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The distribution of anthropogenic REE in the Dutch distributaries of the Rhine: the role of suspended matter

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In nature rare earth elements (REE) occur in fixed ratios; contamination with a single rare earth element causes a clear deviation from the natural NASC normalized REE-patterns: an anomaly. REE are progressively used in many high technology products and processes. For example, gadolinium-containing chelates have been used since the '80s as contrasting agent in MRI-imaging. The pertaining anomaly is currently used as a tracer for distinguishing waste water from water unaffected by anthropogenic contamination. In the Dutch monitoring program in the Rhine-Meuse distributaries, total (10% HNO $_3$ digested) and dissolved (< 0.45 μ m) fractions in surface water are routinely analysed, and with two-week intervals suspended matter samples are collected with a centrifuge. Since 2008, the set of analysed elements was extended with REE, enabling this study.

Lobith, the entry point of the River Rhine in The Netherlands, shows an annual oscillation in the magnitude of the lanthanum (La) anomaly. This positive La-anomaly was reported by Kulaksiz and Bau in 2011; they identified the point source as a production plant for catalysts used in petroleum refining in the German city of Worms. Since the spring of 2011, samarium (Sm) is used in the same process, resulting in matching La- and Sm-anomalies.

The anthropogenic La and Sm concentrations are predominantly present in the total fraction, which suggests that the anthropogenic La and Sm concentrations are associated with suspended matter. The anthropogenic La and Sm concentrations are lower in the suspended matter samples collected with the centrifuge, suggesting a bias of these La and Sm concentrations in the finer fraction of the suspended matter. The anthropogenic La en Sm concentrations remain relatively constant throughout the rivers, but close to Lake IJsselmeer and the North Sea, sedimentation causes a sharp decrease in the anthropogenic concentrations. Detailed sampling of sediments, suspended matter and water could give a clear insight in the sedimentation rates in the area. The off-set between the introductions of the two anthropogenic contaminants can be used throughout the Rhine catchment downstream of Worms to distinguish new suspended matter and resuspended older sediments and the sedimentation of these two fractions. Although the La- and Sm-anomalies largely disappear towards the North Sea, the La-anomaly in the sediments is still larger in the coastal areas than at the more distant sampling points. In order to gain more insight in the processes that take place at the freshwater-saltwater interface (e.g. desorption and sedimentation), more research is planned.