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Use of spatio-temporal water quality data to conceptualise tracer based hydrological models in mesoscale river basins

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Tracer based hydrological models have to face the spatial heterogeneity of landscape organisation, when applied to hydrochemically differentiate runoff sources at greater scales. This heterogeneity leads to additional runoff sources, which is particularly the case in anthropogenically impacted basins. It furthermore results in spatially varying hydrochemical runoff source compositions due to catchment characteristics like bedrock lithology, soil cover and land use. In this study synoptic sampling of stream waters was applied at different flows to record the spatio-temporal variability of water quality as an effect of catchment heterogeneity. Sampling sites range from monolithological headwaters of different bedrock types to the point source dominated main stream of the catchment. Samples were collected at low flow (summer), high flow (winter) and at intermediate flow conditions (spring). The study area is the Dill catchment (692 sqkm), located in the low mountainous regions of Hesse, Germany. It is of highly heterogenous lithology and anthropogenically impacted at the lower water courses. The water samples were analysed for a set of 21 stream water solutes by ICP-MS. Subsequently principle component analyses (PCA) of the water quality variables and hierarchical cluster analyses (HCA) of sampling sites were conducted for each of the sampled flows. The results reveal that hydrochemical patterns of stream waters can be ascribed to the influence of point source inputs and the different lithological signals of the catchment at low flow conditions. At high flow the different lithological signals loose their individuality due to dilution processes. Beyond this the results show that tracer studies, including catchment wide field surveys and analysis of multiple tracers

combined with multivariate statistical techniques are useful tools towards systematically conceptualising the knowledge about catchment functioning. This knowledge comprises information about the controls on stream water quality at different flows, the delineation of hydrochemically emergent runoff components, the choice of meaningful tracers and implications on the type of hydrochemical mixing model to choose for water source apportionment. The outcome of this study will form the basis for a soft data calibration experiment for the Dill catchment, using a mesoscale semi-distributed model.