fe contents may explain these relationships and also confirms the major role of Fe in phosphate  
459 adsorption onto sediments (Krom and Berner, 1980b, 1981; Sundby et al., 1992; Jensen et al., 1995). Lambert  
460 (1968), and Karickhoff et al, (1979) have found the partition coefficient to be linearly related to the organic matter  
461 content, which is mostly associated with the fine fraction.

462 However, the results of individual sites show that a wide range of  $K_p$  values was observed over the narrow  
463 range of each parameters in sites with low and high contents of fine fraction (respectively Bay of Seine and  
464 Penzé estuary). In contrast, good correlations were found only in the Loire and Gironde estuaries, characterized  
465 by a wide range of fine fraction and Fe content. In these two estuaries,  $K_p$  can be simply calculated from either  
466 of the two main sediment characteristics with limited uncertainty. In general, however, partition coefficients  
467 have to be assessed in each area at various stations in order to define the local behavior.

468 When  $\text{exch-P}$  and  $K_p$  have been determined for a sediment, its ability to adsorb or release phosphate can be  
469 inferred if the concentration of phosphate in the water in contact with the solid is also known. Indeed, the  
470 theoretical equilibrium water phosphate concentration ( $C_{the}$ ) corresponding to the  $\text{exch-P}$  concentration can be  
471 computed ( $C_{the} = \text{exch-P}/K_p$ ) and compared to the actual overlying water phosphate concentration. Note that  $C_{the}$   
472 corresponds to the so-called ‘equilibrium phosphate concentration, or  $\text{EPC}_0$ ’ determined experimentally by many  
473 other authors (Froelich, 1988; Slomp et al., 1996). An example is given in Fig. 7 for the Bay of Seine where  
474 overlying water phosphate concentrations were available.



475

476 **Fig. 7.** Theoretical equilibrium water phosphate concentration ( $C_{the}$ ) computed from the partition coefficient  
 477 ( $K_p$ ) as:  $C_{the} = \text{exch-P}/K_p$ ) compared to actual overlying water phosphate concentration at typical stations of the  
 478 Bay of Seine at various seasons. When the actual overlying water phosphate concentration is lower than the  
 479 theoretical one, adsorbed phosphate (exch-P) is liable to be released into the water column, which is generally the  
 480 case here.

481 In February, the sandier sediments (stations 10, 12), have overlying water phosphate concentrations close  
 482 to theoretical concentrations (Fig. 7). A steady-state between solid and liquid phase may thus be assumed since  
 483 the sediments of this area are subject to little resuspension (Avoine, 1986). In addition, the low phosphate  
 484 consumption in winter confirmed by low chlorophyll  $a$  values ( $0.5\text{-}1 \mu\text{g L}^{-1}$  vs up to  $9 \mu\text{g L}^{-1}$  during spring blooms;  
 485 Aminot et al., 1998) are not likely to disrupt the equilibrium. In the Seine mouth (stations 15, 16), subject to intense  
 486 particulate inputs and strong hydrodynamic conditions (Marmin, 2013), overlying phosphate concentrations are  
 487 up to 7 times lower than theoretical concentrations. This suggests the presence of freshly deposited sediments,  
 488 with high exchangeable phosphate concentrations which are not yet in equilibrium with overlying waters. This is  
 489 consistent with the sudden increase of the Seine flow from about  $200$  to about  $600 \text{ m}^3 \text{ s}^{-1}$  during the week before  
 490 sampling. Desorption from particles should occur in case of superficial sediment resuspension.

491 During spring and summer, all sediments are in large excess of phosphate when their equilibrium  
 492 concentrations are compared with that of the overlying waters (Fig. 7). The consumption of phosphate by the  
 493 phytoplankton blooms from April to July (chlorophyll  $a$  up to  $13 \mu\text{g L}^{-1}$  in April 92), with subsequent recycling in

494 the surface sediment layers, contributes to unbalance the equilibrium (especially in spring and summer) and to  
495 maintain phytoplanktonic growth through phosphate release if other nutrients are still available.

496 The above global approach of  $K_p$  is an example. Keeping in mind that exchangeable phosphate was  
497 preferentially associated with the fine particles ( $< 63 \mu\text{m}$ ; Andrieux-Loyer and Aminot, 2001), a determination of  
498  $K_p$  on the fine fraction subject to resuspension would be necessary in a more specific ecological field survey.  
499 Experimental  $K_p$  determination on this fraction should even show an amplified impact of phosphate desorption to  
500 the phytoplankton trophic level of coastal waters.

### 501 **5.3. Maximal Adsorption Capacity ( $Q^o$ )**

502 Continuous loading of external phosphorus to a coastal ecosystem could decline its sediments buffering  
503 capacity as a result of saturation of the exchangeable phosphate sites on sediment surface. However, Polyzopoulos  
504 et al. (1985) questioned the notion of maximal adsorption capacity. They noted that, in most experiments dealing  
505 with adsorption of phosphate onto solids, maxima are experimentally determined by placing the solid in solutions  
506 of increasing phosphate concentration, expecting to reach the concentration for which the solid does not adsorb  
507 phosphate any more. However, due to solid heterogeneity and the ability of certain minerals to accept multiple  
508 layers, the adsorbed amount increases continuously without plateauing to a maximum value. The notion of  
509 maximal capacity is thus quite difficult to define.

510 To tentatively overcome the problem of solid saturation experiments, we used a mathematical application  
511 of the IDE data, originally intended to determine  $\text{exch-P}$  concentrations, for computing  $Q^o$  by equation (18).  
512 Indeed, the Langmuir adsorption isotherm, which includes the notion of maximal adsorption capacity, was  
513 expected to be a relevant alternative to estimate a theoretical adsorption maximum. However, the results show that  
514 reliable values of  $Q^o$  were not obtained because of cumulative experimental and calculation uncertainties, despite  
515 precise phosphate determinations. The results are altered by large uncertainties and are not significantly distinct  
516 from  $\text{exch-P}$ , even though some larger values were found. Consequently, the values found may not reflect the true  
517 maximal adsorption capacity of the coastal sediments into consideration. Our study points out the difficulty of  
518 determination of  $Q^o$  by application of the Langmuir equations using the batch IDE results. This is attributed to the  
519 propagation of errors due to the necessity of working, in this kind of experiment, with low phosphate  
520 concentrations and sediment amounts (increasing the effect of the sediment inherent heterogeneity). However, the  
521 unsatisfactory determination of  $Q^o$  does not invalidate those of  $\text{exch-P}$  and  $K_p$  determined with an acceptable  
522 precision by the IDE method using the Langmuir equations.

523 Our observations about  $Q^o$  values may explain why they are among the lowest values reported in literature:  
524 1-98  $\mu\text{mol g}^{-1}$  (Bubba et al., 2003; Jalali and Peikam, 2013); 3-12  $\mu\text{mol g}^{-1}$  (Wang and Li 2010; Li et al., 2013).  
525 Difficulties in the estimation of the maximal adsorption capacity of phosphate onto solids, by direct experimental  
526 or indirect mathematical methods, highlight a significant challenge in the study of adsorbed phosphate  
527 geochemistry. However, coastal sediments and waters are relatively poor in phosphate compared to fresh water  
528 and soils, which minimizes the importance of this factor.

529

## 530 6. CONCLUSION

531 This work aimed to determine the principal data associated with the adsorption-desorption processes of  
532 phosphate, an essential nutrient potentially implied in eutrophication events in coastal and estuarine sediments.

533 There is an extremely wide literature on phosphate adsorption/desorption processes, but most studies deal  
534 with soils characterized by very high phosphate and organic matter concentrations in a complex matrix. In soils,  
535 processes are very different from those observed in sediments from coastal environments, or even lakes. In  
536 addition, most studies use adsorption experiments which essentially determine the equilibrium phosphate  
537 concentration ( $\text{EPC}_0$ ), a parameter used in steady state models, but not suitable for dynamic ecological models.  
538 Moreover, one-step extractions using varying solutions and solid concentrations were shown to fail to produce a  
539 correct value of exchangeable phosphate (Aminot and Andrieux, 1996).

540 Our approach relies on the Langmuir theory, adapted to solid-water exchanges in batch laboratory  
541 treatments, that we checked as a tool to obtain several parameters governing the exchange of phosphate between  
542 water and sediment in coastal environments. Essential data are thus available from the IDE experiment, such as  
543 the amount of exchangeable phosphate and the partition coefficient with a precision acceptable for environmental  
544 models. First, the amount of exchangeable phosphate determined using our method strictly meets its Froelich's  
545 definition (1988). In addition, the knowledge of the partition coefficient, coupled with surrounding water  
546 phosphate concentrations, brings first information on the ability of sediments to interact with the water phase to  
547 sorb or release phosphate. These data, obtained by the simple Langmuir theory can be easily applied in ecological  
548 models.

549 Using the same data set that was used for the determination of  $\text{exch-P}$  and  $K_p$ , the Langmuir equations (17)  
550 and (18) were used to compute the maximum amount of phosphate potentially sorbed ( $Q^o$ ) on the sediments. This  
551 was expected as a simple mathematical alternative to sediment saturation experiments subject to criticism.

552 Unfortunately, with high uncertainties, the equations fail in the satisfactory determination of  $Q^o$  and our results do  
553 not allow to conclude that  $Q^o$  is greater than  $\text{exch-P}$ , in most cases, as expected from literature results relying on  
554 experiments on phosphate sediment saturation (i.e., Li et al, 2013).

555

556

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### 563 **Appendix A. Supplementary data**

564 Supplementary data to this article can be found online at:

565

566 **Author contributions** The two authors have participated in the research and article preparation (Study's  
567 conception, acquisition of samples, phosphate analysis, writing of the manuscript).

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570 **Data availability** The data presented in the current study are available from the corresponding author upon  
571 request.

572 **Conflict of interest** The authors declare that they have no conflicts of interest.

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574

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### Figure captions

748 **Fig. 1.** Map of surveyed areas and location of sampling stations. A: The Bay of Seine; B: The Penzé estuary; C: The  
749 Loire estuary; D: The Gironde estuary.

750 **Fig. 2.** Comparison of exchangeable phosphate concentrations obtained by the Infinite Dilution Extrapolation  
751 (IDE) method, using Phosphate-Free Seawater (PFS) and bicarbonate solution ( $2.5 \text{ mmol l}^{-1}$ ) for various sediments  
752 from the Bay of Seine. Sediments were sampled at different periods of the year (size fraction  $< 63 \mu\text{m}$ ,  $< 0.1-3 \%$ ;  
753 loss at  $500^\circ\text{C}$ ,  $1-2 \%$ ).

754 **Fig. 3.** Kinetic experiments performed at  $20^\circ\text{C}$  for two typical coastal sediments.

755 **Fig. 4.** Application of the IDE experiment to the determination of exchangeable phosphate of a coastal sediment  
756 from the Loire estuary; size fraction  $< 63 \mu\text{m}$ , 93 %. Exchangeable phosphate is mathematically treated by A: an  
757 asymptotic function (equation (13)), B: a linear function (equation (15)).

758 **Fig. 5.** Partition coefficient ( $K_p$ ) as a function of A: the  $< 63 \mu\text{m}$  sediment fraction and B: the Fe content in the  
759 studied French coastal and estuarine areas.

760 **Fig. 6.** Comparison of exchangeable phosphate (exch-P) and maximal adsorption capacity ( $Q^0$ ) in the studied  
761 French coastal and estuarine areas. Confidence intervals of exch-P are generally within the corresponding open  
762 symbol

763 **Fig. 7.** Theoretical equilibrium water phosphate concentration ( $C_{the}$ , computed from the partition coefficient ( $K_p$ )  
764 as:  $C_{the} = \text{exch-P}/K_p$ ) compared to actual overlying water phosphate concentration at typical stations of the Bay of  
765 Seine at various seasons. When the actual overlying water phosphate concentration is lower than the theoretical  
766 one, adsorbed phosphate (exch-P) is liable to desorb into the water column, which is generally the case here.

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### Table caption

**Table 1** Nomenclature used herein.

**Table 2** Exchangeable phosphate (exch-P) and partition coefficients ( $K_p$ ) in surface sediments of the studied French coastal and estuarine areas.

**Table 3** Relationship parameters of  $K_p$  vs percent of  $< 63 \mu\text{m}$  particles and total Fe-content of studied site sediments

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### Highlights

- Langmuir theory and its constants for exchangeable phosphate in coastal sediments
- A simple linear model to obtain exchangeable-P from the Infinite Dilution Experiment
- Partition coefficient, a criterion for sediment-water phosphate exchange
- Is the determination of the maximum adsorption capacity reliable ?

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**Declaration of interests**

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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