Geophysical Research Abstracts
Vol. 18, EGU2016-7641, 2016
EGU General Assembly 2016

Implementing a GLUE-based approach for analysing the uncertainties associated with the modelling of water mean transit times using tritium

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The use of tritium in catchment water mean transit time (MTT) studies has recently been claimed as necessary, because it can demonstrate the contribution of old water not identified by stable isotopes. Recent analytical developments have substantially improved the precision of tritium activity determinations. This improvement may reinforce the use of tritium in hydrological investigations, taking advantage of the end of the interference caused by past nuclear weapon tests.
TEPMGLUE, a Generalised Likelihood Uncertainty Estimation (GLUE) based approach was developed for analysing the uncertainties associated with the use of lumped parameter models for investigating water MTTs. The approach consists of two different steps; first, the analytical precision of tritium determination in both the input and catchment sample water analyses is taken into account, and subsequently the lumped model parameter identification issue is considered. This methodology was implemented using the exponential-piston model in the Vallcebre research catchments where several water samples were analysed for tritium in 1996, 1997 and 1998 (low analytical precision), and 2013 (high analytical precision).
For every site and sample set, the TEPMGLUE approach provided two outcomes: first a map of the relationships between the ratio of exponential to total flow (model parameter f) and the MTTs and, second, a likelihood weighted cumulative density function for a range of MTT values instead of a single optimal one. This allowed the estimation of the statistical significance of differences observed in MTTs among diverse water sample sets using a resampling test.
The results showed that MTTs were poorly sensitive to the model parameter f. Most of the uncertainty was due to parameter identifiability issues, whose contribution decreased from more than 90% for the older samples to less than 50% for the 2013 samples. The contribution of the analytical errors rose to 47% in the latter samples, despite their improved analytical quality. When only the 2013 samples were used, the likelihood weighted cumulative density functions showed multi-modal patterns that were well simulated by mixing several normal distributions. These multiple solutions issues may be fixed if the sites are resampled in a few years thanks to the gradual temporal stabilisation of tritium in rainfall.
Finally, the results allowed the classification of the sampled waters in three main groups which were consistent with the geological setting of the area: shallow open aquifers in the soils showed MTTs of nearly 5 years, whereas spring and stream base flow waters showed MTTs of about 7.5 years in one of the sub-catchments and nearly 12 years in the other one.