



Sediment fingerprinting experiments to test the sensitivity of multivariate mixing models

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Sediment fingerprinting techniques provide insight into the dynamics of sediment transfer processes and support for catchment management decisions. As questions being asked of fingerprinting datasets become increasingly complex, validation of model output and sensitivity tests are increasingly important. This study adopts an experimental approach to explore the validity and sensitivity of mixing model outputs for materials with contrasting geochemical and particle size composition. The experiments reported here focused on (i) the sensitivity of model output to different fingerprint selection procedures and (ii) the influence of source material particle size distributions on model output.

Five soils with significantly different geochemistry, soil organic matter and particle size distributions were selected as experimental source materials. A total of twelve sediment mixtures were prepared in the laboratory by combining different quantified proportions of the $< 63 \mu\text{m}$ fraction of the five source soils i.e. assuming no fluvial sorting of the mixture. The geochemistry of all source and mixture samples (5 source soils and 12 mixed soils) were analysed using X-ray fluorescence (XRF). Tracer properties were selected from 18 elements for which mass concentrations were found to be significantly different between sources. Sets of fingerprint properties that discriminate target sources were selected using a range of different independent statistical approaches (e.g. Kruskal-Wallis test, Discriminant Function Analysis (DFA), Principal Component Analysis (PCA), or correlation matrix). Summary results for the use of the mixing model with the different sets of fingerprint properties for the twelve mixed soils were reasonably consistent with the initial mixing percentages initially known. Given the experimental nature of the work and dry mixing of materials, geochemical conservative behavior was assumed for all elements, even for those that might be disregarded in aquatic systems (e.g. P). In general, the best fits between actual and modeled proportions were found using a set of nine tracer properties (Sr, Rb, Fe, Ti, Ca, Al, P, Si, K, Si) that were derived using DFA coupled with a multivariate stepwise algorithm, with errors between real and estimated value that did not exceed 6.7 % and values of GOF above 94.5 %.

The second set of experiments aimed to explore the sensitivity of model output to variability in the particle size of source materials assuming that a degree of fluvial sorting of the resulting mixture took place. Most particle size correction procedures assume grain size effects are consistent across sources and tracer properties which is not always the case. Consequently, the $< 40 \mu\text{m}$ fraction of selected soil mixtures was analysed to simulate the effect of selective fluvial transport of finer particles and the results were compared to those for source materials. Preliminary findings from this experiment demonstrate the sensitivity of the numerical mixing model outputs to different particle size distributions of source material and the variable impact of fluvial sorting on end member signatures used in mixing models. The results suggest that particle size correction procedures require careful scrutiny in the context of variable source characteristics.