

## Composition and Chemical Reactivity of an Iron-Phosphorus-Manganese Phase in a Freshwater Estuarine Sediment

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Recent studies on natural iron-rich colloids indicate that the formation of iron phosphate compounds might be a crucial process in freshwater environments. Here, we report on the presence of a mixed phase of iron, phosphorus and manganese which was identified in an intertidal freshwater sediment of the Scheldt estuary (Belgium). In the upper 15 cm depth of the sediment, this phase represents, on average, 24%, 63% and 87% of total Fe, Mn and P, respectively. The phase was characterized using both chemical (ascorbate and HCl extractions) and physical (XRD, microprobe, Mossbauer spectroscopy) techniques.

The rates of release of Fe, P and Mn from the sediment during ascorbate extraction were proportional to one another. That is, the build-up in solution of the three elements were characterized by constant ratios, with P/Fe, Mn/P and Mn/Fe molar ratios of  $0.71 \pm 0.04$ ,  $0.11 \pm 0.01$  and  $0.08 \pm 0.01$ , respectively. Microprobe analyses of the mixed phase revealed very similar molar ratios of  $0.78 \pm 0.03$ ,  $0.13 \pm 0.02$  and  $0.10 \pm 0.01$  for P/Fe, Mn/P and Mn/F, respectively. Thus, ascorbate stoichiometrically extracted the mixed phase. The Fe oxide phases hematite and ilmenite were also identified with Mossbauer spectroscopy. However, these phases were not ascorbate extractable and represented a relatively unreactive Fe pool in the sediment. Furthermore, microprobe analyses showed that these Fe oxides carried little P and Mn.

The concentration of the mixed phase decreased with depth, with a 50% lower concentration at 12-14 cm depth compared to the upper 0-2 cm of sediment. The decreasing solid phase concentration, plus the pore water dissolved  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and phosphate concentration profiles indicate that the dissolution of the mixed Fe/P/Mn phase, rather than Fe oxide phases, controls the remobilisation of Fe, P and Mn in the sediments. The chemical and microbial reactivity of this phase is therefore crucial for biogeochemical cycling of Fe, P and Mn in the freshwater portion of the estuary.