## Validating the 1D saturated zone modelling approach

The one-dimensional solute transport modelling approach for the saturated zone adopted in this work is based on the following assumptions: (1) average flow rates derived from particle tracking are suitable for use in the 1D solution of the ADE to derive solute breakthrough, (2) the groundwater flow field and hydraulic gradients are sufficiently uniform to allow the flow field to be represented

by a 1D model, and (3) transverse horizontal and vertical dispersion are negligible relative to the longitudinal dispersion. For the purpose of demonstrating the validity of the proposed approach, we use a hypothetical, though realistic, problem whereby solutes are introduced to the aquifer via recharge (similar to case study scenario) and move laterally to a groundwater extraction bore. The extraction scenario was purposely used to create curvilinear flow paths of varying lengths along which solute particles would travel at different rates. Solute breakthrough was calculated with the 1D analytical solution along every path that contributed to solute delivery to the extraction point (within a defined time period). The contribution from each BTC along a given travel path was summed to define total solute breakthrough at the extraction point. Since the governing solute transport equations and the initial and boundary conditions are linear in C, the superposition principle is applicable (Toride et al., 1995). We then compare the results in terms of solute breakthrough with those derived from a fully 3D numerical groundwater flow and solute transport model implemented in MODFLOW and MT3D. When the summation of analytical BTCs along individual solute trajectories agree with the MT3D BTC at the extraction point, this means that the analytical BTC along any individual path is correctly predicted. We recognise that the conditions for the validation exercise are different from our case study where the flow fields are natural (i.e., not altered by groundwater extraction), the purpose is demonstrating that solute transport along a 1D curvilinear flow path of known length and flow rate can be modelled with existing analytical solutions of the ADE that assume a linear trajectory.

A Visual MODFLOW model (Waterloo Hydrogeologic) was set up (1) to provide flow paths and flow rates required by the 1D analytical solution (similar to what is done in the regional model), and (2) to provide the flow fields for MT3D that would generate the independent validation data. The 1000m-wide by 2000m-long synthetic MODFLOW model includes a constant head boundary along the eastern side while the remaining sides are no-flow boundaries (Figure S1). Recharge was introduced to the upper half of the flow domain with cells 1-100 receiving 100 mm/year with the exception of Cells 10-14 that received 200 mm/year. Two extraction wells with a pumping rate of 1000 m3/day were introduced at L1=100 m and L2=200 m from the constant head boundary; note that only one pump was activated at a time for each of the two extraction scenarios (L1 and L2). A concentration observation well was introduced at the extraction well to monitor solute breakthrough. Steady-state flow conditions for each extraction scenario were established and used as initial head distribution for the transient MODPATH/MT3D simulations. In order to provide independent validation data for the MT3D simulation, solutes were introduced with the recharge flux during the first 500 days of the 3000-day simulation thus representing a solute pulse with unit concentration (mass/m3) at every recharge cell with the exception of cells 2, 3, 4, 5, which had concentrations of 2, 3, 4, and 5 (mass/m3) unit concentrations, respectively. The input of solutes was varied both temporally (as it is a pulse) and spatially (different rates at some cells) to demonstrate the versatility and validity of the method. For the MODPATH simulation, fifty tracking particles were introduced along a 500 m long section of the constant head boundary. One particle was released in the centre of each of the 10 m-wide cells, starting north of the cell opposite to the extraction point. The MODPATH simulation period was 3000 days to ensure that the number of tracking particles used is sufficient to capture all tracks that may contribute to solute delivery at the extraction point within the 1000-day MT3D reporting period (period during which results from the two approaches are compared).

Solute breakthrough calculations using the hybrid approach are described herein. Since we are trying to replicate the MODFLOW-MT3D reference data and define breakthrough at the extraction wells, an identical discretisation was used when implementing the hybrid model whereby an analytical solution is invoked for every MODPATH-derived flow path. A BTC typically describes concentration versus time *C*(*t*), however, since we are superimposing BTCs for multiple flow paths to derive an effective BTC at the extraction wells, we define BTCN as solute mass versus time (solute flux) for each flow path. The boundary condition for solving the analytical solution Eq. 2 is a direct delta function (Boundary Value Problem; Toride et al., 1995) defined by the solute flux from a recharge cell, which is given by:

$Sf\_{n}=A\_{n}×Re\_{n}×C\_{n}$ (Eq. S1)

where *Sfn* is solute flux through entering any recharge cell *n* (mass/day), *An* is cell area (for all domain cells *A*n 100 m2), *Ren* isrecharge rate for any recharge cell *n* (m/day), *Cn* is recharge solute concentration for any recharge cell n (mass/m3).

Solute breakthrough (concentration versus time) at the extraction wells is obtained by superimposing multiple BTCns (mass/day) collected from all flow paths (corresponding to every tracking particle used in the MODFLOW model), which are then normalised by the pumping rate *P* of the well (m3/day) to produce concentration (mass/m3) versus time data:

$C\_{t}=\frac{1}{P}\sum\_{T=1}^{n}BTC\_{n}$ (Eq. S2)

where *Ct* is concentration (mass/m3) as a function of time *t* at the extraction point, *BTCn* is solute mass versus time (solute flux) for each flow track, *T* isparticle flow track, and *n* is the number of flow tracks contributing to solute transport during the simulation period. Note that using a larger than required number of paths ‘n’ would not compromise the results as one would be adding zeros to Ct, that is, paths starting from very distant points would not reach the extraction point within the 1000-day period and hence contribute nothing to solute delivery (Ct) to the extraction point.

## Validation of the hybrid solute transport modelling approach

The hybrid solute transport modelling approach adopted here used MODPATH-derived flow paths to generate groundwater flow velocities to run the 1D analytical solution of the advection-dispersion model as implemented in CXTFIT. This approach is similar to consideration of individual stream tubes along each of the particle paths, without solute interaction between stream tubes (Jacques et al., 1997; Vanderborght et al., 2006). Here we validate this approach to generate an average BTC at an extraction well by comparison with the average BTC generated with the MODFLOW-MT3D reference approach.

First, the particle path lines are discussed. Contours of the steady-state pressure heads for the two extraction scenarios (same pumping rate but different well location) are shown in Figure S2 (blue lines). Contours were derived from the imposed boundary conditions and stresses relating to the synthetic MODFLOW model. Figure S2 also shows the paths of 50 released particles with only 33 and 40 particles arriving at the extraction wells after 3000 days of travel time for L1=100 m and L2=200 m, respectively. For each of the particles arriving at the well, MODPATH provided the exact arrival time and flow path length, from which the flow rates were calculated (see Figure S3).

Figure S4 shows excellent agreement between the superimposed BTCs generated from applying the 1D analytical solution with velocities from Figure S3 (that is the hybrid approach) and the use of a 3D numerical solution through MT3D. For extraction well L1=100 m 33 individual BTCs were used to calculate the average BTC, whereas at well L2=200 m 40 BTCs were used for calculating the average. There is a very good agreement between both methods, with a maximum discrepancy of 7% across the entire simulation period. The slightly higher concentrations for the hybrid approach for well L1=100 m was likely due to the absence of lateral dispersion between the individual stream tubes. For well L2=200 m the path lines are longer therefore longitudinal dispersion in the hybrid approach has reduced concentrations to values very close to those of the 3D numerical model. The magnitude of the discrepancies in peak concentration was only 1.3% and 0.12% for L1=100 m and L2=200 m scenarios, respectively. As the peak concentration was the key prediction in this work, the accuracy of the proposed hybrid approach was deemed to be excellent.