# BACKGROUND AND DETECTION OF FLUORESCENT TRACERS IN KARST GROUNDWATER

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**ABSTRACT**

A set of specific fluorescent organic susbtances are commonly used for tracer tests in hydrology, particularly in karst environments where the recognition of flow connections is a prerequisite to any further investigation. The detection of these tracers has been considerably improved by the development of spectrofluorometric techniques. The instrumental limits of detection are always far below those of salt tracers. The fluorescence background of water at the sampling site may however interfere and limit the chance of identifying a real breakthrough of the tracer. This background may originate from both natural or anthropogenic sources. Though these problems are likely to occur in any kind of aquifer, they are obviously emphasized in karst aquifers, due to highly variable hydrodynamics and hydrochemistry as well as higher susceptibility to organic contaminations. A better understanding of the fluorescence of DOM (dissolved organic matter) including both natural substances and organic contaminants is one of the leads that are followed at the moment. Using 2D and 3D fluorescence spectra allows us to discriminate between the background and the tracer itself. Unfortunately the interferences are more often insidious and their evaluation somewhat subjective. The application of more rigorous tracing protocols, as well as the development of an instrumentation suitable for higher sampling rates (i.e. field fluorometers), give us another promising opportunity for studying the time variations of the fluorescence. Those variations can then be used for the discrimination between the background and the breakthrough of the tracer itself. At the light of several case studies recorded in the belgian karst, this paper focuses on the possible combined use of spectra and time series of fluorescence to identify tracers. This approach seems to be especially attracting for tracer tests when environmental or drinking water concerns require a compromise between the reliability of the results and the use of the lowest amounts of tracer.

**Key words**: tracing, fluorescence, background, limit of detection, karst

## 1. INTRODUCTION

The input of artificial tracers in groundwater is commonly achieved for studying water flow (Käss, 1998; Schudel *et al.*, 2002), in particular for the identification of pollutants routes and for the protection of water supply (Meus, 2002). Fluorescent organic dyes are considered as appropriate tracers in most situations. They are normally absent from the environment and readily detectable using fluorometric techniques. In Switzerland, where tracer tests are controlled (Office Fédéral de l'Environnement, 2005), approximately 70 % of the tests performed between 1984 and 2003, were using fluorescent dyes, among which 40 % with the most popular tracer uranine (Acid Yellow 73). In Wallonia, during the last decades, 67 % of the tests in carbonate aquifers were performed with fluorescent dyes (30 % with uranine). Fluorescent tracers own better instrumental limits of detection (LOD between 0,001 and 0,1 ppb, Schudel *et al.*, 2003) than any salt tracer. In Wallonia, for more or less the same proportion of successfull tests (60 %), the total mass of fluorescent tracers needed represents only 23 % against 77 % of salts. To give an idea, a total mass of 160 kg of uranine was estimated to be used in this region.

However, the main concern with tracer tests remains to demonstrate that the tracer significantly exceeds the background, and more precisely that the identified tracer is well that from the intended trace (Smart and Karunaratne, 2002), a simple fact that raises a few complex points regarding the use of fluorescent tracers:

- the input of organics into groundwater could pose an environmental threat at a given level which is not totally under control at this stage, even if several studies (Field, 1995; Behrens *et al.*, 2001) have demonstrated that several dyes are toxicologically safe in

"normal" conditions of tracing. This obviously should encourage hydrologists to minimize the quantity of tracer used, but in turn is also compromising for the detection of the tracer;

- the long lasting use of fluorescent dyes, together with their low capacity of degradation underground, continuously increases the level of background especially in aquifers with lower turnover time. These contaminations has been early recognized by Parriaux *et al.* (1990) and represents an additional component to the general problem of interference. Contaminations through all the sampling procedure (through samplers or bottles) is also frequent;
- natural organic matter (NOM) present in water contains a range of fluorophores (Baker and Lamont-Black, 2001; Baker and Genty, 1999) that may interfere, especially in the case of short wavelengths tracers. Even if there are some attempts to appply corrections to these signals, the assessment of their variations remains a difficulty;
- many domestic organic products, industrial products, or their by-products, also contains fluorophores which may interfere in quite an insidious manner in groundwater. These products may originate from different contaminant sources including leachates and plumes of landfills (Riediker *et al.*, 2000; Baker and Curry, 2004; Menzel *et al.*, 2002), farm wastes (Baker, 2001) or sewages (Baker *et al.*, 2003). Petrochemical as well, mainly PAHs, (Groner *et al.*, 2001; Pharr *et al.*, 1992) and pesticides also contain potentially interfering fluorophores. The detection of these substances is until now better known in surface water than in groundwater. They are often generic substances that can be hardly recognized individually. Their behaviour, thus the variations of fluorescence that they introduce, is not sufficiently documented until now to be taken into account when searching fluorescent tracers;
- from the analytical point of view, because of all the above mentioned interferences, the chance of identification of the breakthrough of an injected tracer does not only depend on the instrumental performances (sensitivity, selectivity) but also on a pertinent judgement of the operator (Smart and Karunaratne, 2002).

No objective protocol, like a statistical one for instance, have been until now defined for the search of fluorescent tracers in groundwater. On another side, it is likely that such a protocol, if not written in a sufficiently flexible way, may be misunderstood and applied with a blind confidence, thus compromising a good interpretation. Much experiments have always to be dealed with case by case. This paper is intended as a guidance to help the practitionner to fill the gap between the field and the laboratory. It is a common mistake that those two aspects are treated in separate ways while they should obviously be part of a complete procedure. If the interrelations of the data to the problem are faulty, the conclusions drawn may also be faulty (Collective, 1980).

As a consequence, a clear distinction must be made between the detection of the substance itself in a single sample and its identification in a chronological serie of samples as a probable breakthrough originating from an actual injection.

The results below are all extracted from karst aquifers case studies. This type of aquifer has been choosed as a worst case because of its highly variable quality and its high susceptibility to contaminations. Data are issued from the authors experience as well as several thousands of analyzed samples collected through the practice of the laboratory EWTS. The tests mainly concern the identification of the three fluorescent tracers mostly used in Wallonia: uranine, sulforhodamine B (Acid Red 52) and naphtionate[1]. However, a great deal of the conclusions may be extrapolated to the other dyes and other types of aquifer.

## 2. MATERIALS AND METHODS

The approach is based on a classical sampling procedure for water tracing, eventually complemented by an in situ monitoring of water fluorescence.

[1] 1-naphthylamin-4-sulfonicacid sodium salt hydrate

Most of the sampling and monitoring sites are wells, galleries and karstic springs in the Carboniferous and Devonian limestones aquifers in Wallonia.

Samples were usually collected through automatic samplers (ISCO 3700 in most cases) on a minimum daily basis, with some samples taken manually as controls. The periods of sampling are ranging from 1 to several months. Wells were pumped at a constant rate except where the exploitation required another modulation.

A few more specific investigations were focusing on the variations of natural background fluorescence of groundwater. These were part of a student work (Gourdin, 2003) in the Carboniferous limestones of the Néblon valley (Ourthe river) and of an on-going research on the Chalet spring (Amblève river) in the Devonian limestones.

All samples were analyzed in standard quartz cell on a HITACHI F-2500 fluorescence spectrophotometer. The default parameters settings for such low fluorescence measurements were excitation/emission slits of 5 nm and photomultiplier voltage of 700. In the case of trace concentrations, these settings revealed to be a good compromise between the sensitivity and a suitable wavelength resolution of spectra.

Standards solutions of the studied fluorescent tracers were prepared using known dry powders and dilutions by fresh ultrapure water. Anyway, all the results are gross intensity values except when specified.

Three successive analytical methods were used according to the depth of information needed in each case. The basic measurements were made with the so-called "stand-by" method which measures the fluorescence intensity for fixed excitation/emission (EX/EM) wavelengths corresponding to the optimum of the fluorescence of the tracers. Those wavelengths for naphtionate, uranine and sulforhodamine B were respectively 320/415 nm, 491/511 nm, and 564/584 nm. For the search of naphtionate in the presence of a high background, three more wavelengths couples were used according to the possibility of measuring a maximum of six couples simultaneously. The choice of these wavelengths was determined by a judgement based on the variations observed in a representative set of spectra of groundwater. A second method is the "dual synchronous scanning" that allows the best visualization and separation of the fluorescent tracer peaks. The method, also called "of the constant step" has been proposed by Behrens in 1969. It has been tested by Charrière (1974) and its advantages are detailed in Käss (1998). In the present study, two kinds of synchronous spectra were used for covering the whole set of the studied tracers, with a 20 nm shift[2] for uranine and sulforhodamine B, and a 95 nm shift for naphtionate. Spectra were recorded with a scanning speed of 300 nm/minute. Intensities are normally expressed in function of the excitation wavelength. A third method, whose results are going out of the frame of this paper, is using the total fluorescence[3] by varying undifferently the excitation and emission wavelengths. It was until now not so widely used for identifying fluorescent tracers but it is likely to become an interesting tool thanks to its capacity of fingerprinting natural or contaminant fluorescence.

Fluorescence of groundwater in situ was measured with a flow-through field fluorometer FL30 (GGUN) combined with a TRMC-4F datalogger (Tétraèdre). The system (Schnegg, 2002) is equipped with 4 LEDs, allowing the measurement of turbidity (660 nm LED) as well as the fluorescence in the three searched domains of the electromagnetic spectrum (370, 470 and 525 nm LEDs[4]). The system is also equipped with a conductivity cell and a temperature measurement. It allows the fluorescence signals of the tracers to be corrected for the turbidity. In the present case, only gross signals were used.

Water level, as well as conductivity and temperature, were measured by a TROLL 8000 (In Situ) probe.

## 3. RESULTS AND DISCUSSION

[2] Stokes's shift.

[3] This method is also called Excitation Emission Matrix (EEM).

[4] The 370 nm LED is optimal for tinopal detection. The detection of naphtionate should require a slightly lower excitation wavelength.

A wide range of uncertainties are affecting the final evaluation of any analyte (Collective, 1980). The main problem in searching a tracer is that, like in all environmental analyses, only a signal can be measured and its real correspondance with the searched substance is not univocal. In the case of the identification of traces, these uncertainties are emphasized because of the confusion that may arise between the background and the analyte. Moreover, in tracer tests, the uncertainties are coming both from the analytical procedure and the effective variations in time of the population of samples itself. The question to know if an identified substance is really the one involved in the actual tracer test is an additional problem, maybe more critical to solve in most experiments.

All these uncertainties can thus be matched by reducing the degree of freedom of the problem, that means acquiring as much pertinent data as possible.

In a general way:

- the uncertainties related to the identification of the trace in an individual sample may be tackled by increasing the dimension of the information in the wavelength domain, that means acquiring synchronous, eventually total fluorescence, spectra for a better identification of tracer peaks, while
- the uncertainties due to the identification of the breakthrough of the tracer may be tackled by increasing the dimension of the information in the time domain, that means analyzing time series of samples.

Obviously, such an approach requires that good planning and protocol have been previously defined in order to make these acquisitions posssible, the reason why the degree of confidence on the identication of the breakthrough may vary considerably from one experiment to another.

This paper focuses on the combined use of spectral and time variations.

### *3.1. Identification of tracers through spectra*

For tracer tests where the number of samples is rather limited, the acquisition of spectra, in particular synchronous scanning spectra, is recommended. Anyway the results should be carefully interpreted.

Figure 1 shows the principal causes of variations in the spectra of groundwater which may affect the discrimination of the peaks of tracers. The larger the part of the spectrum is homogeneously affected, the less the interference will be a problem for demonstrating the presence of the tracer. Even if it is frequent in karst waters, turbidity is affecting the signal as a whole and corrections can be made more or less easily (Evans, 2000; Schnegg, 2002). Organic contaminants, and to a less extent natural organic matter, are without any doubt the most problematic causes, without considering the occurrence of someone else's tracer which can only be solved in time domain.

Figure 2 and 3 show two examples of possible misinterpretation due to background when single or very few samples are available.

In the first case (Fig. 2), the signal B is a blank signal coming from a karst spring after a winter flood. The signal A is a standard of 0,01 ppb of uranine prepared with ultrapure water. It is clear that a simple measurement at the optimal excitation wavelength of uranine (491 nm) would lead to the conclusion that the spring is containing uranine. Moreover, in this case, it can also be concluded that the deviation on the spectrum B can be due to uranine peak, while probably this deviation is only due to multiple interferences.

Smart and Karunaratne (2002) have studied the variations of fluorescence through synchronous scanning spectra with 20 nm shift in a surface stream. They demonstrated a frequent occurrence of uranine-like fluorescence variations.

The case of the identication of naphtionate is far more critical. The problem has been reported in Schudel (2003). At shorter wavelengths, the natural background commonly produces peaking around 320 nm that can be easily confused with main naphtionate peak. Signal A (Fig. 3), that can be confused with B, represents a standard of as much as 0,1 ppb of naphtionate.

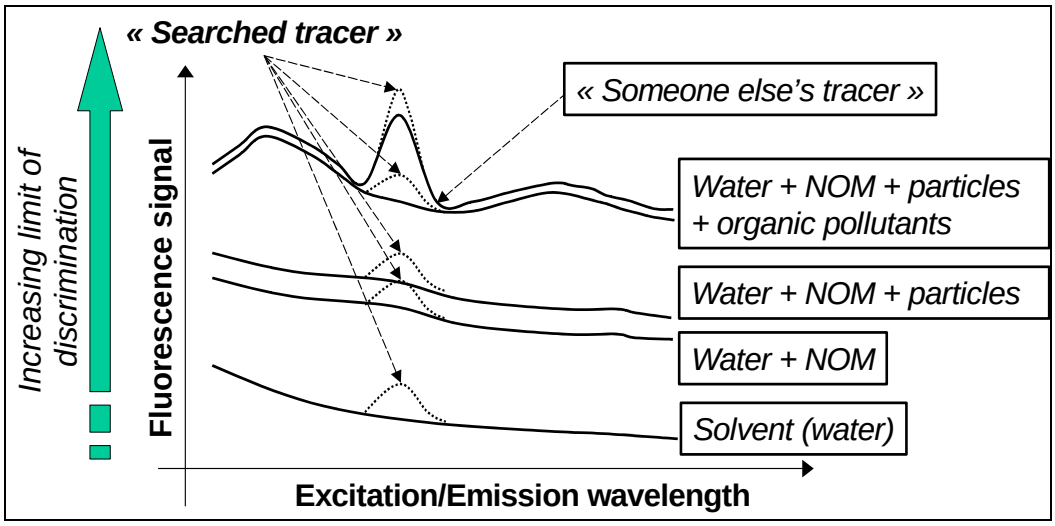


**Figure 1**: Main fluorescence interferences when trying to discriminate a tracer on spectra of groundwater.

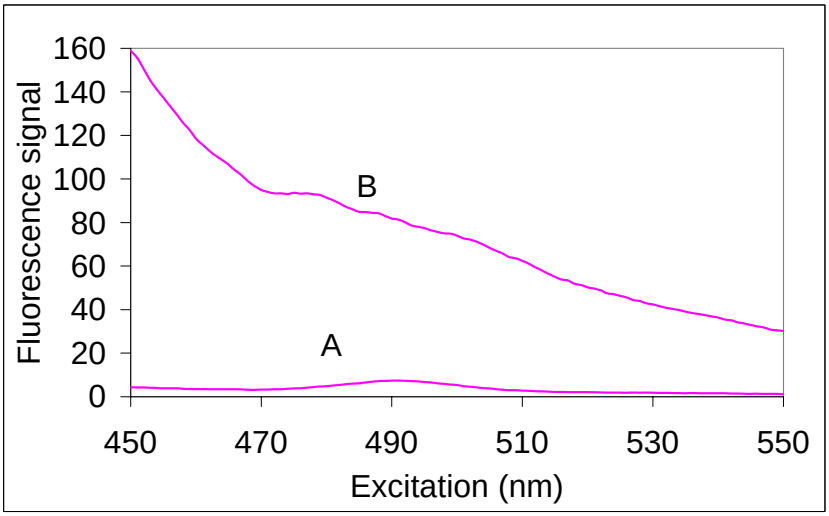


**Figure 2**: Comparison of the synchronous scanning spectra of a uranine standard solution 0,01 ppb (A) and a spring blank sample (B).

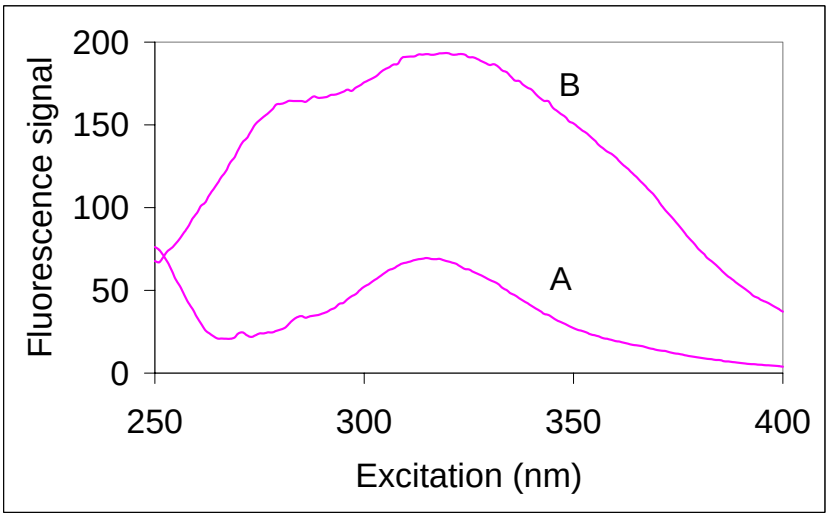


**Figure 3**: Comparison of the synchronous scanning spectra of a naphtionate standard solution 0,1 ppb (A) and a spring blank sample (B).

Smart and Karunaratne (2002) conclude that the strong background observed for in UV-blue region of surface water spectra may not interfere so much with conventional tracers. They probably do not consider here the potential use of napthionate. In Wallonia, and this was the case in many european countries this last years, around 20% of tracer tests are achieved with naphtionate. Naphtionate can indeed interfere mostly with natural organic matter, more precisely with humic-like (fulvic) acids (Baker and Genty, 1999). Those interferences have also been recognized in leachates from landfills (Baker and Curry, 2004). In karst groundwater, it has been demonstrated that these interferences are strongly dependent on the residence time of water (Gourdin, 2003; Batiot, 2002). A longer residence time indeed allows a strong reduction of this background and the amplitude of its variations. In these situations, naphtionate can be used without too much uncertainty in the interpretation.

Other organic contaminants like naphtalenesulfonates used as plasticizers for concrete (Menzel *et al.*, 2002) are also producing confusing peaks for naphtionate.

Petroleum products usually interfere only in a region of the spectra where no conventional tracer is used (i.e. at shorter wavelengths). Groner *et al.* (2001) measured an optimum of fluorescence for these products at EX/EM = 254/320 nm.

Protein (tryptophan)-like fluorescence is also typical around 270/340 nm and me caused by farm effluents (Baker, 2002). In wells situated in the vicinity of farms in the Néblon study (Gourdin, 2003), ammonium has also been proved to be correlated with an increase of water fluorescence around 320/405 nm.

### *3.2 Identification of tracer breakthrough in time series*

In analytical chemistry (Collective, 1980) the limit of the detection (LOD) of a substance is usually referred to as the lowest concentration of an analyte that the analytical process can detect. It is recommended to be at least 3 times the standard deviation of the blank ($3\sigma$). The real problem is however the availability of this blank. If a synthetic blank (i.e. pure water) is used, the LOD[5] can only reflect an instrumental limit which, in the case of spectrofluorometry, is usually far below the effective limit of detection that can be reached when considering also the variability of field background.

Looking at tracer tests, the problem is no more the representativity of an individual sample but that of a time serie of samples that should be separated from the background which is also varying with time. Smart and Karunaratne (2002) didn't missed this problem and they suggest either a premonitoring of sampling sites or the use of analog sites for corrections of background variations. However, they also emphasized that only the experience of the practioner may guarantee a good interpretration of the fluorescence data. These authors, as well as Baker (2003), studied natural variations of surface streams.

The results below are an attempt to give a better appreciation of the possible range of natural background variations in groundwater for the three mentioned tracers, thanks to the sustained acquisition of fluorescence data at optimal wavelengths for each (320/415 nm for naphtionate, 491/511 nm for uranine and 564/584 nm for sulforhodamine B).

Graphics in figures 4, 5 and 6 show a set of time series data measured for springs, galleries and wells in limestones. Fluorescence intensities are only relative signals that were acquired with the same instrumental setups.

It is clear from these figures that the intensities for each tracer can not be dealed with in a similar way. For sulforhodamine B, the standard deviation ranges from 0,1 to 0,48. For uranine, it ranges from 0,29 to 4,34. For naphtionate, it ranges from 4,51 to 133,53. As for the coefficient of variation, it ranges, for sulforhodamine B, from 5 to 31 %, for uranine, from 5 to 47 % and, for naphtionate, from 4 to 47 %. These of course can not be compared to measurements made with other instruments and other settings. It gives a good indication on the opportunity to choose a tracer instead

[5] This LOD is mainly linked to the sensitivity of the instrument (Photon Technology International, 1999) which is an evaluation of the instrumental uncertainty.

of another, according to the background, and suggest us to use a 3σ calculated on a blank serie as a "field LOD" more realistic than the instrumental LOD. In terms of equivalent concentrations of the tracers, this new LOD would give respectively from 0,016 to 0,076 ppb for sulforhodamine B, from 0,003 to 0,054 ppb for uranine, and from 0,11 to 3,32 ppb for naphtionate. Unfortunately some other kinds of errors can disturb this evaluation. For a same instrument, the reproductibility of the signal should also be considered, especially from a date of analysis to another. Also the conservation of samples can introduce a drift in the intensities. It is frequent to observe a drift in a serie, because of the varying age of samples when using automatic samplers.

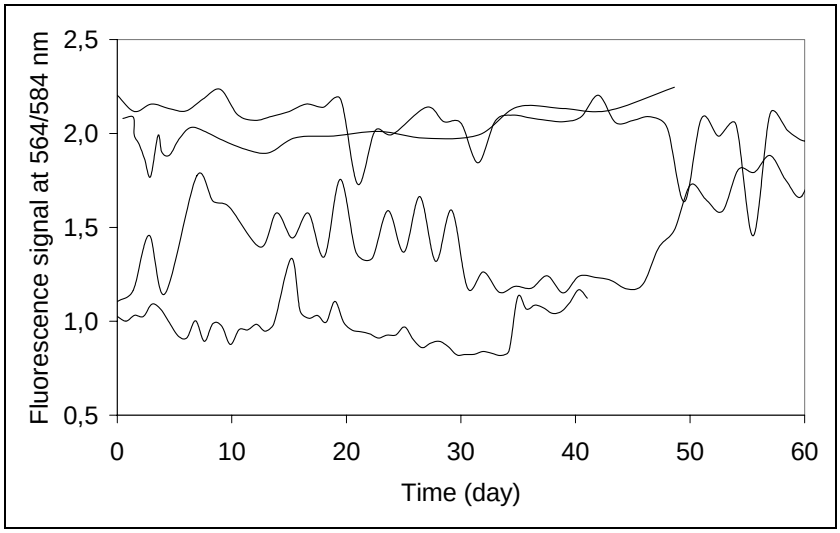


**Figure 4**: Examples of fluorescence time series for groundwater at the optimal wavelength of sulforhodamine B.

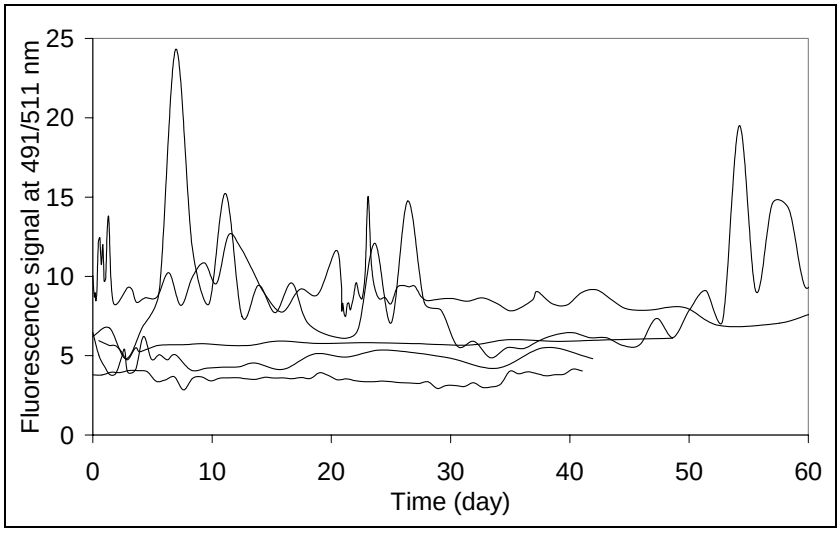


**Figure 5**: Examples of fluorescence time series for groundwater at the optimal wavelength of uranine.

The following example (figure 7) shows how the combined use of time series and spectra may be used to assess the detection of naphtionate. The time serie here presents a shape that can be confused with a breakthrough but the evolution of spectra shows clearly that these variations concern a broad part of the spectra and are probably due to changes of NOM concentration.

This example, which is frequent, is suggesting us that a simpler way for discriminating the tracer should be to measure the evolution of the intensities at a few specific wavelengths. An example is presented in figure 8. Here again, the variations at 320/415 nm make us think about a breakthrough. Anyway, the occurrence of the same variations at shorter wavelengths allow us to exclude the presence of the tracer.

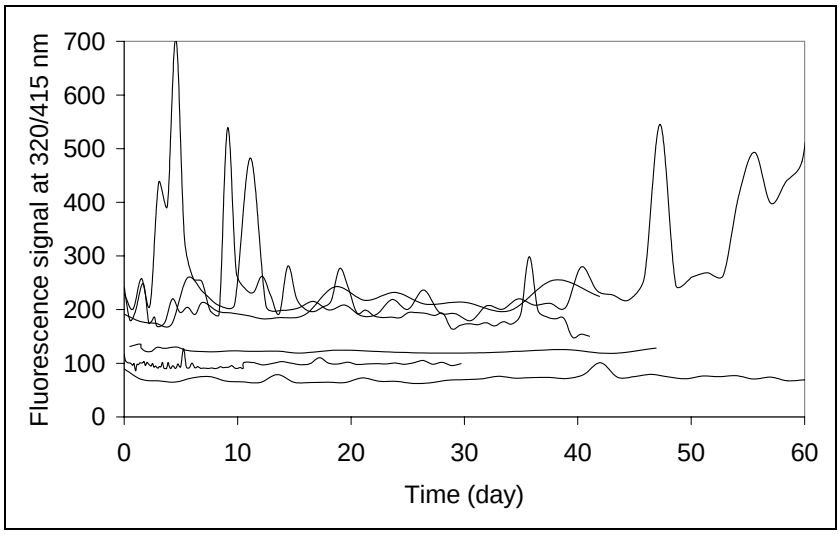


**Figure 6**: Examples of fluorescence time series for groundwater at the optimal wavelength of naphtionate.

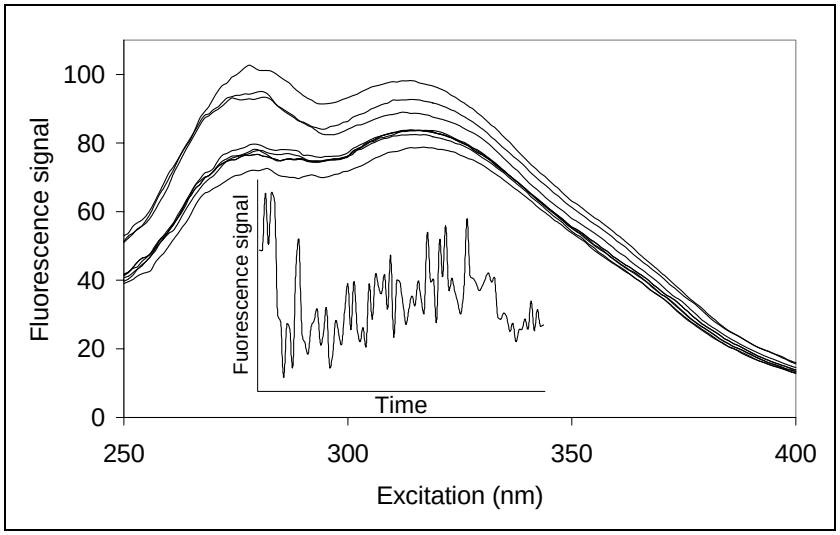


**Figure 7**: Example of the combined use of time serie and synchronous scanning spectra for searching naphtionate in groundwater.

In the case of uranine, such corrections are more difficult to apply because the occurrence of interfering peaks is more random. The example in figure 9 shows that the combined observation of the time serie at 491/511 nm and the synchronous spectra can bring a better certitude regarding the breakthrough of the tracer.

### *3.3. Monitoring in situ*

Previous results suggest that not only the variations of natural background, but principally the causes of these variations should be investigated in order to avoid any false-positive interpretation of the tracers. The recent improvement of field fluorometer techniques (Gouze *et al.*, 2000; Schnegg, 2002) is a good opportunity to make these investigations.

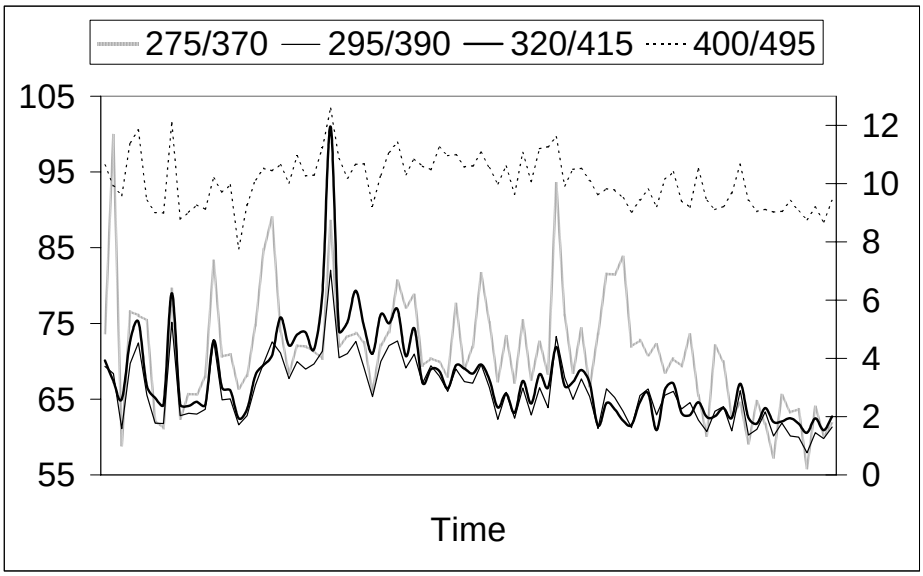


**Figure 8**: Example of the use of time series at different wavelengths for searching naphtionate in groundwater.

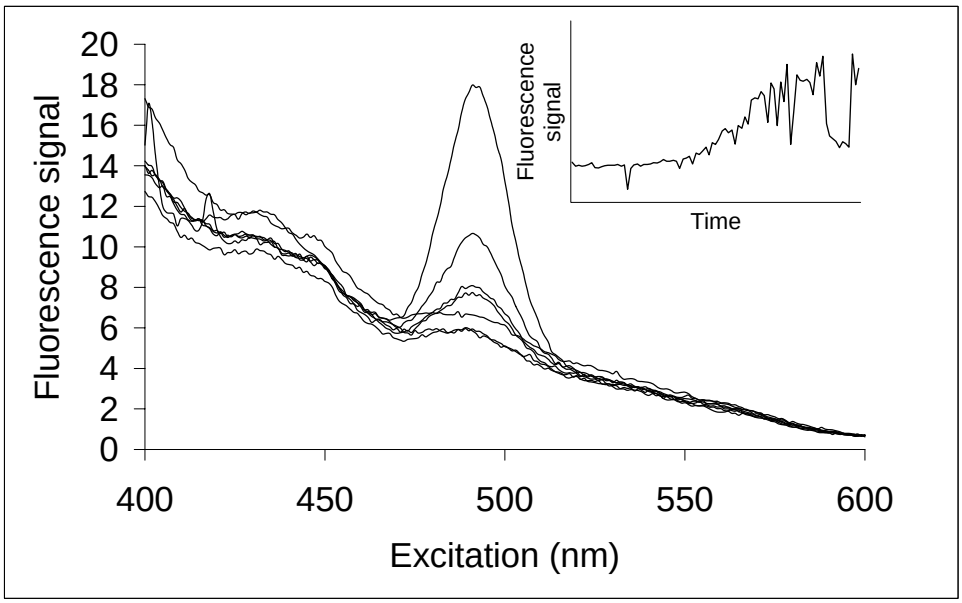


**Figure 9**: Example of the combined use of time serie and synchronous scanning spectra for the demonstration of uranine in groundwater.

The FL30 flow-through field fluorometer, for instance, operates in the three at stake regions of the fluorescence scale. An example taken from the Chalet karst spring is shown in figure 10. It appears that a great deal of the fluorescence in the three wavelength bands can be correlated with the discharge of the spring. The comparison with the 491/511 nm fluorescence measured in samples collected with the automatic sampler is also shown. The correspondance seems pretty good even if some spikes are not clearly in relation to the water level. Some may be linked to an increase of the conductivity[6], while the others not. This can be noticed for water samples, where this can also be due to sampling or conservation processes, as well as for continuous measurements, where they were probably missed by the water sampling.

[6] Not reported on this graph.

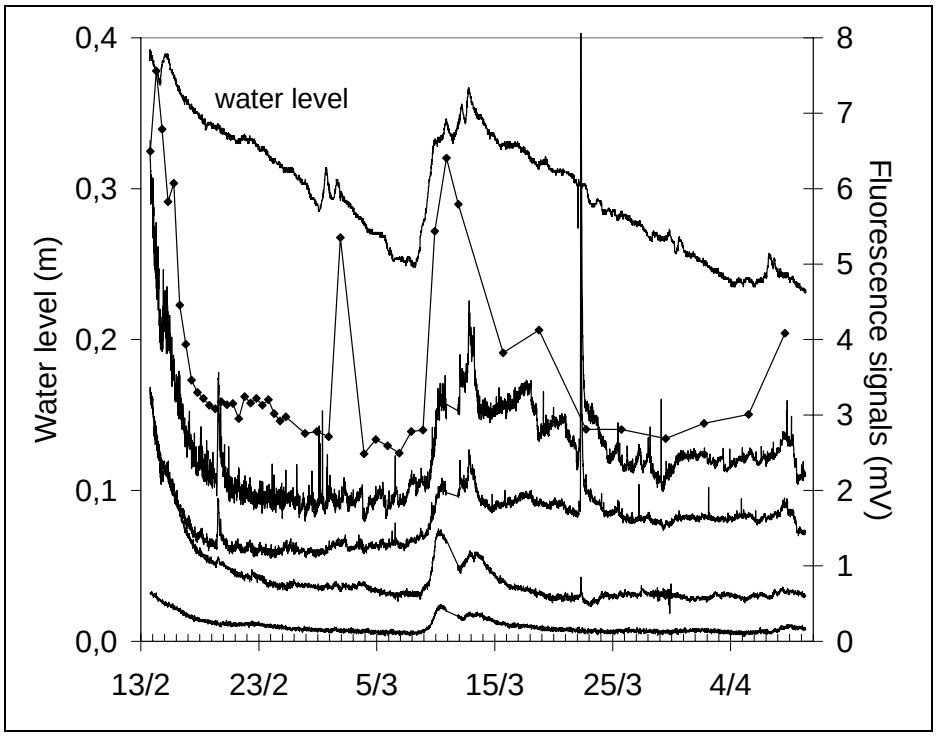


**Figure 10**: Example of monitoring in situ of a karst spring. From top to bottom, the lines are corresponding to: the water level, the fluorescence at 491/511 nm measured by spectrofluorimetry on water samples, the turbidity, the fluorescences measured with the flow-through fluorometer with LEDs at 525, 470 and 370 nm.

## 4. CONCLUSION

The use of fluorescent dyes requires background fluorescence to be carefully considered to avoid false-positive results in tracer tests. These precautions should be taken since the planning phase of the experiment until the final interpretation of the data. Premonitoring of the background is one of the recommended approaches, but uncertainties due to its extrapolation do not exempt from adequate sampling, analysis protocols and processing of the data, in order to reliably discriminate a breakthrough.

A combined approach using synchronous scan spectra and time series of fluorescences at different wavelengths is here proposed. A field limit of detection far more proper to the demonstration of the tracer breakthrough is also suggested.

Monitoring in situ, with field fluorometers, of the fluorescences before and during tracer tests seems to be a good prospect for future tracing.

Especially in karst aquifers, the monitoring of any parameter reflecting natural variations (i.e. discharge rate, conductivity) is also beneficial and should be undertaken systematically around the period of tracing.

All these measures should probably balance any suspicion on the fact that in many cases fluorescent tracers, even if used parsimoniously, remain more performant tracers than salt ones.

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