

Matrix correlation as a tool to identify anthropogenic Gd anomalies in river water samples

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Gadolinium is used since 1988 as a contrast agent in resonance magnetic imaging (RMI) medical exams. Free gadolinium is toxic, so highly soluble and stable synthetic Gd-chelates are administered to patients. The Gd-chelates excreted in the urine remain dissolved during the regular sewage treatment, becoming enriched in the effluents discharged in the drainage system. As a result, many authors reported Gd anomalies in river water and also in shallow groundwater. Gd anomalies are usually identified by means of semi-log plots of rare earth elements (REE) data normalized to a reference (e.g. PAAS).

We studied samples from Atibaia River and Anhumas Creek, in São Paulo state, Brazil. River water samples were filtered through 0.22 μm membranes. Major ions were measured by ion chromatography and acidified samples were used to determine 42 trace elements by ICP-MS, either directly or after a pre-concentration step (REE). The particulate matter retained during filtration was also analysed, after acid digestion.

The results obtained for Gd in water samples ranged between 4.01 and 70.1 ng/L. A correlation matrix was calculated with all analytical data. The naturally occurring REE form a coherent group and very high correlation coefficients (near 1) were obtained as expected. However, Gd results showed very low correlation with respect to the other REE (0 to 0.36), when all samples are considered. The correlation plots of Gd showed both points with a clear trend and scattered data. These last corresponded to the same samples that exhibited Gd anomalies in the REE normalized plots. The trend in the plot represents the natural occurrence of Gd while the samples with anomalous Gd content could be identified without normalizing the REE results. Furthermore, the results of Gd showed high correlations with the results of other soluble constituents like Na^+ , K^+ , SO_4^{2-} , PO_4^{3-} , HCO_3^- , NH_4^+ , and electrical conductivity. The correlation matrix calculated with the results obtained from the particulate matter data resulted in Gd behaving coherently with the other elements of the REE group. As a whole, such results confirm that the anomalous Gd is present in the truly dissolved fraction of the studied water samples.