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Practice Guide for Tracer Tests in Groundwater

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Practice guide for conducting tracer tests in
groundwater

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Titel: Handbuch zur Durchführung von Tracertests im Grundwasser
Stichwörter: Grundwasser, Fluorometer, Tracertest, Uranin


Executive summary

Authors: Dr. Leonard Stoeckl, Dr. Armin Pechstein, Dr. Armin Margane
Title: Practice guide for conducting tracer tests in groundwater
Keywords: groundwater, fluorometer, tracer test, uranine

Tracer tests in groundwater serve for investigating aquifer properties. Tracers, e.g. fluorescent dyes like Uranine or Naphtionate, are injected into groundwater and can be detected at other locations with the help of fluorometers. Depending on the shape of the tracer's break through curve, aquifer parameters like flow velocities, porosities, and dispersivities can be determined. The usage of such tracer dyes as well as the handling of the measurement devices is not trivial, and the test preparation rather complex. This manual is intended to help the user to successfully conduct tracer tests in groundwater, with special emphasis on the use of fluorometers, and provides advice on possible risks and sources of errors.
1. INTRODUCTION

This manual aims at giving detailed explanations on how to conduct tracer tests. It represents a substantial revision and extension of the Practice Guide for Tracer Tests by MARGANE and ABI-RISK (2011) and is, unlike the previous guide, not specific for karstic environments. For more detailed scientific guidance please refer to relevant international literature, e.g. WARD et al. (1998), KÄSS (1998), or LEIBUNDGUT et al. (2009). The manual provides a number of useful tips and is based on experiences made during the tracer tests conducted in the Nahr el Kalb catchment in Lebanon (MARGANE and ABI-RISK, 2011), the Wadi Wala in Jordan (GASSEN and STOECKL, 2013), and at U Minh in Vietnam. In detail, this document provides:

a) support in planning tracer experiments
b) more detailed and updated information about the calibration and the handling procedure of the Albillia GGNU-FL 30 fluorometer,
c) background information and working procedures for the different data loggers which are available in various BGR projects, and
d) error solving strategies which were obtained by direct communication with the developer of the fluorometer, Pierre Schnegg.

This document describes step by step how to plan a test and how to use specific measurement instruments (i.e. Albillia GGUN-FL30 fluorometers), including the calibration process, field application, and data handling. Practical experience gained during three different technical cooperation projects made it necessary to prepare this new instruction guide in order to ensure the sustainable and successful usage of different types of Albillia GGUN FL30 fluorometers and data loggers.

Currently, one fluorometer (Serial Number 442) is available within the project “Improvement of Groundwater Protection in Vietnam” (IGPVN). In Hannover, Germany, BGR holds 3 fluorometers (SN 640, 641, 642). As different data loggers by Albillia exist and are available in various projects conducted by BGR, we define here:

First type logger - CF card and RS232 port, without display (used by IGPVN)
Second type logger - CF card and RS232 port, with display
Third type logger - Micro SD card and USB port, with display

Certain settings are different for the different logger types, thus we refer to the first logger type always (e.g. available in the project “Improvement of Groundwater Protection in Vietnam”) and give additional information in brackets if different for the other types. This guideline focuses on pumping tracer tests with instantaneous injection.

2. PLANNING A TRACER TEST

2.1 General information

Tracer tests are a common technique to investigate flow pathways and travel times in aquifers, surface waters and the unsaturated zone, or to investigate interactions between the different compartments. The concept underlying a tracer test is rather simple. Water is marked by a tracer at a specific location along the expected flow path.
The tracer concentration is then recorded at certain observation points located downstream from the injection/marking point. The obtained data, i.e. the observed tracer concentration as a function of time at the observation point, is subsequently evaluated to estimate and describe hydraulic properties of the investigated system.

Tracer tests may be conducted in karst groundwater where rapid groundwater flow and high discharge quantities might occur to identify flow paths. In streams and rivers, dilution tests with artificial tracers can be used to determine discharge rates (see MARGANE and ABI-RISK, 2011, and references therein). In porous aquifers, tracer experiments are commonly used to determine hydraulic aquifer properties, like effective porosity, dispersivity, or hydraulic conductivity.

Ideal tracer substances are as similar as possible to water, e.g. do not cause density effects, are not subject to sorption, are chemically and biologically stable, and are easily detectable at low concentrations. Thus, groundwater hydrologists commonly use fluorescent dyes, e.g. Uranine (Fluorescein), Na-Naphthionate, Amidorhodamine G, or Amino-G-Acid. These substances also exhibit rather good detection limits, but are not visible over several orders of magnitude of concentrations.

In order to measure the concentration of a fluorescent tracer during a tracer test in water, a fluorometer is needed. Light with a certain wavelength (excitation spectrum) is emitted by the fluorometer. The intensity of the light which is scattered back by the tracer (emission spectrum) is then detected by the fluorometer allowing to determine the tracer concentration in the water.

To support the decision on which tracer meets test requirements best, Table 1 summarizes properties of most common tracer dyes used in groundwater, and groups them into different classes by means of their emission/excitation spectra (first row). Accordingly, only tracers from different classes can be detected at the same time, because the similar spectra cannot be separated by the Albillia GGNO-FL 30 fluorometer.

Conducting a tracer test needs detailed preparation. The success of a tracer study largely depends on the clear definition of the aim of the test and the careful preparation by the field hydrologist. This includes the evaluation of available hydrological data to develop a concept for the tracer test by assessing the overall geological and hydrogeological conditions. Furthermore, preparing a working plan for the test in advance is strongly advised as detailed planning on equipment, involved people, timing, sampling and documentation of test results is required.
Table 1: Fluorescent tracer dyes and their characteristics; with +++ for “very good”, ++ “good”, + “fair”, - “not advisable”, and blanks “unknown” (modified after http://www.albillia.com/Tracers.html)

<table>
<thead>
<tr>
<th>Class</th>
<th>Name</th>
<th>Detection limit</th>
<th>Sorption</th>
<th>Bleaching by light</th>
<th>Quantum yield with acidic pH</th>
<th>Environment friendly</th>
<th>Price</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>Sodium naphtionate</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>III</td>
<td>Tinopal (CBS-X or -CL)</td>
<td>+++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>+++</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Amino G acid</td>
<td>+</td>
<td></td>
<td>+</td>
<td>++</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>Photine</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>Duasyne yellow T</td>
<td>+++</td>
<td>++</td>
<td></td>
<td></td>
<td>++</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>Pyranine</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>I</td>
<td>Uranine (Na fluorescein)</td>
<td>+++</td>
<td>+++</td>
<td>-</td>
<td>+++</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>I</td>
<td>Eosine</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>II</td>
<td>Amidorhodamine G</td>
<td>+</td>
<td></td>
<td>+++</td>
<td>+++</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>Rhodamine WT</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>Sulforhodamine B</td>
<td>++</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

When planning a tracer test, the following points should be considered:

- Tracers might not be readily available and international import regulations may apply.
- The quality of the tracer (composition and purity) might vary.
- Officials and authorities should be involved at an early stage to make sure that necessary permissions are available on time.
- The measurement locations for operating fluorometers and other equipment should be safe, without the instrument or data logger being potentially damaged, vandalized, or stolen, or the logger being flooded.
- High backgrounds e.g. of dissolved organic material in the water might inhibit measurements.
- All participants should be involved in the planning and be aware of their responsibilities during the test.

Additionally to measurements by a field fluorometer, it is recommended to manually collect groundwater samples during the arrival and peak times to be analyzed for tracer concentrations in a laboratory. It is recommended to use brown glass bottles (e.g. 50 ml) which prevent degradation of the tracer by UV light. Irrespective of this, samples should be stored in a dark, cool and dry place. The application of special laboratory techniques (e.g. synchro-scan see LEIBUNGDGUT et al., 2009) may not only lead to an improvement by more precise measurements, but also lowers the detection limit (compared to field devices). Additionally, different tracer substances in a single sample can be more easily separated in the laboratory, if tracers with overlapping emission/excitation spectra are used. However, if taking water samples, a lot of human
resources, good logistical as well as time management are needed to carry out a tracer test successfully.

Especially when planning tracer tests in subsurface environments, it is important to recognize that flow paths and travel times are often unknown beforehand. The arrival/travel time of the tracer may differ considerably from expected travel times, being much shorter or longer as initially predicted. Different scenarios and corresponding timetables for field work should thus be prepared with regard to logistics and test realization. The sampling intervals (especially for manual samples) should be more frequently during expected times of a) first tracer arrival and b) maximum (peak) concentration. As mentioned above, these times are not always easy to predict, thus probabilities and personal experiences (if available) should be included as well.

2.2 Estimate the tracer mass and preliminary calculations

The initial tracer mass for a tracer experiment should be carefully estimated. In doing so, the aim of the test, type of tracer dye, and the overall hydrologic framework need to be considered. In general, the amount of the injected tracer substance has to be large enough to produce a concentration peak at the observation point which can be easily detected and resolved.

When working with the Albillia GGUN-FL30 fluorometer in the field, concentrations less than 1 ppb were found difficult to detect. Furthermore, it should be noted that the presence of colored dissolved organic matter (CDOM) may cause a high background in the excitation spectrum of Amino-G-Acid or Tinopal. If using these tracer dyes CDOM concentrations of the water should be checked in advance.

Non-reactive transport in groundwater is described by the three-dimensional dispersion equation, which can be solved numerically. Using simplifications, analytical solutions of the dispersion equation are available for 2D and 1D groundwater flow. Corresponding 2D solutions allow e.g. to evaluate tracer tests in porous aquifers under natural flow conditions. When combining a tracer test with a pumping test, groundwater flow becomes convergent to the pumping well, which further simplifies the analytical solution to 1D (e.g. LEIBUNDGUT et al., 2009). The freeware TRAC (GUTIERREZ et al., 2013) assembles various analytical solutions for tracer experiments in 2D and 1D. TRAC is easy to handle and can be used to simulate and design tracer tests, as well as for their evaluation.

However, it is important to keep in mind that analytical solutions represent simplified systems, e.g. assuming aquifer homogeneity. This increases the uncertainty when estimating the initial tracer mass to be injected under natural, more complex conditions. Nevertheless, using analytical solutions is favored to empirical equations, which may also provide a first guess for the initial tracer mass. In order to demonstrate the estimation of the initial tracer mass by using TRAC (v1.7-r4), the following exemplifies corresponding calculations for a combined pumping-tracer test.

The configuration of a combined pumping-tracer test is presented in Figure 1. Accordingly, the tracer is injected in a monitoring well at distance $x$ [m] from the pumping well. Both wells, the injection and the pumping (monitoring) well are completely screened in a homogeneous aquifer of thickness $b$ [m]. The aquifer is assumed to be infinite (i.e. unbounded). The pumping well is discharged at a constant
rate \( Q \) [m³/h] for the entire duration of the test. The tracer is injected quickly (Dirac pulse) into the monitoring well. The observation point to detect the tracer is the pumping well where a fluorometer is installed to analyze and record the tracer concentration of the pumped water over time.

![Figure 1: Conceptual sketch of a tracer experiment which is combined with a pumping test.](image_url)

To estimate the initial tracer mass by using the TRAC software, information on the geometry and performance of the test is needed as input for the calculations. As the tracer experiment is combined with a pumping test, a cone of depression develops and groundwater flow is radially convergent to the pumping well. Accordingly, the settings “radial converging” dimension, “brief (Dirac)” injection, and “infinite” milieu are chosen “formula” slide of the software TRAC. In the parameter tab, estimates of the hydraulic aquifer parameters (effective/kinematic porosity, longitudinal dispersivity), as well as \( b \), \( x \) and \( Q \) are needed to perform preliminary simulations to calculate the tracer concentration at the observation point, i.e. at the pumping well. By varying the initial tracer mass or using the corresponding dialog in the “dimensions” tab, the most suitable amount for tracer injection can be calculated. In this regard, the recovery rate of the tracer mass needs to be estimated. Consider that recovery rates are seldom 100% of the initially injected tracer mass. Bounds of e.g. 10% and 80% may thus be used for preliminary calculations.

Figure 2 presents the simulated tracer concentration at the pumping well for six different scenarios (colored lines), and compares the simulated scenarios to the actual retrieved tracer concentration in the field (black line). With regard to the recovery rate of the tracer \( (R) \), the scenarios mentioned above were used (i.e. 10% and 80% of tracer recovery). In each scenario, hydraulic aquifer properties were varied: effective porosity \( (n_e) \) was 5% and 15%, and longitudinal dispersivity \( (\alpha_L) \) was 1 m and 10 m. Estimates for hydraulic parameters may be available from previous field investigations, or may be taken from the literature if no field data is available.
The possibility of adjusting hydraulic aquifer parameters and varying recovery rates makes TRAC a good tool for preliminary calculations. After simulating the described scenarios, it was decided to use 500 g for the respective tracer test. With this amount, a “worst case” ($R = 10\%$, $n_e = 15\%$, $\alpha_L = 1$ m) concentration peak of 6 ppb is reached 10 days after tracer injection, which is still detectable by the field fluorometer. Whereas, the scenario which produces the most distinct peak of 143 ppb at 3.3 days after injection ($R = 80\%$, $n_e = 5\%$, $\alpha_L = 1$ m) will have negligible impact on the environment. The test should not be finished before the concentration decreased to at least 50% of the maximum concentration. Be aware that tailings might take a lot of time. Note that the scenarios also show that the field hydrologist should prepare for a long test period, as indicated e.g. by the dashed blue line in Fig. 2.

Figure 2: Simulated tracer concentrations at the observation point (pumping well) for different scenarios with tracer recovery rates $R$ of 10% and 80%, effective porosity $n_e$ of 5% and 15%, and longitudinal dispersivity $\alpha_L$ of 1 m and 10 m. Simulated concentrations (colored lines) are compared to the actual retrieved concentrations (black line).

Figure 2 also shows that preliminary calculations are normally based on a rather simple understanding of the investigated system. Multiple peaks in the actual measured tracer concentrations (black line) suggest that aquifer heterogeneity may have a strong impact on groundwater flow at the investigated site. However, predicting the response of complex systems is normally not feasible at this stage of investigations.

2.3 Tracer injection

Different considerations have to be taken into account for a successful tracer experiment, in particular when testing groundwater environments:
The tracer needs to be injected into the flow path. That is, for groundwater related tracer experiment, the tracer should be injected over the entire thickness of the aquifer to satisfy the 2D or 1D condition of analytical solutions.

The tracer should be injected at screen depth. Just pouring the tracer into the well is not an adequate procedure, in particular when testing deep wells where the tracer would have to move a long way downwards to enter the aquifer.

Tracer injection is done in three phases. First, the injection well is flushed to establish groundwater flow into the aquifer. Second, the dissolved tracer is injected. Third, the well is flushed again to make sure that all the tracer enters the aquifer.

Tracer injection should be conducted as quick as possible, in order to satisfy the “Dirac” condition of an instantaneous (pulse) injection.

If several tracers are used (multiple injection points), several sets of equipment are needed for tracer injection to prevent cross-contamination.

In order to realize a tracer injection as summarized above it is highly recommended to install injection pipes in the injection well which are perforated over approximately the same depth as the well. The injection pipes are then connected to a pump, and are used for tracer injection as well as for well flushing (Figure 3). Amounts of water to flush the well before and after tracer injection should be estimated beforehand. Persons who weigh/prepare/inject the tracer are requested to wear protective clothing and disposable gloves, and should leave the site immediately after tracer injection to prevent potential cross-contamination.
3. Operating the fluorometer

3.1 Getting started

Before conducting a tracer test with fluorescent dyes, the fluorometer has to be connected to a PC, initialized and calibrated. Therefore,

- Install the programs FLUO and GigaTerm from the provided CD which comes with the fluorometer

- Connect the data logger via the cable with the fluorometer (of the same serial number, if you have more than one device).

- Insert the correct card into the logger (either a micro SD or a compact flash card, depending on the device type). These cards have to be initialized by Albillia, so only use the appropriate cards. Depending on the type of card there are slight differences for the operation (e.g. for correct operation, a provided file called flashcar.dat has to be present for the logger types one and two, while a cal.dat file must exist on the SD card for the logger type 3).

- Switch to the applicable settings on the data logger e.g. for a type 1 logger without display and RS232 port set 2 1 1 1 1 (for a type 2 and type 3 logger with 6 digits use 2 1 3 1 1 0). The first number on the logger always displays the Sampling Rate (SR). For the type 1 logger the following four numbers resemble the four lamps of the fluorometer. For the other logger types,
additional information on the settings can be found inside the lid of the data logger.

- Establish a connection between the data logger and the PC via USB cable. (Some data logger come with a RS232 serial cable. A RS232-to-USB adapter should be provided by Albillia, otherwise you have to buy one). Install the driver on your PC.

- Connect a 6V or 12V battery to the data logger and turn it on. (Note that some loggers are turned on by a switch, others are turned on by simply connecting the battery, e.g. type 3 logger).

- Now check the COM port where the logger is installed on your PC (“devices and printers” using Windows).

- For a first communication between the PC and the logger open GigaTerm, as this is more robust than the program FLUO. Select the right COM port which is in use and a baud rate of 9600 (Figure 4). Then select the “open” box. If a connection is established, recordings will appear. If no connection was established see chapter “trouble shooting” at the end of this manual.

![GigaLog Terminal 903](image)

**Figure 4: COM Port and Baud Rate Settings in the GigaTerm Program**

- Click on the first yellow box on the left (arrow up). Some lines will appear in the main window ending with “no cf”.

- Click on the fifth yellow box with the clock symbol to send the computer time to the logger.

- If a communication with GigaTerm is possible and the date and time is set, close the program and open the FLUO program.

- FLUO communicates with the logger via the file “calibrat.dat”. This file is located in the same folder as the FLUO.exe program and has to be specified for a correct communication with the logger, as well as correct performance in the field (see section calibration). It is the basis for the correct conversion of the
millivolt (mV) signal from the logger into a correct tracer concentration (ppb). Note, that spaces should not be changed in the calibrat.dat file.

- Open the calibrat.dat file with the editor of your choice (e.g. notepad++). Change the serial port in use to the correct COM port, where the cable is plugged in, i.e. in around line 50 of the calibrat.dat file “Serial port in use (usually 1)”. Save this file under the same name and location!

- Switch the slider in FLUO to “New acquisition” (bottom left). Now the red lamp should start blinking and mV as well as the converted ppb data should be received in the respective yellow boxes. Note that if all tracers and turbidity (top line) are selected, the temperature is hidden in a left column in the yellow mV box. Also note that the electric conductivity is only shown if a sensor in the fluorometer is available and if this is indicated in the calibrat.dat file (i.e. 001. instead of 000.).

3.2 Fluorometer calibration

Calibration of the fluorometer before each tracer test is a must. Each fluorometer must be calibrated separately for each location using the local waters. Note that calibration is a time consuming process and might take several days, depending on the number of fluorometers, stations and repeat calibrations. Repeat your calibration (at least once) in order to be sure your calibration is correct, before installing the fluorometer. Even if used at the same location, the calibration should be repeated at least after a duration of 6 months.

Before calibration, different calibration solutions have to be prepared. For this process water from the source where the test will be conducted has to be used. The solutions of different tracer concentrations (e.g. 100, 10, and 1 ppb) and pure water have to be inserted into the fluorometer and measured.

The respective measurements (in mV) have then to be inserted in the calibrat.dat file. The calibrat.dat file is necessary for a correct functioning of the FLUO program which calculates the tracer concentrations in ppb from the millivolt (mV) signal recorded by the fluorometer.

3.2.1 Preparation of calibration solutions

In general you prepare three solutions; 100 ppb, 10 ppb and 1 ppb for each tracer. If you measure at different locations, different solutions have to be prepared using the water from each individual sampling location. This is, because background values might vary (contamination, different water input, etc.) and therefore the tracer signal might be altered.

To prepare the solutions one will need:

- high-precision balance (max ~200 g; e.g. Mettler-Toledo ML 203)
- one 500 ml volumetric flask for each tracer, one for each station (see step 1 below) Note: Do not use Erlenmeyer flasks, as they don’t allow high precision in measuring water quantity.

- at least two 500 ml volumetric flasks for steps 2 and 3

- at least two 100 ml graduated cylinder glasses

- automatic pipette as shown in Figure 5 (e.g. Eppendorf 10 ml) or glass pipettes 5 ml (e.g. Wertheim, Germany)

- sampling bottles 100-200 ml

A set of solutions is prepared in five steps:

step 1: 0.500 g tracer in 500 ml water >> 1g/l solution
(keep solution until calibration is final)

step 2: 5 ml of 1 g/l solution in 500 ml water >> 10 mg/l solution

step 3: 5 ml of 10 mg/l solution in 500 ml water >> 100 ppb solution
(store at least 100 ml for calibration; keep 1 bottle to prepare 1 and 10 ppb solutions if required later)

step 4: 10 ml of 100 ppb solution in 100 ml water >> 10 ppb solution
(store 60 to 100 ml for calibration)

step 5: 10 ml of 10 ppb solution in 100 ml water
5 ml of 100 ppb solution in 500 ml water >> 1 ppb solution; or
(store 60 to 100 ml for calibration)

The “stored” solutions prepared in steps 3 to 5 will be used for the calibration process of the fluorometer. Keep them at a dark, cool place and calculate how much of each solution you might need before starting to prepare the respective solutions. The interior of the fluorometer does not have to be filled to the top. The tube holds approximately 20 ml, however 15 ml are sufficient for reliable measurements. If you plan to support fluorometer measurements by tracer analysis in the lab it is also recommended to keep some additional calibration solution.
3.2.2 Configuration of the calibrat.dat file

The calibrat.dat file is located in the same folder as the FLUO program. It can be opened and configured with an editor of your choice (e.g. notepad++, do not use WORD here). In the calibrat.dat, L1 to L4 indicate the values (always in mV) recorded by each of the four lamps (L) inside the fluorometer; for pure water (without tracer), for each tracer, and for turbidity (NTU). During the calibration, these values have to be measured and replaced for water and each of the tracers with a concentration of 100 ppb. A maximum of three different tracers can be used during a single test. If only one or two tracers are applied, the other canals can simply be ignored during the calibration process. The aim of calibration is to translate the recorded mV signal into the correct concentration signal, depending on the excitation spectrum of the different tracers.

The calibrate.dat file is configured as follows:

- Copy the calibrat.dat from the FLUO folder in a separate “calibration folder”. Generate another copy and call it calibrat_new.dat. Always use the last calibrat.dat file for a calibration. If you are not sure or do not have it use the original calibrat.dat which is usually stored on a second card delivered by Albillia and the installation CD. Make sure you are using the calibrat.dat assigned for the correct fluorometer and data logger (serial number) if you are working with more than one fluorometer.
- Set the data logger 2 1 1 1 1 (or to 2 0 3 1 1 0 for type 2 and 3 loggers, respectively) and start the logger.
- Synchronize with PC-time with GigaTerm and close that program (see section “getting started”).
- Open the FLUO program and switch the slider to “new acquisition”.
- Unscrew the upper and lower cap of the fluorometer. Use the rubber stopper to plug the bottom of the inner fluorometer tube.
- Clean the interior of the fluorometer well before you start and each time you use different tracer solutions.
- Start filling the fluorometer subsequently with the first solution (e.g. pure water from your sampling location). It is recommended to always start the calibration with the lowest concentration (e.g. pure water or 1 ppb tracer solution) since you do not need to rinse the fluorometer when going to higher concentrations.
- The recommended measuring sequence for the calibration process is:
  a) Pure water from the test location
  b) Tracer 1 – 1 ppb
  c) Tracer 1 – 10 ppb
  d) Tracer 1 – 100 ppb
  e) Tracer 2 – 1 ppb
  f) Tracer 2 – 10 ppb
  g) Tracer 2 – 100 ppb
  h) Then for a third tracer, respectively (if used)
  i) Then repeat with other instruments accordingly
- After filling the fluorometer with pure water or a tracer solution, take around ten measurements (90 seconds) and check if the values in the yellow boxes (mV / ppb) are constant (Figure 6). Press the “stop” button and see if there are any outliers.
Figure 6: Calibration of instrument 531 with the FLUO program for 100 ppb Na-Naphthionate

- Copy the third or fourth line (not an outlier!) of the mV and the ppb signal in the yellow boxes for each calibration solution (pure water, and 1, 10, and 100 ppb for each tracer) into a blank (txt or word) file first (see Figure 7). This file also serves as a back-up if the calibration process fails. These measurement will later be used to rewrite the calibrat.dat file. (According to direct communications with Pierre Schnegg, it is not recommended to calculate averages as described in MARGANE and ABI-RISK (2011) because the UV light of the fluorometer will lead to a constant decay of the tracer solution during measurements. Thus better use the second or third line of mV values recorded by FLUO).

- Use the values of this backup file to replace the respective values in your calibrat_new.dat. This includes the millivolt values for water and the 100 ppb tracer concentrations of the different lamps (L1 to L4) as well as the millivolt values for the different concentrations in the lower section of the file (See red and yellow circles in Figure 8, respectively). Here, “-8” and “-7” indicate a concentration of 10 ppb and 100 ppb, respectively. If you wish to add a 1 ppb measurement to the calibration you can just write another line (“-9”), above (!) “-8”, but make sure, that you keep the blanks in line and that you change the “Number of calibration lines” from 2 to 3 (one more line above).

- Change the date and location in your calibrat_new.dat to be able to identify the correct file at a later stage.

- Save your calibrat_new.dat and rename it to calibrat.dat. Copy it into the FLUO folder (i.e. replace the old calibrat.dat). It is recommended to always store the “old” calibrat.dat files as a backup, in the case the calibration shows worse
values than before or fails completely. If the calibration was successful, values for 1, 10, and 100 ppb are exactly measured with the FLUO program now. A deviation of less than 1 ppb might be considered successful.

- Now repeat the process with your different calibration fluids to double-check calibration quality. Do not forget to clean the fluorometer properly when using a lower concentration or different tracer solution. Generate a second calibrat_new.dat and compare it to your calibrat.dat in the FLUO folder. If the values do not change significantly your calibration can be terminated here.

Figure 7: Backup calibration file with mV and ppb values copied from the FLUO program
Figure 8: Calibrat.dat file of fluorometer 525 with L1 to L4 (red circles) the lamps for water and Uranine (mV values with the 100 ppb solution) and -9, -8, -7 (yellow circles) the mV values for the 1 ppb, 10 ppb, and 100 ppb solutions, respectively.
The number of lamps should always be four (except for a dilution test, see MARGANE and ABI-RISK, 2011), to achieve the most precise measurements by the whole measurement spectrum.

According to personal communications with Pierre Schnegg a two point calibration with 10 ppb and 100 ppb solutions is sufficient, however we always included the 1 ppb solution. Note that the values for water cannot be higher than the values for tracer concentrations and turbidity (NTU), otherwise FLUO will return an error message (sometimes background concentrations in the water might be quite high and may disturb the measurements, see chapter “trouble shooting”).

Also note that what is displayed in the FLUO program is the ppb values based on the previous calibration! To see actual results of your calibration you can restart the FLUO program with the new calibrat.dat, set the slider to “process mV” and open one of your last .mv files which were recorded during the calibration process. Note that every time that you are measuring with the FLUO program the mV measurements are written into .mV file. Determined by the calibrat.dat in the FLUO folder they can be reprocessed at a later point in time. Depending on your operational system, the .mv files might not be stored in the FLUO folder but in a different location (i.e. in c:/Users/your_username/AppData/Local/VirtualStore/Program Files/Fluo/). It is recommended to create a shortcut to this location if not stored in the FLUO folder.

4. FIELD APPLICATION

4.1 Installation of the fluorometer

The sampling location where the fluorometer should be installed, has to be on the assumed main pathway of the groundwater flow. Flow at the measurement location should not be turbulent (preventing development of air bubbles which lead to biased measurements). There should be no major water gains or losses from other water sources in the vicinity of the sampling point. The water should be channeled through the fluorometer either in a flow through cell (or simply a bucket, Figure 9) or by connecting it directly to a tube. If no or little information about pathways is available beforehand, the possibility of installing more than one fluorometer at different sites should be considered.

If the fluorometer is placed in open water or a river, make sure that it is secured, e.g. fixed with ropes. The bottom and top caps of the fluorometer should always be mounted to prevent damage of the inner glass tube. The holes in the top and bottom caps (in- and outlets) should be directed to opposite sides, to enable water flow through the fluorometer.

The connection cable must be plugged in the fluorometer before submersing the fluorometer in water. The location of the logger should be a place which is easy to reach for data readout and changing of batteries and should additionally be safe from flooding.
4.2 Handling the fluorometer

The following provides some suggestions/information on handling the fluorometer in the field:

- Use Sampling Rate (SR) of 2 minutes, a 12 V battery will last for approximately 2 weeks.
- Frequently (at least daily) check if data was recorded and read out the data from the card. Reportedly, the devices are not 100% reliable.
- Also, test how much data can be stored depending on the size of your card as well as the selected sampling rate.
- When measuring, never switch the logger off and on again, as old data will then be overwritten! Only when replacing the card (for readout) switch off the logger.
and turn on again after inserting the new card. Do it quickly, to keep loss of data to a minimum.

- During recording, it might be advisable to have a PC connected to the logger and open the FLUO program, especially for type 1 logger without LCD display. Note that when FLUO is working, the data is not only stored on the card, but also on a separate .mv file on your PC, which might be useful if e.g. the data on the card gets lost.

- Clean the interior of the fluorometer from time to time (after some days, depending on the water quality, turbidity, organics and sediment transport).

- Protect the fluorometer from direct sunlight, as it will heat up the device and lead to biased measurements.

4.3 Trouble shooting

If the communication between the logger and a PC fails

- Check all (!) connections (e.g. the cable in the logger and in the fluorometer, the cable from the logger to the PC)

- Check if the SD or CF card is inserted correctly in the data logger

- Make sure that you use the right settings on the data logger

- Check if the right port is selected

- Check with the program Gigaterm if a connection can be established (see “getting started”).

- When using the program FLUO, check the calibrat.dat file which is located in the folder from where FLUO is executed. In the calibrat.dat, make sure, that
  a. the right port is allocated
  b. no blanks are added to the original file structure
  c. if more than two solutions are used for calibration, this number has also to be changed in the calibrat.dat file.

- If an error message after editing the calibrat.dat appears when starting FLUO, you should check, if the values of your water are still smaller than all other values for the tracers and turbidity, from L1 to L4, respectively.

- If the instrument is still not working directly contact one of the authors of this script or Pierre Schnegg, the developer of the instruments.

Baseline values given in the .mv file are automatically recorded when the FLUO program is set to “data acquisition” and should not exceed 13 mV. To avoid that the baseline is exceeded, the fluorometer should not be near any metallic objects, power lines, etc. The manufacturer recommends not to operate the fluorometer near a notebook connected to a charger (such as would be necessary for calibrations or measurement of manual samples, or the absence of a logger display). However, we cannot confirm that this has any influence on the readings.
It is recommended to format the storage cards (CF or Micro SD) every now and then to avoid problems. The files on the card however, have to be stored on the computer and reloaded after formatting the card. These are for the logger type 1 the flashcar.dat, and for the logger type 2 and 3 the cal.dat. Concerning CF-card readers, we have tried a good dozen different ones. They will all be broken after some time as a kind of built-in limitation but it is highly recommended not to use the cheap readers as you would risk breaking the pins in the CF-card adapter of your logger.

Sometimes loggers will stop recording data for unknown reasons. Thus, it is recommended to collect data as often as possible and change batteries after about one week (if on 2 min time interval) in order to minimize lost data. If a PC is connected and the FLUO program is recording, all data are stored in a .mv file which is continuously written. This file will not be overwritten by the program. A new file is generated on each day the FLUO program is restarted. Another possibility to restore data from the card is to go to “Read FlashCard” in the FLUO program and select “Retrieve previous card content as RETREIVE.DAT file”. Sometimes old data can be restored after the logger was turned off and on again.

5. REFERENCES


