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Towards quantitative speciation of phosphorus in marine sediments by micro XRF mapping

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Phosphorus (P) is a key macronutrient for marine primary production. Anthropogenic inputs of P are thus largely responsible for the recent eutrophication of restricted marine systems such as the Baltic Sea. Burial in sediments represents the major pathway by which P is removed from the marine environment, and prevented from fuelling further primary production. Therefore, understanding the mechanisms and rates of P burial is crucial to the management of nutrient inputs to restricted marine systems. P may be buried in sedimentary organic matter or in a range of authigenic and detrital mineral phases. The respective concentrations of these phases in sediments have traditionally been quantified by sequential extraction techniques. However, the sequential extraction approach has several limitations, most notably the parallel dissolution of multiple P-bearing phases in a single extraction step. Here we present a new approach to the quantification of P phases in marine sediments. Using micro XRF analysis of epoxy-embedded sediment blocks, we generated in-situ 2D maps of multiple elements in Baltic Sea sediment samples. By overlaying the elemental count matrices in multi-dimensional space, we identified the principal P-bearing phases and estimated their contributions to total P counts. Using a series of ground P mineral standards prepared in quartz and carbonate matrices, we then determined sensitivity factors for each mineral/matrix combination, allowing quantification of the phases identified in the samples. Our approach allows the deconvolution of multiple P-bearing phases with varying contributions of Ca, Fe and Mn, including phases expected to be dissolved simultaneously in the sequential extraction. Furthermore, our approach offers the advantages of being non-destructive and facilitating high resolution records of temporal changes in the P speciation of sediments.