

## TRACER PROPERTIES, AND SPIKING RESULTS (FROM GEOTHERMAL RESERVOIRS)

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### ABSTRACT

We take a look at multi-tracer tests conducted for the characterization of deep liquid-based geothermal reservoir candidates in Germany since 2003, and examine how the properties of the tracers used influenced test performance and results.

### MOTIVATION

Tracer tests are supposed to yield two kinds of information essential for predicting thermal breakthrough in fluid-based geothermal systems: the distribution of fluid residence times in the reservoir under given hydraulic regimes, and the density of heat exchange (fluid-rock contact surface) areas. Whether this succeeds in practice depends upon

- A) spiking design considerations, and how these finally get implemented into field and laboratory (including tracer analytics) work,
- B) the selection of adequate tracers, and how well their physico-chemical properties can be known,
- C) the quality of the models used to derive reservoir properties from measured tracer signals.

Once a spiking has been conducted, (A) and (B) can no longer be changed. One can work on (C), or, more dramatically, one can ask for field tests to be repeated or extended under improved (A) and/or (B) premisses. A number of inter-well and single-well spikings conducted during the last few years for characterizing deep HDR systems in the mid- and S-German crystalline basement and in the N-German sedimentary basin provided some key experiences for comparing between the two options.

Further, the idea of using reactive chemicals as “smart tracers”, as described, for instance, by Ptak and Schmid (1996), Licha and Sauter (2002a,b), or by Haggerty et al. (2008), Haggerty (2008), and in particular the idea of using thermo-sensitive solutes to quantify reservoir temperatures, as proposed by Robinson et al. (1984), or by Chrysikopoulos (1993) is worthwhile being given a closer look.

### REMARK ON THE USE OF SINGLE-WELL DUAL-TRACER PUSH-PULL TESTS TO QUANTIFY HEAT EXCHANGE AREAS

The basic idea behind single-well injection-withdrawal (push-pull) tests is that, when natural flow gradients are absent or negligible, the reversal of test-induced flow fields from the 'push' phase to the 'pull' phase should reduce (or virtually eliminate) the influence, on measured tracer withdrawal signals, of advection-dispersion processes, and thus enhance the visibility of influences from other in-situ processes like adsorption, aqueous-phase or mixed-phase reactions (Tomich et al., 1973; Istok et al., 1997; Schroth et al., 2001), or matrix diffusion (Haggerty et al., 2001); a comprehensive review of the various possible applications is given by Neretnieks (2007). Sauter and Herfort (2002) proposed to use the thereby achieved enhancement of diffusion effects in order to quantify heat exchange areas in liquid-based geothermal reservoirs. Here, we examine only some basic factors governing the determinability of heat exchange areas from solute and/or temperature withdrawal signals in single-well push-pull tests, relying on adsorption and/or diffusion.

Figure 1 shows simulated tracer withdrawal signals from a typical push-pull test with tracers undergoing first-order kinetic exchange processes at or through the surfaces whose density needs to be determined. To be noted, matrix diffusion can also be regarded, formally, as a superposition of first-order kinetic exchange processes (with equal values for  $K_{in}$  and  $K_{out}$ ). The type-curve parameters  $TP$  identifying each curve in Fig. 1 are equivalent to the negative logarithmed product of the underlying process coefficients (assumed to be known for each tracer) with the area density  $\sigma$  to be determined. Increasing  $TP$  means the characteristic time scale of the respective process increases (exchange becomes slower). For a given geo-reservoir (given value of  $\sigma$ ), solute tracers will generally plot in the upper range of Fig. 1 (high values of  $TP$ , slow exchange) while temperature signals will generally plot in the lower range of Fig. 1 (low values of  $TP$ , rapid exchange). Tracer signals are sensitive w. r. to changes of the

area parameter  $\sigma$  only for a limited range covering no more than three orders of magnitude ( $TP$  values between approximately 9 and 12, for the definition used in Fig. 1). In other words, in any test setting, values of  $\sigma$  below a certain level will not be determinable from solute tracer signals, and values of  $\sigma$  exceeding a certain level will not be determinable from temperature signals.

Furthermore, despite flow-field reversal, ambiguity between advection-dispersion (characterized by Peclet number  $Pe$ ) and kinetic exchange processes persists especially for the solute tracers, as can be seen from Figure 2. In principle, determinability can be improved by using contrasting-property tracers simultaneously, however the optimum sensitivity range for  $\sigma$  can never be told in advance.

Figure 3 shows simulated tracer withdrawal signals from a typical push-pull test with tracers undergoing equilibrium exchange processes (characterized by a single, dimensionless, retardation factor  $R$ ) at the surfaces whose density  $\sigma$  needs to be determined. Here, the sensitivity of tracer signals w. r. to  $\sigma$  (on which  $R$  depends quadratically) remains uniform over a greater range, and there is less ambiguity between retardation and advection-dispersion processes (in principle, it suffices to have one reference tracer for which  $R = 1$  is known with certainty).

Further aspects limiting the use of solutes to quantify rock surface areas in geothermal reservoirs are as follows:

- (i) adsorption rates generally decrease with temperature (Licha and Sauter, 2002a,b); meaning that a particular adsorption process showing equilibrium at room temperature may become kinetic at reservoir temperature (loss of parameter determinability as one moves from Fig. 3 to Fig. 2), and it may start resembling matrix diffusion (adding further ambiguity of process identification), and kinetic process rates may in turn become too low to produce unambiguous effects in short-term testings (upper part of Fig. 1);
- (ii) even though solute diffusion coefficients increase with temperature, they still remain orders of magnitude lower than heat diffusion coefficients in tight rock, which limits the depth scale at which solutes are able to characterize heat transfer, while in turn rendering them much too sensitive w. r. to heterogeneities on a space scale that is irrelevant to heat transport;

some more will be mentioned in the sequel.

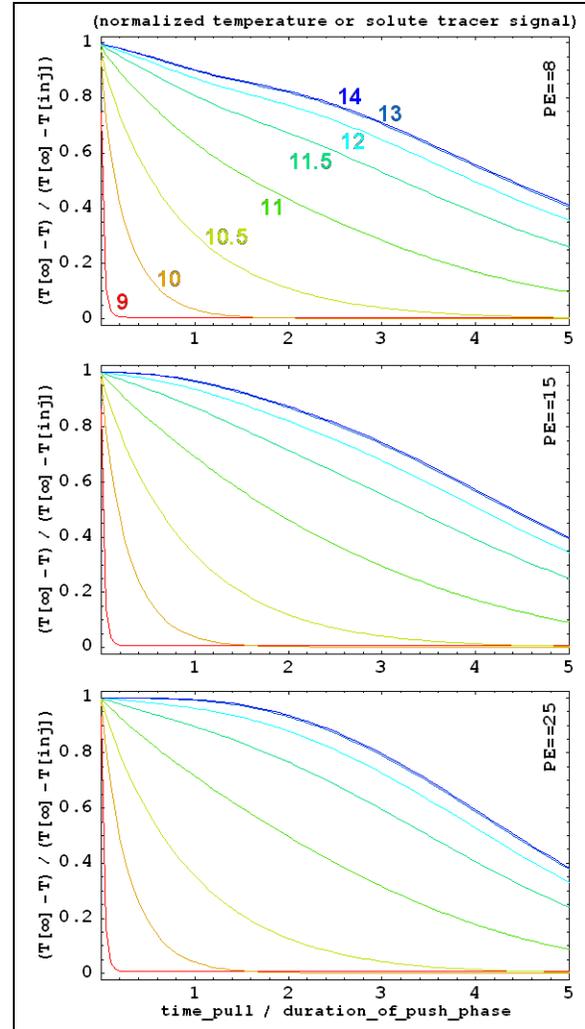


Figure 1: Simulated 'pull' signal families of tracers with kinetic exchange or matrix diffusion processes (characterized by 'type-curve' numbers as shown in color), for three different values of the Peclet number.

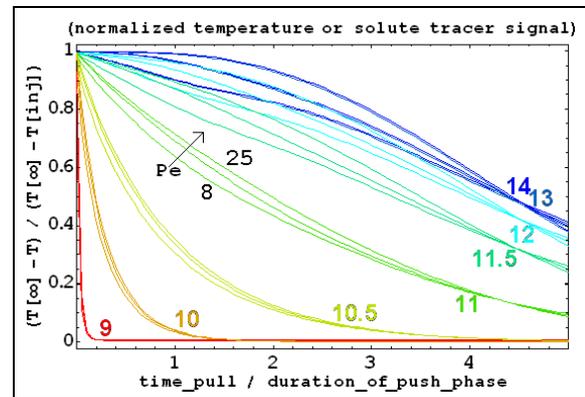


Figure 2: Process identification ambiguity between advection-dispersion (characterized by  $Pe$ ) and kinetic exchange (characterized by 'type-curve' numbers as shown in color).

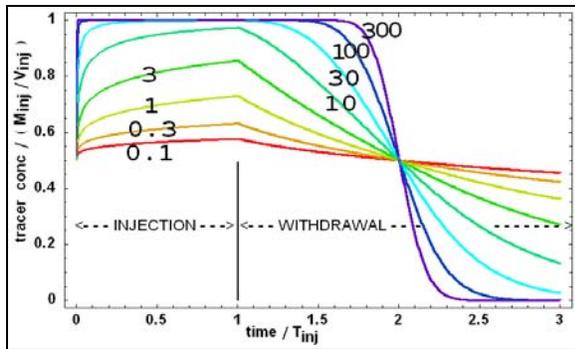


Figure 3: Simulated 'pull' signals of tracers with only equilibrium exchange processes (different retardation coefficients, of which the 'type-curve' numbers shown are a rational function).

### DUAL-TRACER APPLICATIONS FOR CHARACTERIZING CANDIDATE GEOTHERMAL RESERVOIRS IN GERMANY

We review three examples of tracer uses for characterizing candidate geothermal reservoirs of HDR type in Germany. Single-well spiking were conducted at geothermal well Urach-3 in the Southern-German crystalline basement, at the pilot hole (KTB-VB) of the Deep Continental Drilling ("Kontinentale Tiefbohrung") in the mid-German crystalline basement, and at Horstberg (pilot site for demonstrating a single-well multi-layer heat extraction concept described by Jung et al., 2005) in the Northern-German sedimentary basin. Details of test execution, results and interpretation are presented elsewhere (e. g., Jung et al., 2005; Ghergut et al., 2007). Here, we present only the most curious of the aspects specifically concerning the *tracer substances* used in each test.

#### Urach-3 (2003): incomplete tracer dissolution?

Figure 4 shows the measured breakthrough curves (BTCs) of fluorescein di-sodium (abbreviated as *uranine* in the sequel) and of naphthalene-1,5-disulfonate (NDS) from the withdrawal phase of a short-term push-pull test conducted (2003) in cooperation with local Communal Services, ETH Zürich and EGI Utah. The tracer recoveries calculated from the values of Fig. 4 were found to be 55% for uranine, and 33% for NDS, by a time at which approximately the threefold of the flushing volume (the fluid volume injected behind the tracers) had been recovered from the well.

How can this huge difference between the BTCs of two organic tracers, uranine and NDS be explained? Tracer concentrations in fluid samples were analyzed by Laboratories at ETH Zürich and at EGI Utah; they

were double-checked and there is no doubt that these laboratory determinations are correct.

*Is the BTC difference due to adsorption?*

- If yes, then (regardless of temperature effects on adsorption intensity) the adsorptive tracer must be the one showing lower return at early times (despite a popular belief about push-pull tests, stating that "the more retarded tracer has a shorter distance to travel..."; cf. also Fig. 5). According to Fig. 4, the adsorptive tracer would be the NDS. But, firstly, there is good reason to expect that NDS should behave more conservatively than uranine under the prevailing reservoir conditions. Secondly, the relative shape of NDS and uranine signals (their more or less constant ratio, cf. lower section of Fig. 4) does not fit the simulated pattern of two tracers with different adsorption intensities (cf. Figures 1 and 2 in the previous section).

*Is the BTC difference due to matrix diffusion?*

- NDS is indeed supposed to have higher, but not dramatically higher diffusion coefficients than uranine (by virtue of its smaller ion size, though it might be more hydrated). In order to produce such a BTC difference by matrix diffusion only over a period of approximately 12 days (including the shut-in period that had preceded the outflow phase), in a HDR structure with two or three open fractures, an enormously large surface should have been available for matrix diffusion. But, again, the relative shapes of NDS and uranine signals are not easy to match to the typical matrix-diffusion and/or adsorption pattern (cf. Fig. 5).

A different possible explanation is that NDS did not dissolve completely into the tracer mixture "slug" as it was prepared for injection, considerable amounts of NDS remaining on the bottom of the mixing tank. It is known that NDS has very good solubility, but it takes sensibly longer time to dissolve than uranine, under the usual working conditions (cold water, inadequate mixing devices). This would imply that the NDS signal from the Urach test cannot be normalized properly, the actual injected quantity of NDS remaining unknown. - To be noted, the mixing procedure used at Urach was quite different from the one used by the Göttingen group at all other sites in Germany (KTB 2004, Horstberg 2004, Groß-Schönebeck 2007, Landau 2007, Ketzin 2008).

The "truth about mass balance" at Urach will probably never be known with certainty: this demonstrates how some of the most trivial details of spiking practice control the entire interpretation of a tracer test.

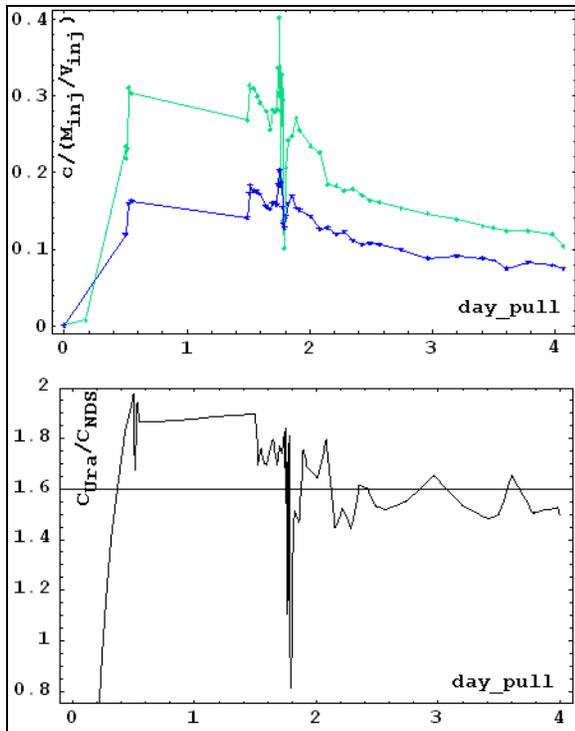


Figure 4: Withdrawal signals of NDS (blue) and uranine (green) from short-term push-pull (2003) at Urach-3 well, and ratio between NDS and uranine concentrations.

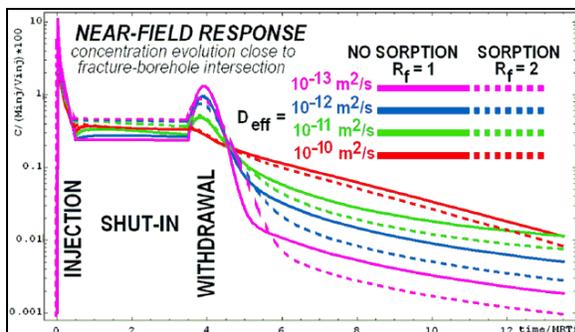


Figure 5: Principle simulations of tracer signals from single-well push-pull tests, for different values of effective diffusion coefficients and of adsorption-related retardation factors.

**Pilot KTB hole: what processes?**

Tracer BTCs produced in push-pull tests at the KTB site (example in Fig. 6) are probably one of the most interesting “multi-tracer” results obtained during the past few years in German hot dry rocks. The differences between BTCs of tracers “with different characteristics” were supposed to enable quantifying the heat exchange area in the spiked system. However, as long as the controlling processes are not yet clarified (sorption? matrix diffusion? diffusive exchange between zones of different fluid mobilities

within the fractures or fissures?) the interpretation of these BTCs remains speculative. According to the present state of modeling for this site (also relying on temperature signals from heat push-pull tests), it seems likely that the processes having the most influence on the measured solute BTCs will become irrelevant for heat transport in the long term.

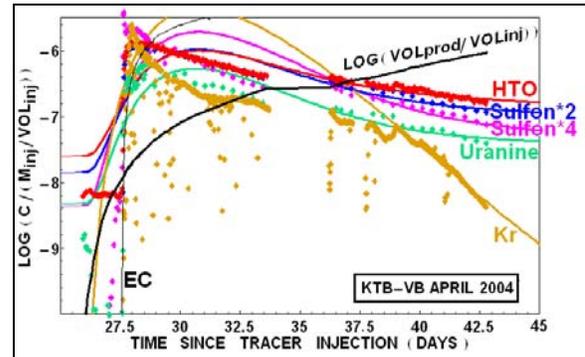


Figure 6: Withdrawal of several tracers in push-pull test (2004) at pilot KTB hole.

By the way, of all tracers injected simultaneously, uranine showed the lowest recovery; the same had been observed in a push-pull test at the Lindau site in South-German crystalline.

**Horstberg: the wrong ‘indicator’ tracer**

A more detailed discussion of this test’s aims and results can be found in Jung et al. (2005), Behrens et al. (2006), Ghergut et al. (2007; 2009) also showing the measured tracer BTCs; here, we just review some aspects specifically relating to uranine behavior.

A tracer mixture consisting of uranine, NDS and tritiated water (HTO) was injected. On-site, a flow-through filter fluorometer for uranine detection was installed in order to get immediate information on tracer breakthrough in the outflowing fluid, and samples were taken frequently for laboratory analysis of all tracers. However, no uranine signal was detected with the field fluorometer (neither before nor after pH adjustment). The laboratory analyses comprised highly sensitive spectrofluorometry for uranine and NDS, and liquid scintillation counting for HTO (the latter being possible only after distillation from brine). Samples showed increasing proportions of native brine, which appeared to be almost saturated with NaCl and had high content of dissolved Fe, Mn and other components, the metals being in solution by virtue of an extremely reduced character of the brine and a pH value around 5.5; in contact with air, excretion of green-brownish precipitates rapidly occurred. While NDS and HTO showed clear BTCs, uranine was found only in trace concentrations in a first series of spectrofluorometric analyses (with pH values adjusted accordingly). With progressing aeration, an increase of the uranine

signals was registered. We explain this phenomenon by the reduction of uranine under the prevailing reservoir conditions (temperatures ranging between 130 degC and 140 degC, very low redox potential) to its non-fluorescent leuco-dye form, which in turn is sensitive to re-oxidation. These reactions can be performed under adequate conditions in the laboratory and enjoy a variety of applications (e. g., in enzyme studies). However, to our knowledge, the uranine reduction to its leuco-dye form has not been documented during water tracing tests hitherto. The intricate brine behavior (precipitation, influence of unidentified ingredients) did not allow exact quantitative determination of the original uranine concentrations, but after partial re-oxidation in the laboratory a plausible uranine BTC was obtained: tracer recoveries amounted to 6.4% (uranine), 7.4% (HTO), 10% (NDS), after an outflow volume of about 2.8 times the injected chaser volume. To be mentioned, also, an interesting correlation was seen between the amount of uranine 'missing' in each sample and its 'maximum possible' amount (taking the other tracers, NDS and HTO, as a reference).

It thus turned out that “uranine disappearance” was not primarily by adsorption onto rock surfaces (the more so as adsorption is generally expected to decrease with temperature), but by *reactions taking place in the aqueous phase*.

Uranine is most popular for its ease of on-site, real-time detection, and on-site filter-fluorometer readings are often taken as a basis for deciding when to discontinue sampling; during the Horstberg test of 2004, the absence of any uranine signal on-site has *scarcely failed to trigger a wrong decision* (under the impression that “the whole tracer have flown to diverging directions”).

#### **REMARK ON THE USE OF THERMO-SENSITIVE TRACERS FOR QUANTIFYING RESERVOIR TEMPERATURE CHANGES**

Robinson et al. (1984), Chrysikopoulos (1993) and other suggested to develop and use thermo-sensitive solutes for quantifying temperatures (or temperature changes) in remote reservoir domains not accessible to direct measurement. This is a very promising approach, which also wonderfully incarnates the idea of a “smart tracer” defined by Haggerty (2008) as “... *to be able to measure the same things as a conservative tracer but also have the tracer provide some more information about the processes going on in between where you inject the tracer and where you detect it again. (...) the way to get this extra information is with a chemical compound that changes irreversibly into a second compound when it encounters the particular conditions you want to investigate. So you start out injecting compound A*

*and downstream you end up with compounds A and B and the proportion of the two tells you something about the process you are studying*”. Yet unlike the 'smart tracer' proposed by Haggerty et al. (2008) for surface-water investigations, the thermo-sensitive solute approach requires more careful examination before it can be applied in deep-geothermal practice (cf. also the US DoE 2008 Report).

Figure 7 shows the simulated tracer return, at the production well of a geothermal doublet, for two (imaginary) thermo-sensitive substances (added at the re-injection hole) whose thermal “decay” obeys Arrhenius Law with lower (l.-h. s.) or higher (r.-h. s.) rates. This was simulated for several possible temperature profiles in the reservoir (shown in the upper section, r.-h. s. identical to l.-h. s.). Reaction-rate profiles resulting from the assumed temperature profiles are also plotted (middle section of Fig. 7). The practical need for indirect temperature sensing (i. e., for using something like the thermo-sensitive solutes) occurs especially in the situation marked by an asterisk (temperature profile in orange) on Fig. 7, when already a large-scale cooling occurred in the reservoir but still no significant temperature drop is seen at the production well. The troubling finding from the simulations in Fig. 7 is that the “thermo-sensitive” solutes are not sensitive w. r. to precisely this situation; the “high-rate” solute no better than the “low-rate” solute.

Logically, for every imaginable temperature profile and fluid residence times, one can calculate a set of Arrhenius-Law parameter values that would be optimal for revealing precisely that temperature profile. But neither is the temperature profile known in advance, nor do we have ready-to-go thermo-sensitive substances with Arrhenius-Law parameters equaling any desired values. Further, it seems difficult to guarantee that thermal decay parameters quantified under laboratory conditions will remain predictable under reservoir conditions.

#### **ONE MORE REMARK**

Water tracers are being used since over hundred years in a variety of ways for a variety of purposes relating to geo-system characterization. The amount of work deployed for improving each of the components (A), (B) and (C) listed in the first section has been increasing unceasingly. However, in spite of objectively increasing knowledge (theoretical and practical) and of steadily improving technical, laboratory-analytical and modeling capabilities, it does not look like “playing with tracers” could ever become “uninteresting routine” in the realm of deep geo-hydrology. Each new spiking application remains (on the average) as challenging as the ones before.

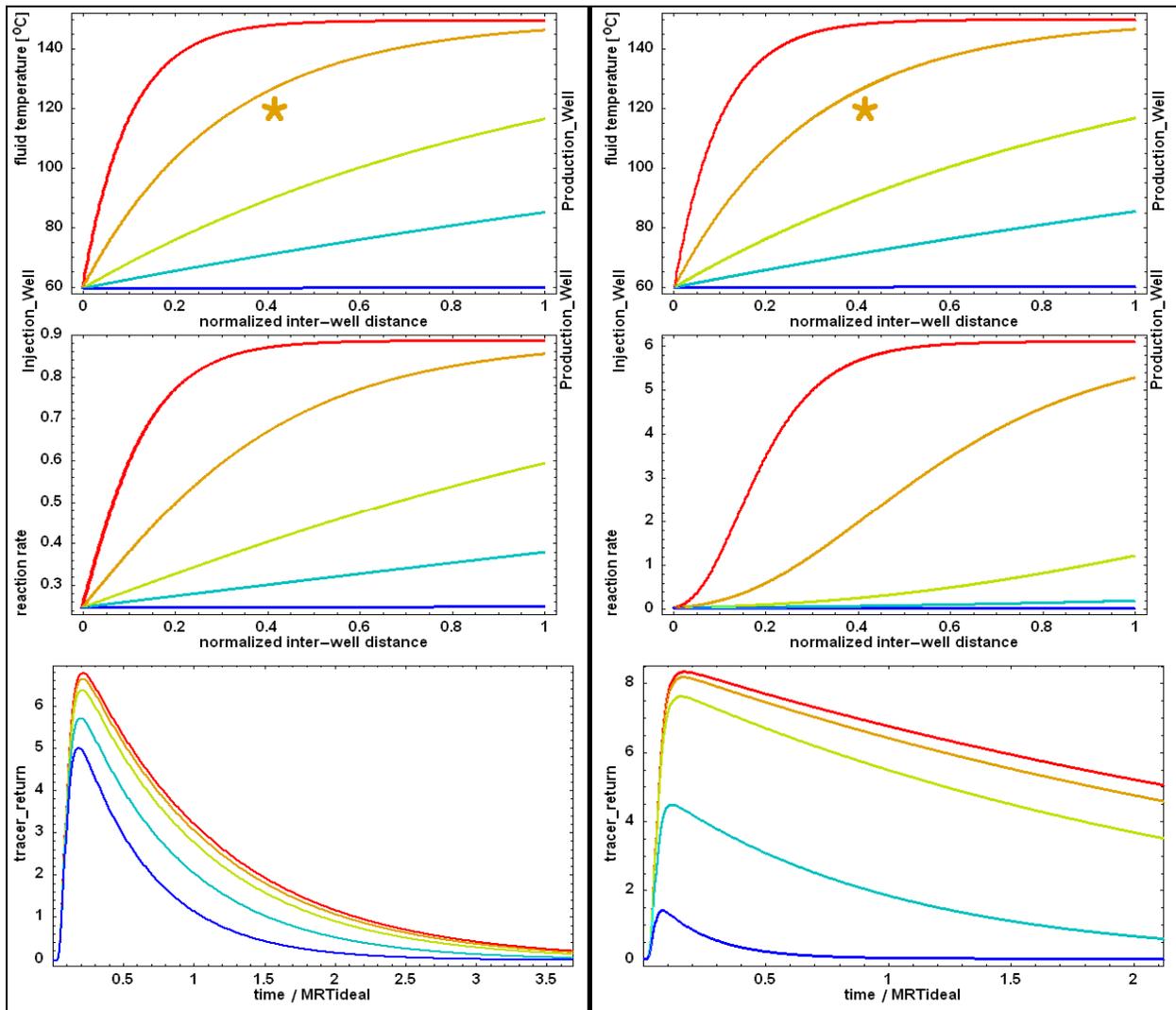


Figure 7: Simulated return of thermo-sensitive solutes for various temperature profiles between the wells of a geothermal doublet.

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