Geophysical Research Abstracts Vol. 15, EGU2013-11481, 2013 EGU General Assembly 2013 © Author(s) 2013. CC Attribution 3.0 License.



## Solute pathways and travel times: implications on water quality in the Neckartal transect model study

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The interactions between subsurface- and surface waters and their quality are not well understood at the catchment scale. The goal of this study was to quantify the factors that influence geochemistry of soil, seepage water, rocks and groundwater and link them to water flow paths and travel times in the subsurface. The model MIN3P was used in this numerical study, coupling variably saturated water flow, solute as well as gas transport and geochemical interactions from precitation to river discharge. Solute travel time distribution is delineated, in combination with a novel approach to compute the transient evolution of flowpaths.

Results show that subsurface water residence times range from approximately two to 2000 years. Different zones are to be expected with respect to the development of mineral equilibria, namely purely atmospherically influenced, as well as open and closed system carbonate dissolution. The extent of reducing conditions is controlled by the presence of organic rich layers such as peat deposits, the dissolution kinetics of aquifer organic matter and the subsequent mixing with oxygenated water by hydrodynamic dispersion.

Only slight shifts of concentrations could be observed due to transient flow over the course of a year. Transient flow conditions, however, were found to influence concentration breakthrough at particular, usually shallow, locations, as could be seen in the hillslope bottom profiles. Natural flow focusing zones at the hillslope/valley interface, hyporheic zones and heterogeneities in the valleys are such potentially dynamic spots. Non-equilibrium conditions along the flow paths and changes in aqueous saturation altering gas transport, were both found unlikely to cause the observed shift in concentration time series. Particle backtracking in such a transient flow field is useful to find the origin of flow pathways and was able to explain the observed concentration shifts resulting from transport pathways.