An inexpensive flow-through field fluorometer

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Abstract

In order to simplify sampling dye tracers in water streams without having to invest money in expensive systems, we developed a highly sensitive flow-through field fluorometer. This apparatus was tested successfully in the field with fluorescein and sulforhodamine. A submersible probe is connected to a digital data logger and the data is written to a PCMCIA memory card allowing 2 weeks of unattended recording at 1 sample every 4 minutes. A sensitivity as low as 0.05 ppb has been achieved. Simultaneous concentration measurements of 2 tracers is possible, at the expense of reduced sensitivity, however.

Résumé

Dans le but de faciliter et d'automatiser la mesure *in situ* de la concentration de divers traceurs fluorescents, nous avons développé un fluorimètre de terrain dont la sensibilité avoisine celle d'un appareil de laboratoire. Ce fluorimètre a été testé avec succès lors de traçages à l'uranine et à la sulforhodamine. La sonde submersible est reliée à un boîtier d'acquisition et les données sont écrites sur une carte PCMCIA permettant deux semaines d'enregistrement à raison d'une mesure toutes les 4 minutes. Le niveau de sensibilité est de 0.05 ppb. La séparation de 2 traceurs simultanés est possible, moyennant une diminution de la sensibilité.

1. Introduction

The design of a new flow-through field fluorometer, able to be put in a stream or a spring to measure small dye concentrations was initiated at the request of researchers at our university. Similar equipment is already commercially available but at a cost prohibitive to academic grants. We designed an automatic, inexpensive device, with the idea of replacing a mechanical sampling system. The advantage of our system is that it replaces the sampler in most situations, provided there is no need to keep the water samples for further analyses. Although it was initially designed for uranine (fluorescein) dye tracer, we also tested it with sulforhodamine, and with a mixture of both.

2. Description of the fluorometer

The apparatus is made up of two parts, a data acquisition box and a waterproof, metallic cylinder which contains the optical system. A 15 metre cable, with waterproof connectors links the 2 parts. Set-up of the fluorometer is possible in most of the conditions found at the water's edge (Photo 1).

The fluorometer

The optical system used for the fluorescence excitation and detection is a standard one: The light emitted by a lamp is filtered to select only the wavelenghts corresponding to the excitation band of the dye. The light is then focused on a transparent tube through the middle of which the water flows freely (Fig. 1). The natural waterstream is sufficient to insure an almost instantaneous movement of the fluid across the optical system, with whatever orientation the fluorometer has relative to the stream. The tube is bent at both ends to prevent daylight from entering.

The fluorescence from the dye is collected at a lens on the photodetector. Excitation light residuals, which always occur in spite of different excitation and emission axes, are removed by another filter. The photodetector current is amplified within the sensor box. The output signal is fed to the datalogger through the cable. Tests done with calibrated concentrations have a linearity and reproducibility that are close to 1%.

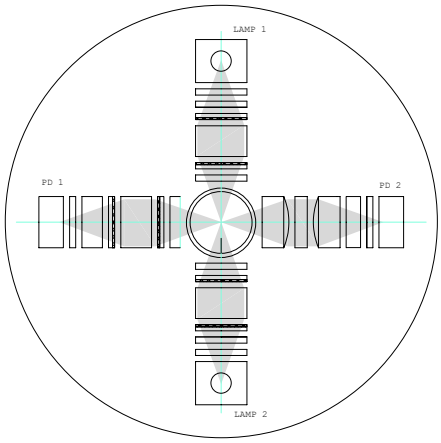

Fig. 1 : Fluorometer optical system with 2 perpendicular excitation and detection axes. Water flows perpendicularly in the central tube.

Practical experience indicates that it is often necessary to measure the water turbidity, since it can considerably alter the measurement in the following ways:

1) by reducing the excitation light and fluorescence through absorption by suspended particles.

2) scattering of excitation light toward the detector.

To measure the turbidity, we mounted a second detection axis in which the emission filter was replaced by an excitation filter. In clean water, even in the presence of dye, the signal of this axis is very small. It corresponds to natural scattering of water. The presence of suspended particles scatters light in all directions, giving rise to a signal proportional to the turbidity.

In water tracing experiments, it is often interesting to use two dyes simultaneously. In order to separate their

fluorescence signals, we installed a second excitation axis, identical to the first, but with a different filter. The new filter is designed to favor the excitation of the second dye at the expense of the first. Thus, 4 independent values can be sampled by combining the two light sources and the two photodetectors.

Data acquisition

The datalogger box contains the acquisition electronics and a battery. Every 4 minutes, a 2-second measurement cycle is initiated. The lamps are successively switched on and off. Six values are collected: the 4 discussed above, and the values at zero excitation (this measure gives the photodetector baseline). All the information is written to a PCMCIA memory card. This data medium can be easily and safely read in a portable computer. Battery and memory card capacities allow for 2 weeks of unattended data recording.

3. Performance

The detection threshold of the fluorometer (used in the real situation of a quiet stream) is 5 x 10^{-11} g/ml for uranine. Sensitivity is 200 mV for a concentration of 10^{-7} g/ml. In clean water, the residual noise level is 0.1 mV. The analogue-digital conversion dynamics is 16 bits.

Several tracer tests have been done during which the data from the fluorometer was compared to the samples taken and measured subsequently in the laboratory. The results of two of them are shown in Figs. 2a and 2b. The first difference concerns time resolution. The high sampling rate of the fluorometer allows detection of faster variations in dye concentration. Second, the tracer arrival time and the position of the maximum concentration reach an accuracy of as short as 4 minutes.

A summary of the properties of the sampler and the fluorometer is given in the Table 1.

Advantages of the field fluorometer compared to samples measured subsequently in the laboratory

The autonomy of operation, the readings every 4 minutes and not having to visit the site are the principal advantages of the field fluorometer. In the case of the mechanical sampler, however, the bottles filled with the water samples must typically be handled at the site at the end of each series. This operation is always error prone and there is a risk of contamination even if the greatest care is taken. Then, the samples must be analysed by bringing them about to a laboratory, which costs more and has inevitable delay. Moreover, the storage of the samples prior to analysis can lead to variations in the dye concentration. Also, in the case of tracer tests using several dyes, chemical cross-reaction can occur. It is also been documented that sulforhodamine G is adsorbed by clay in an hour (MDAGHRI ALAOUI, 1992).

Two advantages of the fluorometer relate to mechanical aspects: unlike the water sampler, the fluorometer has no moving parts, and therefore no wear. Also, because it is always completely submerged, freezing cannot prevent water from flowing through the system window.

Measuring fluorescence is done on the flowing water. The flow may have particles particularly during a fast rise in water level. Water turbidity then becomes an influencing component of the dye concentration measurement. This is never the case with laboratory analyses, where care can be taken to allow the water to settle before analysis. Up to some threshold, the turbidity effect can be removed from the signal, since one of the photodetectors is permanently measuring it. The sensitivity threshold is directly related to water clarity. Therefore, laboratory measurement will detect a smaller dye concentration compared to *in situ* field fluorometer measurements.

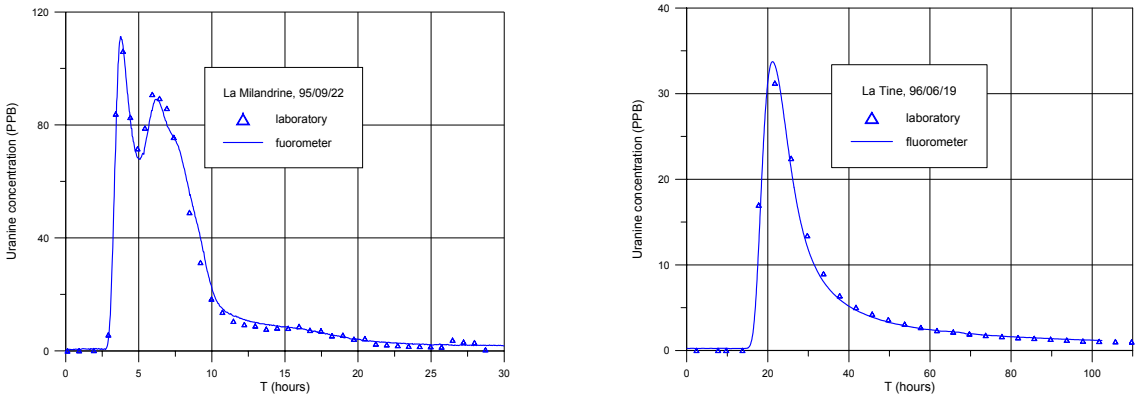

Fig. 2 a & b: Comparison of the results from the fluorometer (line) and the sampler (triangles) at 2 sites.

	Sampler	Fluorometer
Time resolution	bottle filling time	2 seconds
Field duration	number of bottles x sampling period	2 weeks
Work expense	large: many visits necessary	low: set-up and removal
Subsequent handling	sample analysis in the laboratory	none
Result availability	up to several days	immediate
Error by contamination	possible	impossible

Errors by tracer degradation	possible	impossible
Moving parts (wear)	yes	none
Freezing sensitivity	yes	no

Turbidity sensitivity	none if samples filtered	yes
Saturation threshold	none	1.25 x 10^{-6} g/ml
Usable tracers	all, incl. biological	dyes
Number of simultaneous tracers	>2	2
Detection threshold (uranine)	2 x 10^{-11} g/ml	5 x 10^{-11} g/ml

Table 1 : Comparison of a water sampler and field fluorometer performance. Disadvantages are shaded.

Disadvantages

The maximum detection level of the fluorometer is determined by the amplifier gain. In a tracer test, this gain is kept fixed. However, it can be decreased before the test, if it is desirable to measure larger concentrations.

Using a water sampler allows analysis for all tracers, including the biological ones (JEANNIN *et al.*, 1995). Furthermore, the separation of simultaneousy injected tracers (dyes and others) is a straightforward task using samplers. The fluorometer works well with one dye tracer at a time but also can separate uranine and sulforhodamine values.

Simultaneous use of 2 tracers

To be able to separate 2 tracers, the fluorometer must be calibrated. The coefficients c_{11}, c_{12} correspond to a signal under excitation by source 1 of the uranine and sulforhodamine at a concentration of 10^{-7} g/ml, whereas c_{21}, c_{22} corresponds to source 2. The expressions

$$[u] = \frac{c_{22}x_1 - c_{12}x_2}{c_{11}c_{22} - c_{12}c_{21}} \qquad [s] = \frac{c_{11}x_2 - c_{21}x_1}{c_{11}c_{22} - c_{12}c_{21}}.$$

give the concentration of uranine (u) and sulforhodamine (s). The values x_1, x_2 are the voltages measured on the photodetectors.

Note that careful choice of excitation and detection filters is important to ensure a good separation of the tracers. Combinations that result in too small values of the denominator must be avoided. However, the same filter set can be used for various combinations of dye tracers, as long as the denominator rule is observed. Laboratory tests show that it is possible to separate 2 tracers with good accuracy, provided their individual response is known (Fig. 3).

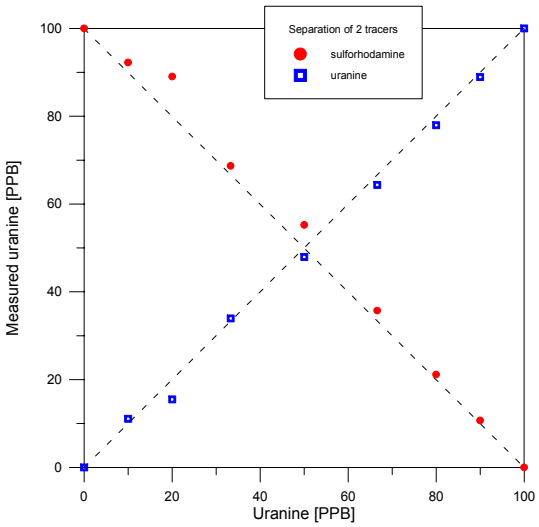

Fig. 3: Separation of 2 tracers. Determination of their concentration in the mixture. The real uranine concentration is on the horizontal axis (inverted scale for sulforhodamine) and measured concentration on the vertical axis.

Conclusion

The flow-through field fluorometer represents an economical alternative to commercial fluorometers and to mechanical sampling systems. Compared to the latter, it has the advantage of dramatically reduced surveillance and maintenance (one set-up and one removal). Its short time resolution should allow an new approach to hydrogeological issues that where neglected with the use of samplers.

The data availability is immediate. If needed, the content of the memory card can be read into a laptop computer at any moment, and the tracer test still carried on. Laboratory delays and expenses are not needed. Simultaneous use of several tracers is current practice. To develop further this instrumentation, an effort should still be made to optimise the excitation/detection filter sets. In addition, the advent of laser diodes in the green part of the spectrum will allow new sources for the selective excitation of uranine.

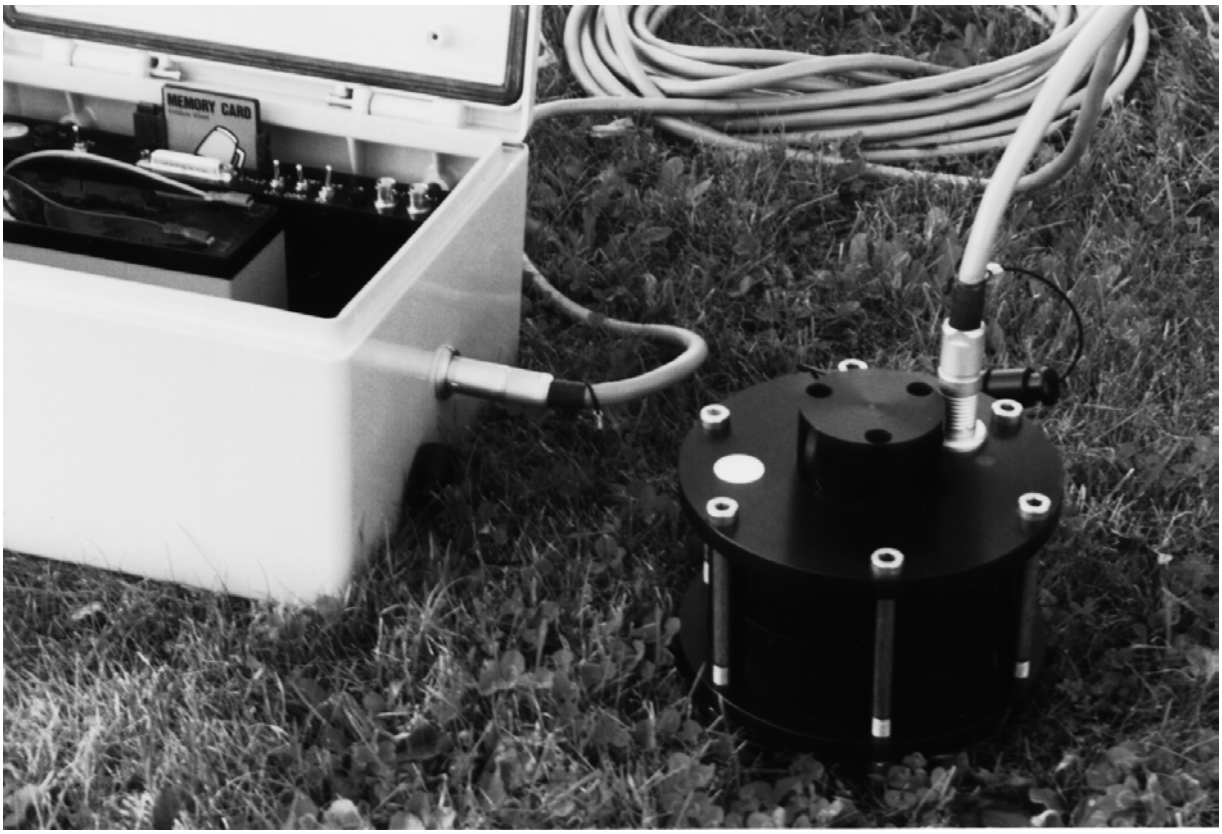

Photo 1 : Fluorometer with its data acquisition box.

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