



## **Sediment dissolved iron:phosphate ratios as indicators of phosphate fluxes and benthic processes in two temperate small estuaries.**

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Nitrogen is known to be the most limiting nutrient in marine ecosystems. However in transition areas such as estuaries, phosphorus can locally and seasonally play an important role. In these shallow areas, the sediment might act as a phosphorus sink, then liberating phosphate ( $\text{PO}_4$ ) under specific conditions (e.g. dissolution of iron-bound  $\text{PO}_4$  under anoxia, desorption of adsorbed  $\text{PO}_4$  in case of sediment resuspension...). The released  $\text{PO}_4$  may significantly increase the biologically available pool of phosphorus in the water, counteracting decreases in the external loads. One method to evaluate the contribution of benthic phosphorus is to measure phosphorus forms in the sediment matrix. Such extraction methods are robust but time consuming. Alternatively, other authors have suggested using dissolved Fe : P ratios as indicators of  $\text{PO}_4$  release to oxic waters.

This study aims to investigate the relationships between dissolved Fe : P ratios in pore waters and  $\text{PO}_4$  fluxes at the sediment-water interface in two macrotidal estuaries (Aulne and Elorn, NW France).  $\text{PO}_4$  and  $\text{Fe}^{2+}$  pore waters concentrations and  $\text{PO}_4$  diffusive fluxes were evaluated during a seasonal cycle.  $\text{PO}_4$  fluxes increased from the outer to the inner estuary and from February to July (up to  $300 \mu\text{mol m}^{-2} \text{d}^{-1}$ ).

In upper estuary,  $\text{NH}_4$  :  $\text{PO}_4$  and dissolved Fe : P ratios, significantly higher in the Aulne than in the Elorn, indicated a higher availability to retain P in the Aulne Estuary.

In both estuaries, high dissolved Fe : P ratios ( $> 2 \text{ mol/mol}$ ) in the surface layer of the sediment, especially in February, indicated insignificant or low  $\text{PO}_4$ -release and high  $\text{NH}_4$  :  $\text{PO}_4$  flux ratios. The lowest ratio generally occurred in July and corresponded to the highest  $\text{PO}_4$  fluxes and the lowest  $\text{NH}_4$  :  $\text{PO}_4$  fluxes. These Fe : P ratios, lower than the theoretical value of 2, suggested that there were not enough diffusing  $\text{Fe}^{3+}$  to retain  $\text{PO}_4$ . However relationships between Fe : P ratios and  $\text{PO}_4$  fluxes were specific of each part of the estuary and differed between the two estuaries in inner and mid areas. This could be explained by high hydrodynamic conditions and by the different morphology of the two estuaries. Nevertheless, dissolved Fe : P ratios could be efficiently used to predict  $\text{PO}_4$  fluxes in outer estuaries. In addition, our findings suggested differences in the exchange dynamics between these two estuaries, with potential implications for nutrient limitation.