DYE TRACER TESTS WITHIN THE SCHOLLBERG UNDERGROUND LIMESTONE QUARRY: EXPERIMENTAL AND HYDROGEOLOGICAL IMPLICATIONS

by Werner Balderer (1) & Fanny Leuenberger (2), ETH Zurich, Switzerland, 8093 Zurich, Geological Institute, Engineering Geology, (1) balderer@erdw.ethz.ch, (2) fanny.leuenberger@erdw.ethz.ch

Abstract

A Large scale tracer test was performed in fissured rocks in the Swiss Pre-alpine Area in an underground limestone quarry adjacent to the alluvial plain of the river Rhine valley. The artificial fluorescent dyes: Uranine, Sulforhodamine and Naphthionate were used as tracers. The implications of this tracer test result in establishing a feasibility study for a planned underground waste disposal site to be situated within the existing limestone quarry. During an observation period of about 3 years groundwater samples were periodically taken from 10 observation boreholes. They were analysed by luminescence spectroscopy in a first step and additionally by HPLC combined with fluorescence detection in a second step. Since the results of the tracer identification and quantification were strongly dependent on the applied analytical method, it created substantial implications on hydrogeological interpretation as of configuration of flow paths and flow velocities. As a consequence of this study it is strongly recommended that every tracer test should be analysed by two different techniques. The most commonly used technique (fluorescence spectroscopy) may be used as a first screening method.

1. Introduction

In order to clarify former hydrogeological investigations (Schlegel, 1995, Weber, 1998) large scale tracer tests were performed in a fissured limestone area within the exploited part of an underground limestone quarry (Balderer, Leuenberger, 2003). For this tracer test the synthetic fluorescent dyes Uranine, Sulforhodamine B and Naphthionate were used. The aim of the tests were i) to determine fast preferential pathways in fissured rocks, ii) to discover possible connections to the adjacent alluvial aquifer in unconsolidated sediments and iii) to determine experimentally by real scale experiments the effective flow velocities and flow paths of the groundwater and to verify the range of existing hydraulic conductivities. Another aim of the test in fissured limestone was also to quantify the possible effects regarding an existing groundwater pumping station for drinking water supply (PW) within the alluvial aquifer. The outcome of these tracer experiments would have implications on the feasibility of setting up a waste disposal site in the disused part of this underground limestone quarry.

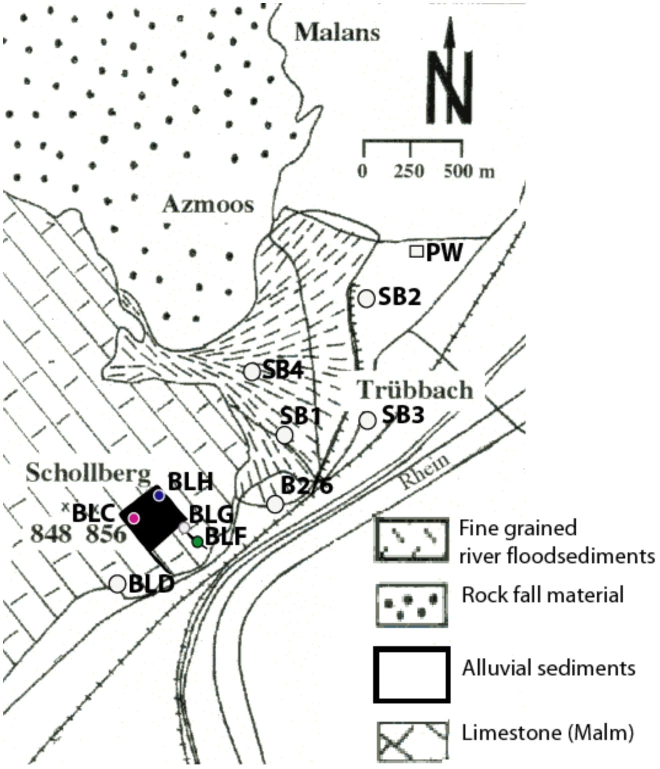

Fig.: 1 Geological Situation of the investigated area with the injection and observation boreholes

Within the investigated area (Fig. 1) a hill formed structure named Schollberg consisting of cretaceous limestone crops out (Fig. 2). This structure belongs to the helvetic nappes, to the so-called structure of the Axen-Nappe (representing the base of the nearby Saentis - Nappe). The axis of this folded structure (overturned fold) dips towards the North-East with a slope of 30°. Within the valley of the River Rhine this limestone bedrock is widely eroded by the combined action of glacial and fluvial erosion and the subsequent filling with fluvial-glacial unconsolidated sediments. With respect to the hydrogeological situation this limestone structure of the Schollberg (Fig. 2) in which the shafts of the underground quarry are driven represents a fractured rock of quite low hydraulic conductivity. According to the hydraulic testing (of packed intervals) in 4 drilled unlined boreholes within the limestone quarry values in the range of $1*10^{-6}$ m/s to $1*10^{-5}$ m/s resulted (for the borehole BLG). For the adjacent alluvial sediments the following values were found by pumping tests: $2*10^{-3}$ m/s (borehole SB1) to $1*10^{-2}$ m/s (for the boreholes SB2 and SB3). These values are representative of fluvial-glacial gravel aquifers. In the borehole SB4 the alluvial sediments contain more fine grained components with a somewhat lower hydraulic conductivity in the range of $5*10^{-4}$ m/s. More adjacent to the limestone hills this gravel aquifer is overlain by fine grained river flood sediments of very low hydraulic conductivity with thicknesses in the range of 16 m (SB1) to 42 m (SB4). Below the gravel aquifer fine grained lake deposits were also encountered in borehole SB 4 (yielding a thickness of 23 m), overlying directly the limestone bed rock of the Malm (Quintnerkalk) which represents the direct continuation of the axial descending folded (nape) structure of the Schollberg hill. The chemical composition of the groundwater within the alluvial gravel aquifer is of Ca-Mg-HCO_3-SO_4 type, with a total mineralization of 422 to 526 mg / l (boreholes SB1 to SB4 and Dornau Pumpimg station). The water of the river Rhine is of similar water type, however, with a lower mineralization of about 390 mg/l. The water sampled in the boreholes within the Schollberg limestone Quarry shows quite varying mineralization but mainly the same chemical composition. For the water of the borehole BLD results a quite similar composition and total mineralization (420 mg/ l) analogous to that of the gravel aquifer. For the other boreholes more distant from the alluvial aquifer quite different mineralization were measured: the lowest mineralization was found in borehole BLC (187 mg/l), BLG contained 770 mg/l, and BLF had the highest values with 1400 mg/l.

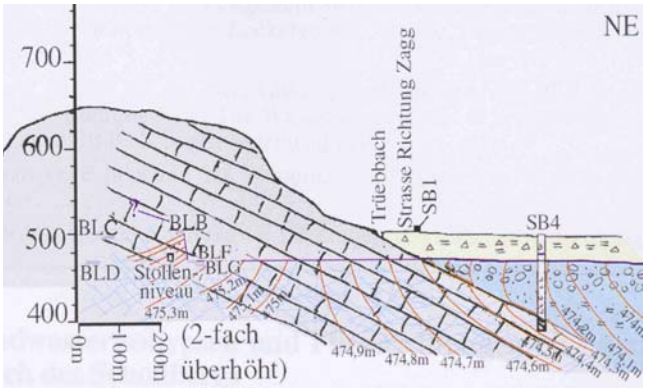

Fig. 2 Schematic cross section through Schollberg to the alluvial sediments (Weber, 1998)

Naphthionate, Sulforhodamine B and Uranine used for the tracer experiment were introduced in 3 boreholes (Fig.1) drilled into the fractured limestone rock of the underground quarry. The injected amounts of dye were as follows: 10 kg Naphthionate into borehole BLH, 2 kg Sulforhodamine into borehole BLC and 2 kg Uranine into borehole BLF. In order to study the propagation of the tracers by advective flow, groundwater samples were periodically collected over a period of 3 years from 10 observation boreholes: BLG within the quarry, BLD in the limestone rock just outside of the quarry and from the following boreholes situated within the alluvial sedimentary filling downstream of the Schollberg quarry B2/6, SB1, SB2, SB3, SB4 as well as from the nearby groundwater pumping station PW. (Fig.1 and Fig. 12). The water sampling out of the observation boreholes was done with a small ubmersible pump after renewing at least twice the borehole volume.

2. Materials and Methods

Performing tracer tests in fractured rocks and porous aquifers normally yield low recovery resulting in concentrations near the detection limits of the methods. At these very low levels, natural or artificial fluorescent contaminants (originating from natural swampy waters, industrial plants or waste effluents) can mask the fluorescence intensities and therefore often yield erroneous results. Therefore it is very important to confirm the results acquired with a conventional technique by a more substance specific method. This concept was used in the way that the samples from naturally out flowing springs and boreholes were analysed successively by two methods. First the samples were screened by fluorescence spectrophotometry (which is the conventionally used method of fluorescent dye analysis, Käss, 1992, 1998, Behrens, 1982). In a second step they were analysed by HPLC coupled to a fluorescence detector (representing a more substance specific method, Lutz & Parriaux, 1988, Lutz, Parriaux & Tissières, 1987).

Table 1: Instrumental Setting of the LS 50B Spectro-fluorometer

Excitation and Emission Maxima of the Tracer Dyes			
Tracer Dye	Maximum Excitation wavelength (nm)	Maximum Emission wavelength (nm)	Detection Limit(ppb)
Na -Naphthionat	330	430	0.03
Sulforhodamine B	564	600	0.01
Uranine (Na - Fluorescein)	491	520	0.01

Table 2: Technical properties of the HPLC system

Pump	P580 Low pressure gradient pump
Column	C18 Reversed phase (0.46cm x 25cm)
Flow-rate	1ml/min
Injector Volume	100µl
Eluent (for naphthionat and sulforhodamine B)	20 mM Na - Acetate, pH 5.2
Eluent (for uranine)	20 mM Na - Acetate, pH 5.8
Gradient Eluent	70% Acetonitrile
Detector	RF-2000 Fluorescence detector
Autosampler	GINA 50 with variable injection volumes
Data System	Dionex CHROMELEON software
Post Derivatization unit (for uranine)	500mM NaOH
Detection Limit of Na – Naphthionat*	≥ 0.1 ppb
Detection Limit of Sulforhodamine B*	≥ 0.1 ppb
Detection Limit of Uranine (Na -Fluorescein)*	≥ 0.1 ppb

*with reference to standards and blanks from pre-test groundwater

The instrumental tools used in the analyses of the fluorescent dyes are two-fold: a) a conventional screening method using a spectrofluorometer (Perkin-Elmer LS50B) which measures the fluorescence intensity of the excited species at a given wavelength (details are described in table 1) and b) High

Performance Liquid Chromatography (HPLC) combined with a fluorescence detector and analysed using the DIONEX-CHROMELEON data system (details are described in table 2).

3. Results

Examples of measured dye concentrations using spectrofluorometry are shown in Fig. 3 and 4 for samples from the boreholes BLG and BLD According to the analytical possibilities of the LS50 instrument (as represented in table 1) the useful analytical range was 0.01 to 2 ppb for Uranine and 0.3 to 5ppb for Naphthionate and Sulforhodamine using external standards.

Blank signals were obtained using water taken before starting the test.

Using chromatography technique the dyes of interest can very well be separated from interfering species in the sample. Coupled with a fluorescence detector this technique provides a highly sensitive substance specific analytical method. Since fluorescence intensity is also affected by interfering substances in the water samples, all samples showing a positive fluorescence signal using spectrophotometry were further analysed by HPLC in order to confirm the presence of the dye. The samples with confirmed presence of the dyes by the HPLC method are presented in table 3. The reliability of the conventional spectrofluorometric method (as by the LS50 instrument) is limited by interference due to fluorescent substances in natural waters or other disturbing macromolecules and not by the detection limits of the dyes of interest. Although HPLC has detection limits analogous or slightly higher than ones obtained with a spectrofluorometer (as the LS50), it has the great advantage of providing separation of the water constituents by the chromatography process before detection and quantification (table 2).

In Fig. 5 an example of a HPLC Chromatogram for Naphthionate of the sample BLG72 (from 8.3.01, resp. 250 days since injection) is represented. On this chromatogram the trace line of the sample BLG72 itself (black line) does not coincide with the lines of standard 1 (0.1 ppb, blue line and of standard 2 (standard 2 (0.3 ppb, brown Line). This is a clear proof that in this sample BLG72 there is no trace of the Naphthionate (as compared to the standards 1 and 2).

In Fig. 6 the HPLC chromatogram for Sulforhodamine in the sample BLG78 (from 17.4.01, resp. 390 days since injection) is represented. On this chromatogram one observes that the trace line of the sample BLG78 itself (black line) nearly perfectly coincides with the line of standard 1 (0.3 ppb, blue line. This is now a clear indication that in this sample BLG78 Sulforhodamine (according to the standards 1) is present. In order to demonstrate the quantitative performance of this HPLC analytical technique the corresponding calibration curves for Naphthionate and Sulforhodamine of the chromatograms of Fig. 5 and 6 are represented on Fig. 8 and 9.

Considering the results of the measured tracer concentrations as represented in the diagrams of figures 3 and 4 which were obtained by fluorescence spectroscopy, quite convincing breakthrough curves seem to be revealed from all investigated observations boreholes and even for the most distant pumping station.

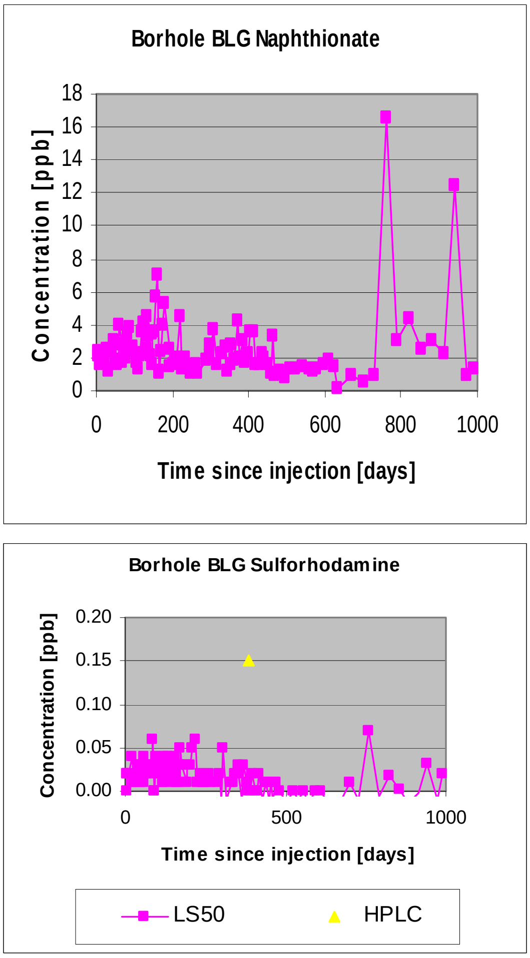

Fig. 3: Resulting concentrations of the water samples from borehole BLG by fluorescence spectrophotometry for Naphthionate and Sulforhodamine.

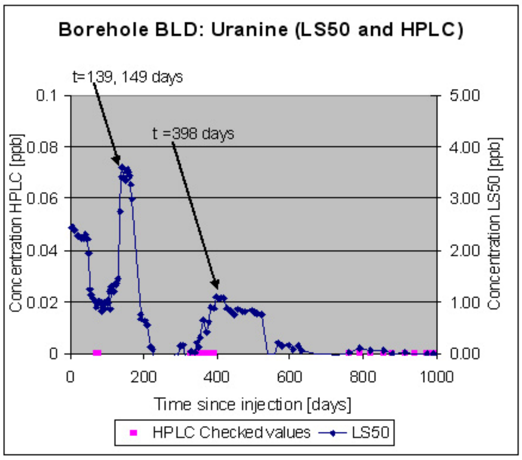

Fig. 4: Resulting concentrations of Uranine of the water samples from borehole BLD by fluorescence spectrophotometry.

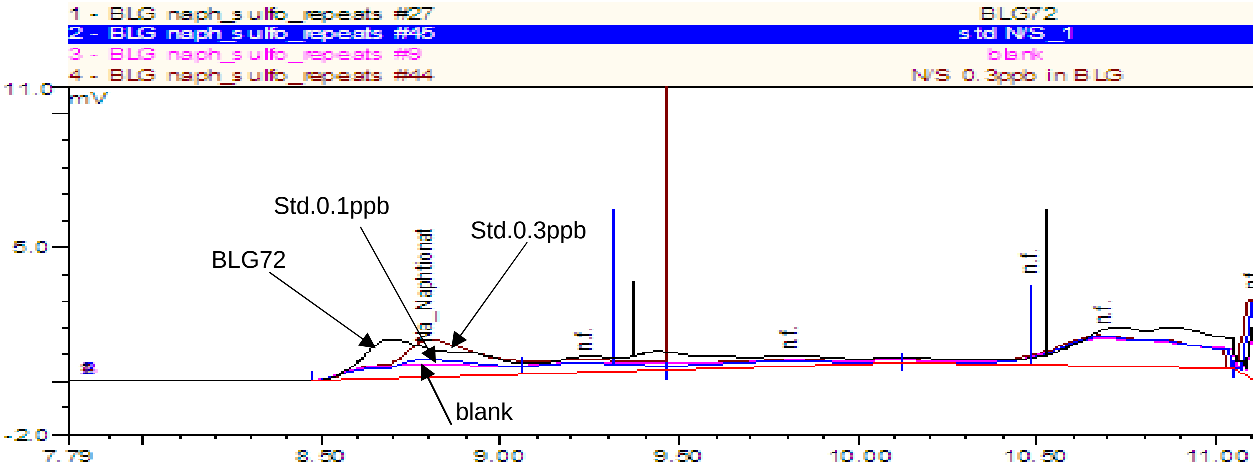

Fig. 5: HPLC Chromatogram for Naphthionate of the sample BLG72 (of the 8.3.01, resp. 250 days since injection, black line) in comparison to standard 1 (0.1 ppb), standard 2 (0.3 ppb) and the blank (water without tracer) according to the analyses of the 18.3.2003

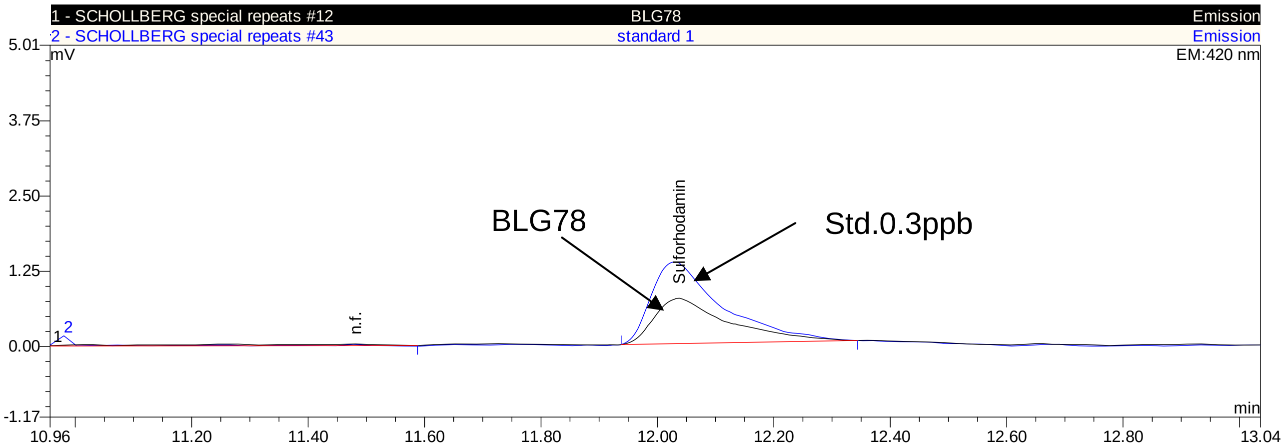

Fig. 6: HPLC Chromatogram for Sulforhodamine of the sample BLG78 (of the 17.4.2001, resp. 390 days since injection) in comparison to standard 1 (0.3 ppb) according to the analyses of the 14.6.2001

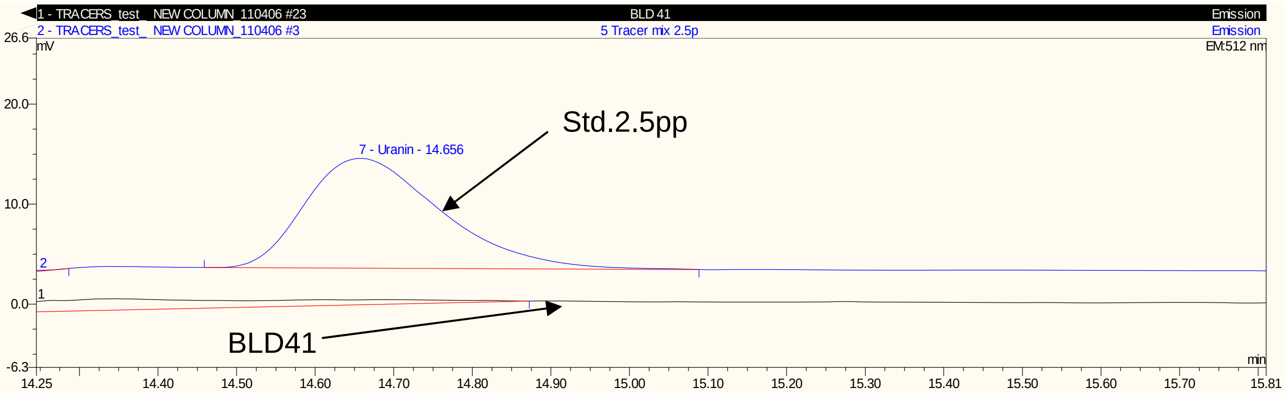

Fig. 7: HPLC Chromatogramm for Uranineinf the sample BLD41 (from 15.8.00, resp. 139 days since injection)) as compared to overlay of the standard chromatogramm (2.5 ppb, blue line), according to the analyses of the 13.4.2006 (For both chromatograms the base line is equal to 0).

But if these results are interpreted as real flow paths of the injected tracers originating from the corresponding boreholes BLC (Sulforhodamine), BLF (Uranine) and BLH (Naphthionate) some discrepancies with respect to the established map of lines of equal head according to the measured hydraulic heads (as represented on Fig. 10) can be recognised. This appears most drastically if the possible flow paths from the injection borehole BLF (Uranine) to the observation borehole BLD are considered, which are apparently confirmed by the diagram of tracer concentration versus time (fig. 4) of fluorescence spectrometric measurements. In this case a tracer flow path would exist along the line of equal head which is hydraulically not realistic.

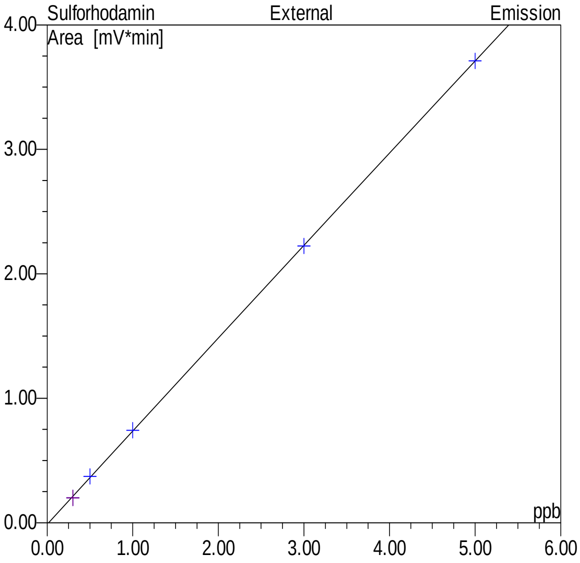

Fig. 8: Calibration curve of the HPLC analyses for Naphthionate (with the reference standards for 0.1, 0.3, 0.5, 1.0 and 3.0 ppb, according to the measurements of the 18.3.2003)

Now if we take into consideration the results of the second analytical technique of HPLC with fluorescence detector (represented in Fig. 4 for Uranine), no one of them reflects any positive substance specific presence of Uranine. As an example the HPLC Chromatogram for Uranine of the sample BLD41 (from 15.8.00, resp. 139 days since injection) is represented on Fig. 7. For this sample which seems to represent on Fig. 4 a real peak with a measured concentration by the LS50 instrument of 3.4 ppb shows on the chromatogram on Fig. 7 not any trace of Uranine if compared to the also represented chromatogram of the 2.5 ppm Uranine standard.

Finally in table 3 all samples with confirmed presence of the dyes by the HPLC method are represented. Considering these results it becomes clear, that the majority of positive break through events of resulting peaks according to the conventional analytical technique of fluorescemnce spectroscopy as would be suggested by the diagrams of the first screening on Fig. 3 and 4 are in reality artefacts caused by other interfering substances present in the sampled groundwater. Therefore these diagrams of fig. 3 and Fig. 4 reveal the astonishing fact, that even such non- identified "background substances" may show quite regular variations emerging from the measured samples like "ghost break through events" which are not or only hardly distinguishable from the behaviour of a real tracer transport phenomena and its resulting break-through curve.

Now if it is admitted that only the results of positive tracer concentration confirmed by both applied analytical methods are real observations of the tracer transport from injection to the identified observation boreholes, one has now also to do the check of plausibility to the given hydraulic situation as revealed by the constructed maps of equal hydraulic heads established by the interpolation of the measured values (according to the head measurements of the 25.2.1998 in all available boreholes) representative for the hydraulic situation in winter / spring season, A. Weber, 1998).

Considering on this map of Fig. 10 the location of the two boreholes with positive tracer recovery BLG and SB4 and the corresponding injection boreholes BLH (Naphthionate) and BLC (Sulforhodamine) it can clearly be noticed, that these flow path according to the tracer results agree very well with the pattern of hydraulic head distribution.

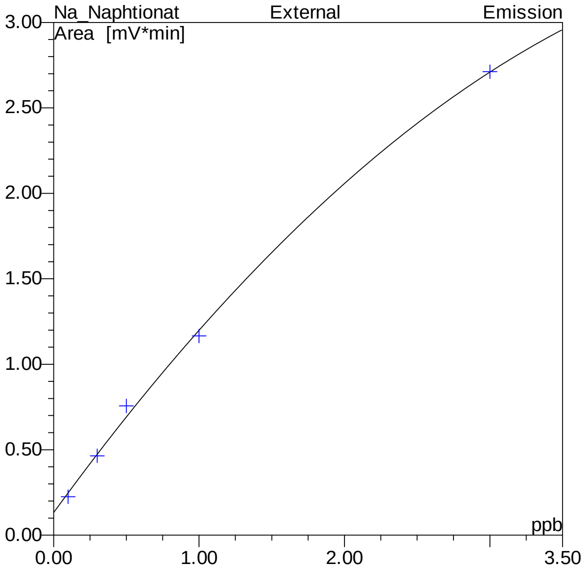

Fig. 9: Calibration curve of the HPLC analyses for Sulforhodamine (with the reference standards for 0.3, 0.5, 1.0 3.0 and 5.0 ppb, according to the measurements of the 14.6.2001)

4. Conclusions

As a consequence from this presented study it is concluded that for low to very low concentration of fluorescent dye tracers the conventional fluorescence spectrometric detection is often not specific enough, especially if other fluorescent substances such as humic acids or other macromolecules are present. In this case a clear substance specific detection and quantification can only be achieved by the combined application of the HPLC technique with fluorescence detection as demonstrated by Fig. 5, 6 and 7.

The possibility of tracer tests is frequently applied to determine flow path in complex hydro-geological situations and for a proof or verification of existing hydraulic connections especially in karstic aquifers.

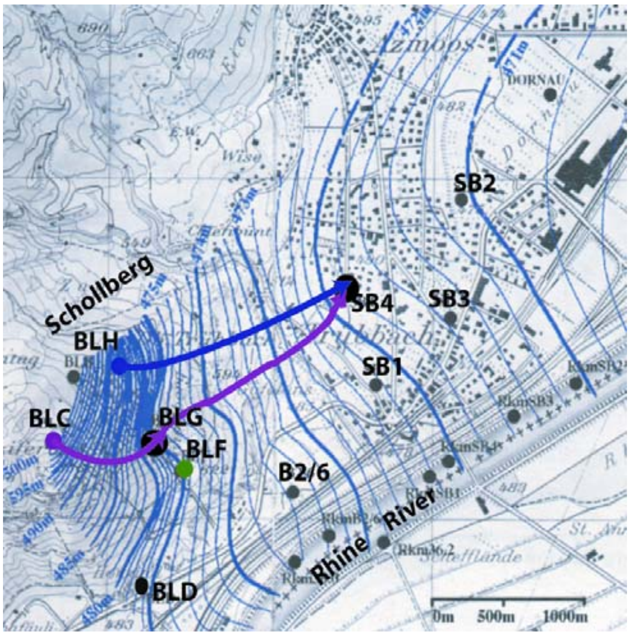

Fig. 10: Resulting flow path of the tracer according to the positive results of the two applied methods as given in table 3.On the map are also represented the lines of equal head according to measurements of the 25.2.1998 in all available boreholes, representative for the hydraulic situation in winter / spring season.

Table 3: Representation of the groundwater samples with positive tracer detection with the HPLC method

Sampled Borehole	Tracer Type	Inject. Bore-hole	Flow-Dist. (m)	Time since inject. (d)	Water sample (Nr.) with pos. Detection	Meas. conc. (ppb) by HPLC
BLG	Sulfo	BLC	290	390	BLG78	0.15
SB4A	Naphth.	BLH	725	173	SB4A42	0.5
SB4A	Sulfo	BLC	940	427	SB4A63	0.1
SB4B	Naphth.	BLH	725	247	SB4B49	0.1
SB4B	Naphth.	BLH	725	331	SB4B55	0.1
SB4B*	Sulfo	BLC	940	203	SB4B45	0.1
SB4C*	Sulfo	BLC	940	398	SB4C51	0.1

*: Positive detection probable with respect to the resulting chromatograms but with resulting concentrations at the limit of detection.

As a consequence of the presented study it is suggested that when interpreting the results of tracer tests the following limitations should also be taken into account:
Failures in the tracer identification may occur due to the analytical limitations of the conventional technique of fluorescence spectroscopy. Such failures may lead to wrong interpretations caused by false arrival times or even in assuming a wrong recovery of a tracer substance, which in reality has never appeared.

Therefore if the the hydrogeological interpretation is based on one conventional analytical technique only it may result in assumptions which provide:

- overestimation of flow velocities (due to too early arriving “peak values”
- underestimation of the effects of hydrodynamic dispersion (due to “high concentrations”)
- wrong assumptions on existing flow path, and hydrodynamic connections, if preferential pathways are assumed which in reality do not exist (if an imaginary but not the real substance is identified no real positive substance specific identification).

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