



## Measurement of the chemical composition of suspended sediment using a handheld XRF analyser

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Measurement of the chemical composition of suspended sediment in rivers usually requires the collection of large volumes of river water to obtain sufficient suspended sediment for analysis. Alternatively, the separation of suspended sediments from the river water can be achieved using a continuous flow centrifuge in the field. A major disadvantage of centrifuging is that it does not recover the finest sediment particles, which typically contain environmentally significant elements.

In this study, we explore the use of direct XRF (X-Ray Fluorescence) measurement of the element concentrations of suspended sediment extracted by filtration using membrane filters, which requires a much smaller sample of suspended sediment (typically 5 – 50 mg) and, therefore, a much smaller volume of river water sample (< 2 litres). We employed an Olympus Delta-50 Premium handheld 50kV XRF analyser (60 sec tests in 3-Beam Soil Mode) for the analysis of the suspended sediment samples. Because the small amount of sediment, the XRF signal was corrected using a correction factor that depends on the mass of sediment on the membrane filter. To derive the correction factor as a power-law function of sediment mass, two Rhine sediment samples of known composition were used. These sediment samples were resuspended in distilled water and different known volumes of the water with resuspended sediment were filtered through 0.45  $\mu\text{m}$  mixed cellulose ester membrane filters. The filters were then analysed using the XRF analyser. Each filter was analysed three times to examine the effect of inhomogeneities in sediment composition across the filter.

To examine the precision of the element concentrations, 13 replicate water samples were collected from the Rhine River near Vuren, the Netherlands, in autumn 2017. The samples were also filtered through 0.45  $\mu\text{m}$  membrane filters and the filters were analysed three times using the XRF analyser.

The XRF analysis yield usable signals for Ca, Cr, Fe, K, Mn, Pb, Rb, Ti, Sr, and Zn; the signals for As, Ba, Cd, Cu, Co, Mo, Ni, Sb, Sn, and Zr, were often or always below the detection limit. The corrected element concentrations are well within the range of the element concentrations in suspended Rhine sediment as measured by Rijkswaterstaat (Dutch Ministry of Infrastructure and Water Management) and Rhine sediment samples collected using a Phillips time-integrated sediment sampler during autumn 2017.

In general, the precision of the analyses expressed as the coefficient of variation varies between 0.13 and 0.22. The Pb analysis is less precise with a coefficient of variation of about 0.4. The majority of the analysis uncertainty can be attributed to the uncertainty in the parameter correction factor function. The inhomogeneities in sediment composition across the membrane filter only contribute for about 10% to the total uncertainty. The precision of the analyses can be improved by a more precise determination of the power-law correction factor function.