# Identification of chemical reactions and their reaction rate coefficients with push-pull tests

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Abstract Determination of chemical reactions and their reaction rate coefficients on a field scale is of concern in many hydrogeological and environmental issues. A push-pull test provides an excellent way to determine this. A simplified method for the interpretation is given in the literature. Here, the accuracy of the method is studied by analysing the observations from a push-pull test performed in the Belgian coastal plain with the simplified method, calculating the confidence intervals for the results and interpreting the observations with TRACER3D, a numerical model. It is shown that by calculating the confidence intervals and using the numerical model, additional usable information can be elicited from the test. Aerobic respiration and denitrification were both derived from the single test together with their first-order reaction rate coefficients.

Keywords denitrification; modelling; parameter identification; push-pull test

### **INTRODUCTION**

A push-pull test is a well test to derive *in situ* chemical processes which occur in the groundwater reservoir. The method consists of a pulse-type injection (the "push") of a test solution into the saturated zone of an aquifer through the screen of a well followed by the extraction (the "pull") of the test solution and groundwater mixture from the same well. The test solution contains a conservative (non-reactive) tracer and one or more reactive solutes selected to investigate specific chemical and/or microbial activities. The concentrations of the reactive solutes are compared with the concentrations of the conservative tracer to deduce reaction mechanisms and rates. This test was used by Istok *et al.* (1997) to study *in situ* microbiological activities. Haggerty *et al.* (1998) developed a simplified method of push-pull test data analysis, making possible the determination of the *in situ* reaction rate coefficient, *k*. Their method is not strongly sensitive to variations in other aquifer parameters such as conductivity, porosity or dispersivity. It is assumed that the injected solution is well mixed within the portion of the aquifer assayed by the test and that the retardation factors for tracer(s) and reactant(s) are identical. Haggerty *et al.* (1998) derived that:

$$\ln\left(\frac{c_d(t^*)}{c_{tr}(t^*)}\right) = \ln\left(\frac{\left(1 - e^{-kt_{inj}}\right)}{kt_{inj}}\right) - kt^*$$
(1)

where  $c_d(t^*)$  is the relative concentration of the reactant (the measured concentration divided by the injected concentration) at time  $t^*$ ;  $c_{tr}(t^*)$  is the relative concentration of the conservative tracer at  $t^*$ ;  $t_{inj}$  is the duration of the pulse injection; and  $t^*$  is the time

elapsed since the end of the test solution's injection. Equation (1) has the form of a first-order equation (Y = A - kX) and an estimate of k can be obtained by measuring the relative concentration of conservative tracer and reactant as a function of the time elapsed since the end of the injection phase using a standard least-square approach.

Here the accuracy of the simplified method is studied. Confidence intervals for the first-order reaction rate coefficients were determined using simple regression. A numerical model simulating flow and solute transport in the vicinity of wells was applied. It was used to verify and if possible supplement the results obtained with the analytical method of Haggerty *et al.* (1998).

#### FIELD TEST AND INTERPRETATION

A field test was performed in the Quaternary sediments of the Belgian coastal plain. Schematization of the groundwater reservoir is given in Fig. 1. A well with the screen situated in fine sands containing organic material is used. Just above the screen, a peat layer is present. A pulse of 505 L of water marked with NaBr and KNO<sub>3</sub> was injected. This solution was prepared in a container open to the air so that the water was also saturated with oxygen. Bromide was used as a conservative tracer and nitrate and dissolved oxygen as reactive tracers. In the injected solution 826 mg Na<sup>+</sup> L<sup>-1</sup>, 228 mg K<sup>+</sup> L<sup>-1</sup>, 266 mg Br<sup>-</sup> L<sup>-1</sup>, 157 mg NO<sub>3</sub><sup>+</sup> L<sup>-1</sup> and 9.5 mg O<sub>2</sub> L<sup>-1</sup> was present. The injection phase lasted 30 minutes whereas the subsequent pumping phase lasted 8 hours. Water samples were taken every half hour and these were analysed for dissolved oxygen content, pH, Eh, electrical conductivity and major anions and cations. The aim of the test was to observe and derive the first-order reaction rate coefficient of aerobic respiration, denitrification and possible other reactions.

The evolution of the calcium, sodium, potassium, bromide, nitrate, bicarbonate and dissolved oxygen concentrations as a function of the extracted volume are shown in Fig. 2. To identify the chemical reactions, enrichment (+) or depletion (–)  $A_x$  (mmol L<sup>-1</sup>) is calculated as a function of the  $Q/Q_{inj}$ :

$$A_x = X - X_{ref} \tag{2}$$



Fig. 1 Schematization of the groundwater reservoir and the two phases of the pushpull test.



**Fig. 2** Enrichment (positive) or depletion (negative) of the pumped water in comparison with the formation water as a function of the ratio of extracted volume (Q) to injected volume  $(Q_{inj})$  for the most important cations, anions and dissolved oxygen.

where X is the concentration of the cation/anion (mmol  $L^{-1}$ ) and  $X_{ref}$  is the concentration in the formation water of the cation/anion (mmol  $L^{-1}$ ).

A reductive environment is present in the aquifer; an Eh of -51 mV was measured as the background aquifer value and an Eh of -126 mV was measured in the over-lying peat layer. Oxygen and nitrate are both important oxidants. During the push-pull test, oxygen is consumed first and its content diminishes sharply to very low values during the first part of the test. Afterwards there is a continuing decrease until about 80% of the injection water is recovered and the dissolved oxygen content is at its background level. This oxygen is consumed by organic matter that is present in the sediments (CH<sub>2</sub>O + O<sub>2</sub>  $\rightarrow$  CO<sub>2</sub> + H<sub>2</sub>O). When most of the oxygen is consumed (from about 80% of the injected volume recovered) the nitrate concentration decreases towards background levels. Before that point no nitrate is consumed relative to the injected concentration and the excess concentration of nitrate relative to the formation water remains constant. The nitrate is most likely consumed by organic matter present in the sediments. This process (5CH<sub>2</sub>O + 4NO<sup>-</sup><sub>3</sub>  $\rightarrow$  2N<sub>2</sub> + 4HCO<sup>-</sup><sub>3</sub> + CO<sub>2</sub> + 3H<sub>2</sub>O) is bacterially catalysed.

First-order reaction rate coefficients are calculated for aerobic respiration and denitrification according to the method proposed by Haggerty *et al.* (1998). For the aerobic respiration, the observations to 5.5 h after the start of the test are used (10 observations). Afterwards, denitrification takes over. Denitrification first-order reaction rate

coefficients are determined on samples taken from 5.5 h after the start of the test onward (six observations). The 90%, 95% and 99% confidence intervals are calculated using simple regression. Results are shown in Fig. 3 and Table 1. The aerobic respiration rate is half that of the denitrification rate. Due to the relatively limited number of observation points the confidence intervals are relatively large.



**Fig. 3** Observations, best fit and confidence intervals of the calculation of the first-order reaction rate coefficients for aerobic respiration and denitrification following the method of Haggerty *et al.* (1998). In the graphs, X equals  $t^*$  and Y is the natural logarithm of the ratio of the relative concentration of the tracer to the reactant.

**Table 1** First-order reaction rate coefficients for aerobic respiration, denitrification and emergence of bicarbonate determined with the push-pull test on the Houtave test site.

	k (h <sup>-1</sup> )	99% conf. interv.	95% conf. interv.	90% conf. interv.
Aerobic respiration	-0.368	$\pm 0.176$	$\pm 0.121$	$\pm 0.097$
Denitrification	-0.731	$\pm 0.349$	$\pm 0.211$	$\pm 0.162$

One of the products of denitrification is bicarbonate. The bicarbonate concentration remains more or less constant before 80% of the injected volume is pumped up. Afterwards this concentration increases. This increase is correlated with the decrease of nitrate. The more nitrate consumed, the larger the enrichment of bicarbonate in the samples. When the nitrate concentration reaches its background concentration the enrichment of bicarbonate in the samples diminishes. Based on the data in Fig. 2, it is not clear if sodium, potassium and calcium undergo chemical reaction, such as for example, cation exchange. There is a very small increase in calcium concentration with reference to the formation water after 80% of the injected volume is pumped up. There is a more or less constant enrichment of sodium in the extracted water until all the injected water is pumped up and the enrichment in potassium decreases in the course of the test.

Finally some calculations with TRACER3D are performed. This is an axisymmetric finite element model which simulates the flow and solute transport in the vicinity of a well (Vandenbohede, 2003; Vandenbohede & Lebbe, 2003) using the methods of characteristics to calculate dispersion. First-order decay and retardation can also be taken into account.



**Fig. 4** Comparison between observations (dots) and calculated breakthrough curves using TRACER3D. Full lines are simulations with no first order decay, dotted line is with first order decay.

The results of the calculations with TRACER3D are presented in Fig. 4. A good fit between observations and calculation is obtained. For bromide, potassium and sodium only advective transport is taken into account. This proves that bromide is indeed acting here as a conservative tracer and that potassium and sodium do not undergo reactions such as cation exchange. In trying to derive a reaction rate coefficient with the simplified method, large confidence intervals were encountered making it impossible to determine if sodium and potassium underwent only non-reactive transport or were reacting chemically. Note that the sodium concentrations of samples taken during the concluding part of the test are spread out. Two calculations are shown for dissolved oxygen. First, tracer breakthrough was calculated without any reactions. This resulted in concentrations that are too high. A first-order reaction rate coefficient of 0.625  $h^{-1}$ was used to fit the observations. This coefficient is slightly larger than that derived with the method of Haggerty et al. (1998) but takes into account the rather large confidence intervals of the latter method. Denitrification is also confirmed by the model. The simulated concentrations are too large after all the dissolved oxygen is consumed. Denitrification starts from the moment the dissolved oxygen is consumed. The observations are fitted using the same first-order reaction rate coefficient as was derived following the method of Haggerty et al. (1998).

## CONCLUSION

The advantage of a push-pull test is that chemical reactions and reaction rate coefficients are studied on a field scale and under field conditions which are difficult to reproduce under laboratory circumstances. Such accurate and reliable information is needed in many hydrogeological and environmental studies, for instance in the design of remediation or sanitation strategies. A push-pull test was performed in the Belgian coastal plain and both the aerobic respiration and the denitrification could be determined. Here, we studied the accuracy and reliability of the method by calculating the confidence intervals for the simplified method and by interpreting the observations with TRACER3D, a numerical flow and solute transport model. The confidence intervals are relatively large but the determination of the first-order reaction rate coefficients were confirmed with TRACER3D. These relatively large confidence intervals are important and must be taken into account for the further use of the reaction rate coefficients (e.g. in the design of a remediation strategy for a contaminated site where such a test is performed). With the simplified method, it was not possible to determine if sodium and potassium concentrations underwent chemical reaction or only non-reactive transport. The latter was confirmed by the TRACER3D simulation.

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