Promises and limitations in the use of sulfonates colourless tracers in hydrogeology

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ABSTRACT. Colourless fluorescent UV tracers are increasingly used in hydrogeological studies in drinking water catchments, in which classical dyes (uranine, sulforhodamines) can sometimes be of significant concern if unexpectedly exceeding the limit of visibility. Among these colourless tracers, optical brighteners and sulfonates (presently naphthionate and amino G acid) are widely used despite lower fluorescence yields, strong interferences with natural organic matter, as well as oxy- or photo-degradation. As a result, higher amounts of tracer are sometimes used, yielding higher concentrations in drinking water and giving rise to the question of their toxicity and the occurrence of their by-products in waterworks. In this paper, several years of practice and improvement of the detection's performance using combined laboratory spectrofluorometric and field fluorometric techniques are summarized and illustrated with several case studies in different aquifers. The developments of UV LEDs optical systems, as well as the increase of time resolution and controllability using telemetric dataloggers, are here considered as main catalysts of this knowledge.

KEYWORDS: groundwater tracing, fluorescence, fluorometer, naphthionate, amino G acid, toxicity, organic matter, telemetry

1. Introduction

The use of UV (ultra-violet) fluorescent tracers in hydrological applications was first suggested in the late 60's (Smart & Laidlaw, 1977). While optical brighteners (stilbenes) were the first type of UV tracers used in groundwater applications, they turned out to be of poor intrinsic quality due to a relatively high detection limit and a tendency to sorb onto soil grains. As an example, Crabtree (1971) reports an application involving stilbene tracers in a karst aquifer. On the contrary, sulfonate UV fluorescent tracers have shown a much higher suitability to groundwater studies, or even to geothermal reservoir applications (Rose et al., 2001). This study focuses on two specific sulfonate colourless tracers: sodium naphtionate (NAP) and amino G acid (AGA). Leibundgut & Wernli (1986) first demonstrated the suitability of naphthionate as an hydrological tracer. Since then, NAP has been widely used, mainly in karst (Käss, 1998). Amino G acid is mentioned in early studies but was afterwards abandoned for a long time (Käss, 1998).

UV tracers have always been appreciated for their complementarity to other dyes (uranine, sulforhodamines…) in multi-tracing applications. In addition, in situations where the coloration of water must be strictly avoided, colourless UV tracers are also typically preferred to other visible fluorescent tracers. The simultaneous use of several UV tracers may even be desired in some cases. The limit of visibility of naphthionate under daylight in a 1 l volumetric flask is about 1 ppm. In the same conditions, that of amino G acid is slightly lower, around 100 ppb, while for uranine the relevant limit is 25 ppb (Käss, 1998). However, the visibility of such fluorescent tracers can be lowered by more than one order of magnitude in surface streams under daylight and their artificial look may attract the attention of a casual observer.

The objective of the present study is to assess the detectability and the limits of quantification of naphthionate and amino G acid in groundwater studies, especially when used simultaneously. In a previous study, Schnegg & Meus (2009) already successfully distinguished naphthionate and amino G acid restitutions in a short distance tracer test in a river. In this paper, three successful applications of NAP and AGA in groundwater tracer tests are reported. The suitability of sulfonate tracers in hydrogeology is also weighted against potential limitations, such as interferences with natural organic matter (making necessary the injection of larger amounts of tracer) or the limited knowledge on the toxicological risks associated with these tracers.

2. Methods

In this study, two independent analytical methods are systematically used. On one hand, water samples (laboratory standards or samples from field tests) are analyzed in the laboratory using a HITACHI F-2500 fluorescence spectrophotometer. These analyses are performed either at fixed peak wavelengths (photometric mode) or through scanning of EEM (Excitation Emission Matrix). On the other hand, field measurements are obtained using GGUN-FL30 fluorometers equipped with UV optical systems (LEDs emitting at 315 and 365 nm) calibrated using laboratory standards. The fluorometers are coupled to Tétraèdre TRMC-5 dataloggers equipped with GPRS telemetry for data collection, storage, and transmission. The system has proved to be very reliable, since data are available in near-real-time, allowing one to quickly identify and address anomalies. The conversion between raw data (in mV) and concentration values (in ppb) is achieved through linear or quadratic calibration curves. The fluorometers also come with a built-in software (FLUO software, see Schnegg, 2002 and Schnegg & Thueler, 2012) which allows the correction of the mutual interferences of each tracer using a specific resolution algorithm.

This algorithm uses a linear calibration of each of the 2 or 3 tracers (coefficients C_j^i of two or three different sets i of lamps, filters and photodiodes for a fixed concentration of 100 ppb of each tracer j) and it solves a set of 2 or 3 equations (each corresponding to the signal produced on each optical detector):

$$C_1^i \alpha + C_2^i \beta + C_3^i \gamma = V_i, \quad i=1,2,3$$ where V_i is the signal (mV) measured on each optical detector

The stability of the solution (concentrations α, β and γ) depends on the optical capacity of separation of the tracers.

Schnegg & Thueler (2012) have compared the capacity of separation of naphthionate and amino G acid with a fluorometer to that of a laboratory fluorescence spectrometer using two distinct separation methods and they conclude that the separation of the fluorometer is even better. However, they draw the attention on the potential adverse effect of turbidity on this capacity of separation.

The main chemical characteristics of sodium naphtionate and amino G acid are shown in Fig. 1. Fluorescence spectra (EEM) are also compared and the respective positions of the fluorescence peaks are shown in Fig. 2. Both tracers can thus be easily identified and quantified when used as single tracers. Naphthionate has two main peaks, the peak at 320/415 nm being usually reported in the literature as the optimal one for analyses. The signal measured with the fluorometer using the LED at 315 nm integrates the fluorescence around this optimum. Amino G acid has three main peaks with slightly longer emission wavelengths than naphthionate. The optimum at 359/450 nm usually reported in the literature would correspond to the observed 350/450 nm peak. However, both other peaks show a higher fluorescence yield. For that reason, the peak at 245/445 nm was preferred for quantifying
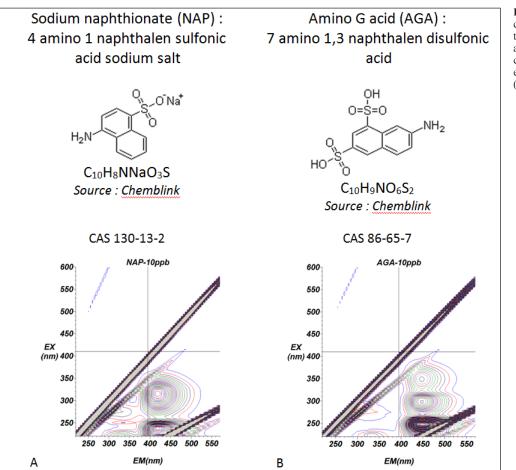
Figure 1. Chemical characteristics of the sulfonate tracers: naphthionate (A) and amino G acid (B) with corresponding fluorescence excitation emission matrices (EEM).

that tracer with the spectrophotometer. On the fluorometer, the most sensitive channel for AGA detection corresponds to the LED at 365 nm.

3. Results

3.1. Mixing test in laboratory

A first series of tests are conducted in the laboratory to assess the capability of the field fluorometer to properly distinguish between both tracers using the LEDs at 315 nm (for NAP) and 365 nm (for AGA). Fig. 3 shows that the tracers, when mixed in varying proportions, can be correctly discriminated using the correction process implemented in the built-in software FLUO. It is likely that the quality of this separation in the field will be affected by factors like temperature, pH or content in other organic fluorescent substances.
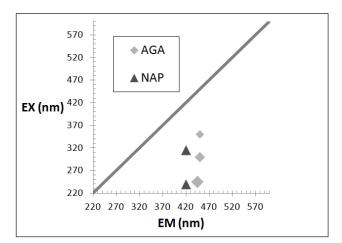
3.2. Field tests

In this section, three different field-scale tracer test applications requiring the simultaneous use of naphthionate and amino G acid for different purposes are reported.

The first case study (Fig. 4) deals with a karst limestone aquifer in which the impacts of a near-by quarry on a drinking water spring had to be assessed. Successive injections of NAP and AGA were made over a period of two years in several boreholes and tracers concentrations were monitored at the spring. The fluorometer was only equipped with a 315 nm optical system, so that a separation between NAP and AGA only based on fluorometer measurements was not possible. However, each breaking slope is indicating the different breakthroughs and laboratory analyses at fixed wavelength allowed a clear separation of NAP and AGA breakthrough curves. One can also see here that the AGA fluorescence signal measured in the laboratory using the spectrophotometer at fixed EX/EM wavelengths is considerably
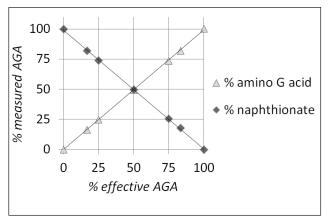

Figure 2. Respective positions of NAP and AGA fluorescence peaks. EX: excitation wavelength. EM: emission wavelength (from EEM data).

Figure 3. Identification of NAP and AGA mixed in different proportions in laboratory solutions, using the fluorometer equipped with LEDs at 315 nm (NAP) and 365 nm (AGA) and with a built-in resolution algorithm.
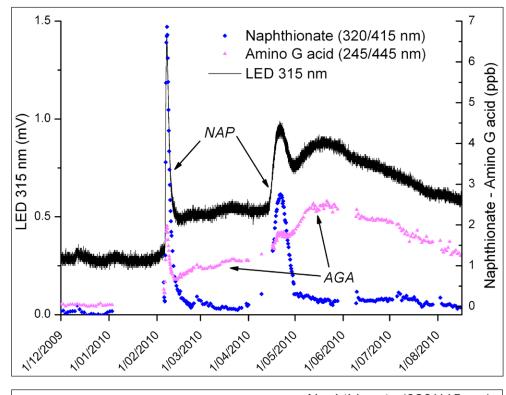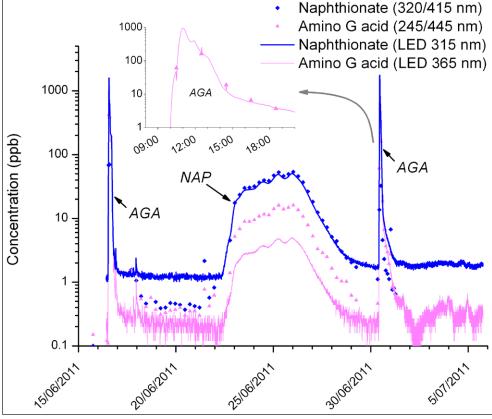
Figure 4. Breakthrough curves of NAP and AGA in a karst aquifer as inferred from the field fluorometer signal (LED 315 nm), compared to laboratory spectrofluorometric data at optimal EX/EM wavelengths.
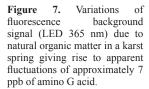

Figure 5. Breakthrough curves (logarithmic scale) of NAP and AGA in a sandy aquifer as inferred from field fluorometer signals (LEDs 315 and 365 nm) combined with laboratory spectrofluorometric data at optimal EX/EM wavelengths.
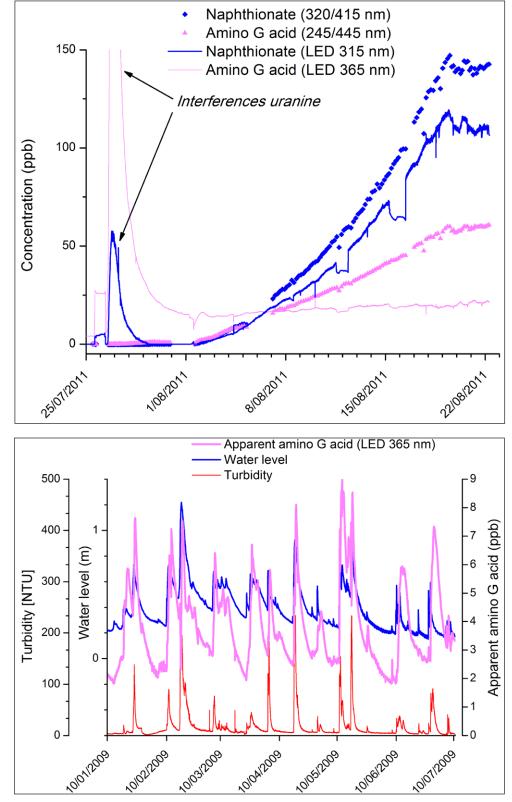
affected by the presence of NAP, while the NAP signal remains unaffected by the other tracer.

The second case study (Fig. 5) deals with the delineation of protection zones in a sandy aquifer. Injections were conducted in boreholes and the tracers were recovered in a pumping well. A single injection of NAP was done, while AGA was injected both at the beginning and at the end of the experimental phase. In this case, the breakthrough curves never overlapped, so that no separation nor correction was required, and an independent quantification of each tracer using single calibrations was sufficient. As a result, when NAP is detected, there is a good correspondence between concentration data obtained from both analytical methods. One can also see that, during NAP recovery,

the AGA fluorometer LED reacted to a much lesser extent than the signal obtained from the laboratory spectrofluorometer analysis at optimal AGA EX/EM wavelengths. The built-in correction algorithm of the software FLUO was not applied in this case. This let us suppose a stronger interference of NAP on AGA signal when using the fixed wavelengths of the spectrofluorometer.

The third case study (Fig. 6) deals with a fissured aquifer contaminated with hydrocarbons, in which tracer tests were conducted in order to design the remediation system. As in the previous case, injections were made in boreholes and recovery in a pumping well with water treatment. Full tracer recovery was not achieved as the maximum technically allowed time for pumping had been exceeded. Uranine was also injected, and its

Figure 6. Breakthrough curves of NAP and AGA in a contaminated fractured aquifer as inferred from field fluorometer signals (LEDs 315 and 365 nm) compared with laboratory spectrofluorometric data at optimal EX/EM wavelengths. The separation of fluorometer signals is made with the FLUO software. A breakthrough of uranine causes some interference at the beginning of the test. *Insert*: EEM spectrum of a sample containing both NAP and AGA.

Figure 7. Variations of fluorescence background signal (LED 365 nm) due to natural organic matter in a karst spring giving rise to apparent fluctuations of approximately 7 ppb of amino G acid.

breakthrough created strong interferences on UV signals recorded during the first week of the test. The analysis of later UV signals highlights the simultaneous breakthrough of both AGA and NAP. The tracers were mixed to such extent in the pumping well that one could not identify the respective peaks of the tracers in the fluorescence spectra of the water samples. The comparison of concentration values obtained in the laboratory and those obtained after correction by the fluorometer is quite useful. One can see that there is a reasonable accordance between both NAP concentration curves. On the contrary, AGA concentration data obtained from the field fluorometer are far lower than those obtained in the laboratory. The higher interference created by the presence of NAP on the AGA signal, probably due to respective

spectral characteristics, is not taken into account when calculating the concentrations using spectrophotometric data, while that interference has been corrected by the software FLUO. In this special case, the use of corrected data from the fluorometer gives better results than the more resolved but uncorrected data from the laboratory.

4. Discussion

Because they are colourless in normal conditions, sulfonates UV tracers appear to be suitable for tracing applications in surface water or involving drinking water, where coloration can be a nuisance difficult to manage for owners. Laboratory and field

	Smart (1984)	Field et al. (1995)	Behrens et al. (2001)	Brüsch-weiler (2007)	Gombert et al. (2010)
		Human risk	Ecological risk		
Naphthionate			L	L	L-M
Amino G acid*	L-M	M	L-M		

*Sometimes confusion can be found in the literature between amino G acid and amidorhodamine G, a more commonly used red xanthene dye

Table 1. Summary of literature on toxicological risks (human, ecological, or undifferentiated) of naphthionate and amino G acid. L: low risk, M: moderate risk, H: high risk (no case reported with this ranking nor any recommendation for avoiding these products).

tests have demonstrated that NAP and AGA can be efficiently distinguished using field fluorometers equipped with two distinct optical systems (LEDs at 315 and 365 nm, respectively), and applying a correction for mutual interferences. In cases where tracer breakthroughs occur simultaneously, spectrofluorometric analyses (EEM spectra) advantageously complement the interpretation of fixed-wavelength data by giving an improved resolution in the spectral domain.

Current limitations about the practical use of these tracers are linked to potential interferences with natural organic matter and a limited knowledge on potential toxicological and ecotoxicological impacts of those tracers. Complex interferences with fluorescent natural organic matter are quite common and are often a major cause of error when no care is taken about the issue (Jozja et al., 2009). The natural fluorescence background associated to organic matter has to be qualified and quantified by taking into account the hydrogeological context and its dynamics, especially in karst systems. As an example, Fig. 7 shows background variations due to natural organic matter in a karst spring, with its equivalent in terms of concentration of AGA, which is around 7 ppb. A clear correlation can be made between the level of the spring and the level of the background fluorescence. The study of the natural fluorescence of water can be considered as in a good progress (Quiers et al., 2011) and analytical methods are also now being perfected. Schnegg & Thueler (2012) have tested the separation of the fluorescence due to natural organic matter from the fluorescence of uranine extracted from active charcoal detectors and they could correctly identify (the charcoal method does not allow a direct quantification) the presence of uranine.

A straightforward solution to the problem of variable background fluorescence consists in increasing the amounts of injected tracers. In that case, the question of the toxicity of the tracer arises. This question seems more critical, as toxicological studies are very limited in number, they are somewhat contradictory, and they are not necessarily suitable for evaluating the risks in situations faced by hydrogeologists. It is also quite common that the opinions on a particular tracer changes with time or differ among authors, as it has been the case for rhodamines and fluorescein in the past in USA and Europe. Some countries have set restrictive lists of tracers which can be used in drinking waters but most of the time the use of tracers is not regulated or requires only an official permission based upon common sense. UV tracers thus remain an option that abstractors may prefer. Table 1 gives some indications about sulfonates toxicity and associated risks. Obviously, the emphasis has only been recently placed on naphtionate. Carre et al. (2007) also conducted such a review of the literature and they concluded, like we do now, that the risks are not well defined. Gombert & Carre (2011) identified, using HPLC, the production of an unknown substance after chlorination of naphthionate solutions in laboratory. Those degraded solutions also showed a significant effect according to ecotoxicological tests on algae. Hence, while there is no reason to forbid the use of any of these tracers, they should all be used with precaution by carefully weighting the need for increased concentrations against potential toxicological or ecotoxicological impacts.

This question can also be addressed by taking advantage of the detection in-situ of UV tracers thanks to the field fluorometer and setting alarms with thresholds which will alert the staff by SMS or will automatically interrupt the distribution. The adjustment of these thresholds can be based on a statistical background and they are usually far below the limits of concern which can be reasonably fixed for drinking water. We have recently, and successfully, experimented this methodology, setting thresholds for the detection of AGA around 1 ppb and a limit of action at 50 ppb.

The experience revealed that further studies on the reliability of the active charcoal method for detecting these tracers would also be helpful for practitioners.

5. Conclusion

Sulfonates are good candidate tracers in hydrology either for complementing other dyes or when a risk of coloration has to be avoided. Naphthionate, a classical tracer, and amino G acid have been evaluated with regard to their detection and separation using combined fluorometric techniques in the field and in the laboratory. These tracers can be most of the time identified in excitation-emission matrix spectra excepted when the content of amino G acid is very low compared to naphthionate. In this latter case, corrected fluorescence data issued from the field fluorometer using 316 nm and 365 nm excitation LEDs give more relevant results. However the simultaneous use of both techniques is advised. These improvements in the detection of sulfonates, as well as systematic studies of fluorescence background and early-warning alarms allowing interruption of the distribution of drinking water, can help in reducing the risks that were previously inherent to the use of excessive amounts of such colourless tracers.

6. Acknowledgements

7. References

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