Optimization of streamflow measurements by the dilution of the food colorant E110

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Abstract This study presents the measurement of streamflows by constant dilution of a yellow-orange food colorant (E110). Field measurements are carried out in the Doria River, a mountain torrent in the Savoie pre-Alps, France. A limnimetric station installed 12 years ago is periodically calibrated by mechanical and chemical measurements. Moreover, simultaneous mechanical and chemical methods allow the statistical validation of the proposed technique. The main advantages of this method are the lack of toxicity, the absence of visible river colouring, comparable to that of aquatic organic matter, and the low detection limit. This method allows high flow measurement under suitable conditions.

Key words streamflow measurement; rating curve; dilution; food colorant; toxicity; concentration determination; Doria River; French Alps

Optimisation de la mesure de débit par dilution du colorant alimentaire E110

Résumé Cette étude présente la mesure de débits par jaugeage par dilution constante d'un colorant alimentaire jaune-orange (E110). Les mesures de terrain sont réalisées dans la Rivière Doria, un torrent montagnard des Préalpes de Savoie. Une station limnimétrique installée il y a 12 ans est régulièrement étalonnée à l'aide de jaugeages mécaniques et chimiques. La mise en œuvre simultanée de méthodes mécanique et chimique permet de plus la validation statistique de la technique proposée. Les principaux avantages de cette méthode sont l'absence de toxicité, l'absence de coloration visible de la rivière au-delà de celle de la matière organique aquatique, et une limite de détection basse. Cette méthode permet des mesures de forts débits dans de bonnes conditions.

Mots clefs mesure de débit; courbe d'étalonnage; dilution; colorant alimentaire; toxicité; dosage; Rivière Doria; Alpes Françaises

INTRODUCTION

The measurement of river discharge using chemical tracers has been in use for a number of years (André *et al*., 1973a; Barnes & Kilpatrick, 1973; Herschy, 1995; Käss & Behrens, 1998), especially in highly turbulent conditions, such as mountain streams, where classical propeller-type current meters are difficult to use.

Still, lack of practice in the use of chemical methods negatively affects the precision of the results and this has perhaps led to the scarcity of its application (Oumedjbeur *et al*., 1993). In France only the electricity company EDF is currently experienced in the method and does some 50 flow measurements a year, in spite of its usefulness also for industrial systems. Precision can be improved by careful laboratory analysis. The analysis of the sources of error in chemical tracer methods indicates that uncertainties can, to a large extent, be caused by the laboratory techniques (ISO, 1990). Masson *et al*. (1987) pointed out that up to 60% of the uncertainty can be attributed to the colorimetric analysis.

Finally, the choice of the tracer has been made more difficult since potassium dichromate, in spite of its numerous technical advantages (Roche, 1963), can no longer be used because of its mutagenic and carcinogenic properties, in addition to its caustic effect on human tissue (INRS, 1987). Since 1877, with the first experiment in dilution gauging based on uranine, a number of fluorescent tracers have been studied and developed (Hadi *et al*., 1997; Käss & Behrens, 1998):

Rhodamine WT, Rhodmaine 6G, Sulpho-Rhodamine Bextra, Erythrosine, Pyranine, etc. However, up to a point, depending on the specific tracer, they all have the disadvantage of photochemical decay as well as a tendency to adsorb on suspended solids or surfaces at very low concentration Herschy, 1995; Hadi *et al*., 1997; Käss & Behrens, 1998; Hudson, 2004). The characteristics of some new fluorescent tracers (such as: Naphthionate, Succinylfluorescein disodium, Carboxy-fluorescein trisodium) with regard to adsorption are better (Leibundgut & Wernli, 1986; Hadi *et al*., 1997; Käss & Behrens, 1998), but at many sites it may be difficult to obtain the authorisation for river colouring. In addition, riverside residents may be rightfully worried. Furthermore, all of these tracers involve potential chemical environmental hazards (Hudson, 2004). Rhodamine B, for instance, has carcinogenic properties (Käss & Behrens, 1998).

Previous studies have already explored the possibility of replacing potassium dichromate, widely used in France, and the fluorescent agents by food colorants (André *et al*., 1973b; Lion *&* Galea, 1975, 1976; Oberlin & Lion, 1978; Audinet, 1995), whose environmental impact is negligible. Indeed, synthetic food colorants are considered, almost by definition, as having low toxicity for humans (Gaunt *et al*., 1974). Direct dosage, without the need for complex sample manipulations (extraction techniques, *a posteriori* chemical reactions), simplifies the measurement of colorant concentration. Lion & Galea (1976) compared three food colorant tracers: Tartrazine (E102), Sunset Yellow FCF (E110 in the European Union) and Cochineal Red A (E124). All were applied to small to medium flows (between 36.2 and 7200 L s^{-1}). The authors found less than 6% difference between the chemical tracer method and the classical mechanical flow measurement.

The present study applies the chemical tracer dilution method to the streamflow from a karstic spring (exsurgence) using Sunset Yellow FCF. The spectral absorbance analysis of the colorant was optimized and a statistical analysis of previous flow measurement results was performed. The spectrofluorimetric characteristics of E110 were also studied in order to enhance the application range of this molecular probe. Field trials were performed on the Doria, a mountain torrent in the pre-Alps Bauges massif, France, where a hydrometric station has been monitored for 12 years by the Centre d'Etudes Eco-Géographiques (CEREG) of Strasbourg University (Ducca, 1993; Najib, 2000).

THE FOOD COLORANT: DOSAGE TITRATION AND LABORATORY VALIDATION

Dosage titration

The food colorant Sunset Yellow FCF is a synthetic molecule without natural equivalent, used in the food industry. Daily acceptable human consumption is 2.5 mg kg^{-1} body weight. The LC50 in rats (Lethal Concentration, the concentration that kills 50% of the animals tested) is 10 g kg^{-1} by oral ingestion (Merck Index, 1996). At the concentration level used in flow measurement (at most 5.0 mg kg^{-1}) it is therefore highly unlikely that the food colorant poses any threat to aquatic life forms, whether plant or animal (Gaunt *et al*., 1974). The azo colorant Sunset Yellow FCF is easily soluble in water (up to 120 g L^{-1}) and its absorbance spectrum is stable between pH 4.5 and 9.5. The water of the Doria River is well within this range. If required, the addition of a surfactant or ethanol can increase the solubility.

The chromophores of the molecule allow direct UV-visible spectrophotometric dosage titration. The absorption spectrum of Sunset Yellow FCF dissolved in ultra-high purity 18.2 MΩ-cm water (Maxima Elga equipment) shows four absorption bands with maxima at wavelengths of 237, 316, 400 and 483 nm (Fig. 1). Conducting absorbance measurements on a sample is easy, and in the future it will be possible to construct portable field equipment for direct measurements during the injection of E110 near the torrent. The UV-visible (200–800 nm) absorption spectra of natural waters in general show a monotonically decreasing signal, with strong absorption band below 230 nm (due to nitrate ions) and a wide band between 250 and 300 nm (due to natural organic matter). These bands are followed by an asymptotic decrease to very low values at visible wavelengths, proportional to the suspended matter concentration.

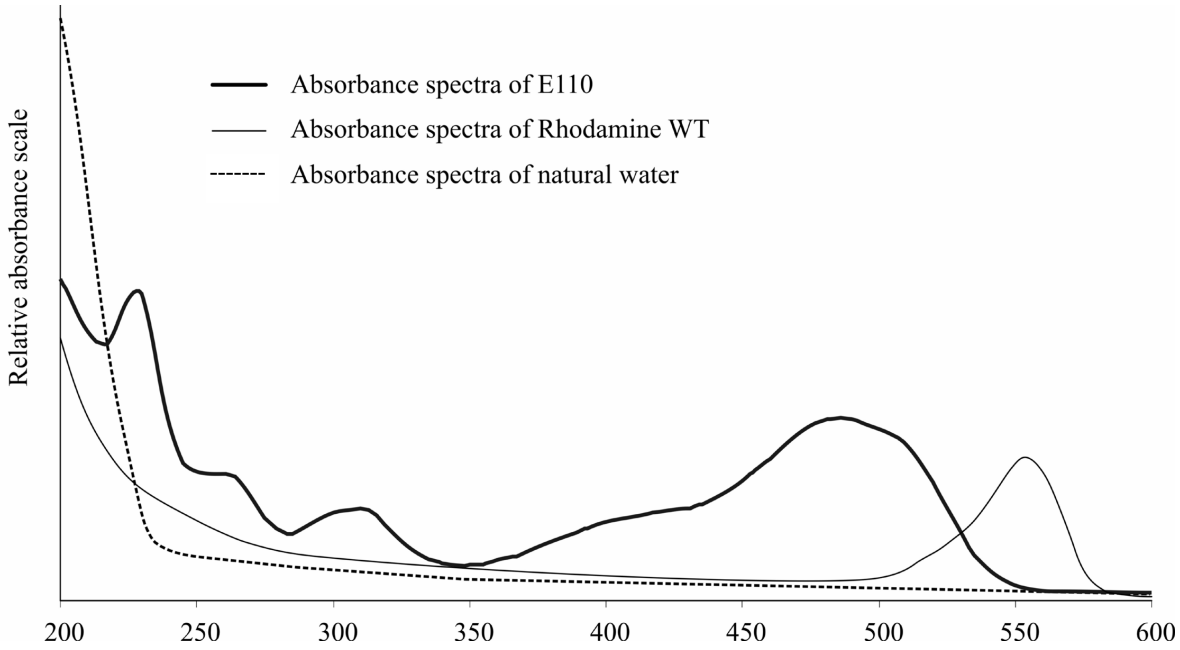

Fig. 1 Absorbance (λex 250 nm) spectra of Sunset Yellow, natural water and Rhodamine WT.

In the ultraviolet part of the spectrum there is interference between the two first absorption maxima (237 and 316 nm) of Sunset Yellow FCF and the absorption spectra of the natural substances in water (Fig. 1). However, at visible wavelengths, the 483-nm band allows dosage titration of the colorant E110. At this wavelength, there is also no interference with the absorption spectrum of traces of Rhodamine WT, used as a pre-tracer to measure the transit time of the cloud (Fig. 1).

However, it is necessary to optimize the dosage titration of E110 in aqueous solution. Many natural surface waters contain suspended impurities or substances that can create variability in the wavelength under scrutiny (by light diffusion or other effects) (Rouessac & Rouessac, 1994). Depending on the importance and variability of this absorption interference, the specific absorption of E110 may be overestimated (Fig. 2). A correction for the baseline derived from the Morton and Stubbs method is required and was used in our work.

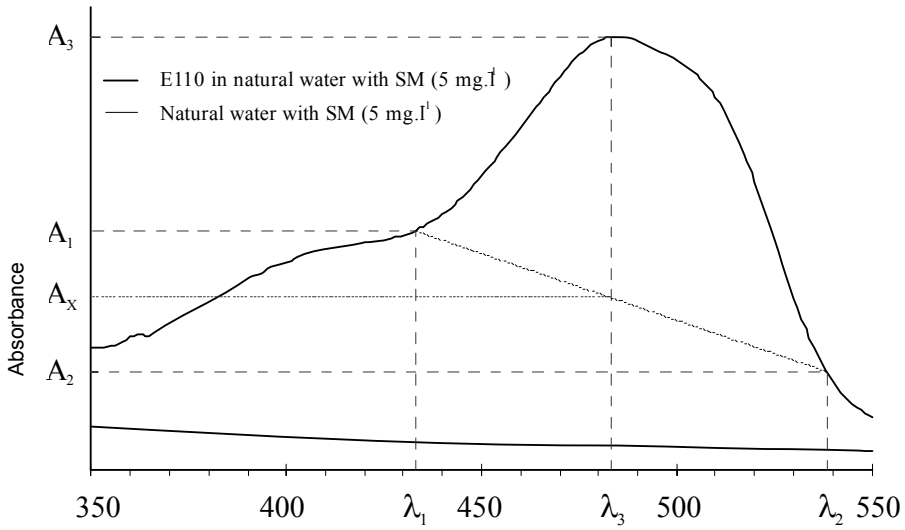

Fig. 2 Specific determination of E110 absorbance in water containing suspended matter (SM).

In order to quantify a substance by its absorption A at its maximum λ_3, one has to subtract the value A_x from the recorded peak A_3. Figure 2 shows the principle of the method. On the basis of a reference spectrum of a pure compound in aqueous solution, two wavelengths λ_1 and λ_2 (433 and 540 nm) are chosen as slope inflection points, thus limiting the measurement band. The reference value used for the dosage titration of E110, in the presence of colloids or suspended matter corresponds to the segment A_3A_x with A_x calculated according to the equation:

$$(A_x - A_1)/(A_1 - A_2) = (\lambda_3 - \lambda_1)/(\lambda_1 - \lambda_2) \quad (1)$$

In our case: $A_x = A_1 - 0.4673\,(A_1 - A_2)$. The calibration of the method is done according to the international standard ISO 8466-1 (ISO, 1990) and the French standard (NF XPT 90-210; Norme Française, 1996) which describe the evaluation phases of the statistical characteristics of the linear function, as well as the limits of detection and quantification. The calibration curve and the characteristics of the method, which corresponds to the relationship between the corrected absorption ($A_3 - A_x$) and the concentration C of E110 in mg L^{-1}, are presented in Table 1. The Beer-Lambert law applies for Sunset Yellow FCF concentrations below 25 mg per litre, which justifies the selected experimental interval between 0.1 and 20.0 mg L^{-1}. All the statistical values used for the calculation of the calibration variables have a 95% confidence level. The detection limit was calculated as three times the standard deviation of 10 measurements of a blank, and the quantification limit as two times the detection limit.

Table 1 Characteristics of the method.

Wavelength (nm)	433, 483, 540
Slope a *	23.26
Intercept b *	0.33
Correlation coefficient	1.00
Detection limit (mg L^{-1})	0.01
Quantification limit (mg L^{-1})	0.02
Confidence interval (mg L^{-1})	0.01

* of straight line [E110] (mg L^{-1}) $C = a\,(A_3 - A_x) + b$

Laboratory validation of the use of E110

Chemical methods for the measurement of river flow are based on a dilution factor between the concentration of the original marker solution and the concentration in the samples. The detection of the sample concentration should only depend on the flow. Other factors such as photochemical degradation, adsorption by suspended matter or river bottom sediments are not supposed to interfere. Knowledge of the properties of the marker in these respects is therefore essential for the final choice of a marker. Light stability of E110 and its adsorption by suspended matter have therefore been tested.

Photosensitivity The light stability of the colorant was tested by exposing a closed recipient containing 100 mL of a 1.0 mg L^{-1} solution of E110 to sunlight for 1 week. The results obtained from daily measurements show that there is no photodegradation of E110. These results are in line with those of a study of E110 Sunset Yellow FCF degradation in beverages, when it is exposed, among other things, to natural conditions (Gosetti *et al.*, 2005).

Adsorption Decrease in marker concentration by adsorption can occur in the time period between the release of the colorant into the river and its analysis in the laboratory. During the flow measurements, adsorption by suspended matter and by river bottom sediments can occur. In contrast there is no interference from adsorption to the glass wall of the sampling vial, nor from compound degradation over time. Two kinds of effects were studied: the suspended matter effect

(5.0 mg L^{-1} of suspended matter of particle size > 0.45 μm, and 0.5 mg L^{-1} of E110) and the influence of sediment (5.0 mg L^{-1} of suspended matter of particle size > 0.45 μm, 150 mg L^{-1} of sediment taken from the river bottom and 0.5 mg L^{-1} of E110). The duration of the test (3 hours) is sufficient to detect adsorption and is comfortably longer than the time range of a flow measurement. Supposing that suspended matter and sediment are always available in excess, the adsorption mainly occurs in the river. The data show that, over the time period studied, there is no adsorption of the marker. The observed fluctuations are not significant compared to the confidence interval of the measurements.

Biodegradability The biodegradability rate of the colorant has been verified by exposing three open receptacles containing 300 ml of a 0.8-mg L^{-1} solution of E110 in the stream water. Samples were stirred and oxygenated by soft bubbling of air. The daily measurements show that biodegradability occurs as early as sampling (10% each 24 h). This result underlines the fact that E110 concentration measurements must be done as soon as possible, ideally by using a field spectrophotometer *in situ*. Five days are sufficient to obtain a degradation of 50% of E110. The concentration is below the detection limit after 10 days of incubation.

Range of use Although the theoretical solubility of E110 in ultrapure water is 120 g L^{-1}, it is difficult to prepare a clear 70-g L^{-1} concentrated solution with natural water. With a quantification limit of 0.02 mg L^{-1} (Table 1) and a dye injection rate of 0.015 L s^{-1}, the maximum flow that can be measured is 53 m^3 s^{-1}, and over 70 m^3 s^{-1} with an injection rate of 0.0029 L s^{-1} and a 30-L tank (with our constant level canister).

VALIDATION ANALYSIS OF SIMULTANEOUS MECHANICAL AND CHEMICAL FLOW MEASUREMENTS

The Doria River catchment and the hydrometric station

The Doria River is part of a karstic system that drains from the southwestern edge of the pre-Alpine hills of the Bauges massif, France. This hydrological unit is part of the Leysse River sub-basin that drains the southern part of the massif into the Bourget Lake after passing through the city of Chambéry.

The hydrometric station is located about 1600 m downstream from the karstic spring (exsurgence) of the Doria, close to the bridge of the Lovettaz Road at an altitude of 576 m a.m.s.l. The flow of the karstic system has to be augmented by the surface runoff of the Hauterivien, made of impermeable shale (1.54 km^2, which corresponds to 10.1% of the entire basin). The morphometric characteristics of the Doria drainage basin (up to the hydrometric station Pont de Lovettaz) are: surface area 15.19 km^2; circumference: 20.69 km; mean altitude: 1311 m; median altitude: 1320 m.

The hydrometric station was installed in February 1989. Initially, water levels were recorded using an OTT X limnigraph (biweekly rotation, reduction 1/10). In 1991, an automated recording station CR2M SAB 600 was installed, equipped with a submerged ultrasound sensor that was coupled to the mechanical limnigraph. The station functions at two recording intervals (5 or 15 min) switching automatically to the shorter interval when the water level exceeds 50 cm. Since November 1995 the station has been linked to the telephone network through a modem. In addition to water level and temperature, the station has been recording conductivity since December 1996, when a Merck conductimeter was added. Conductivity values are average, usually between 260 and 270 μS cm^{-1} (minimum 199 μS cm^{-1}, maximum 319 μS cm^{-1}). Between 1997 and 1999, the physicochemical quality of water in the River Doria has been assessed seven times, under different hydrological conditions. In the Piper classification its waters are calcium-bicarbonated. The average hydrotimetric titre is 16.2 (French scale), total alkaline titre averages 15.3 (French scale), and the average pH is 8.3.

Rating curve of the hydrometric station: flow measurements

The rating curve of the station was established using 48 mechanical flow measurements by a current meter with a C2 (OTT) propeller and a graduated rod and by 42 chemical dilution flow measurements, 17 of which were done simultaneously with mechanical flow measurements. In general, mechanical flow measurement in mountain torrents is difficult because of the presence of large boulders on the river bed.

Out of the numerous gauging methods (Herschy, 1995; Käss & Behrens, 1998; Godley, 2002), dilution gauging is often the one that is recommended (Florkowski *et al*., 1969; Wilson, 1973; Bencala *et al*., 1983; Elder *et al*., 1990; Gees, 1990). However, when possible, in a favourable and quiet section from the torrential stream, mechanical measures can be used. Results are then similar to those obtained through dilution gauging (Airey *et al*., 1984; Gees, 1990; Benischke & Harum, 1990; Käss & Behrens, 1998; Hudson, 2004). In close proximity to the hydrometric station, there is a section that is boulder-free and stable, and this is where the mechanical measurements were performed, thus allowing comparison of the classical method with the dilution experiments using the new tracer.

The chemical dilution was carried out by constant-rate injection with a classical constant level canister as developed by the electricity company EDF. The flow measurement section is 100-m long between the injection point and the sampling point, and it is also close to the hydrometric station. Along the measurement section there are neither significant inflow, nor losses, from the sides that can influence the measurement. The complete mixing of the tracer solution is insured by a series of small waterfalls and by the turbulence associated with the presence of large boulders. The sampling is done on a stable and relatively smooth section.

The transit velocity of the tracer and the passage time of the tracer were determined by Rhodamine WT injections. Before each flow measurement, a blank river water sample was taken, allowing the correction of the baseline in the spectrophotometric calibration. During each flow measurement, 10–12 successive samples were taken, to ensure that the sampling was performed during the stabilization phase of the tracer concentration, and, samples were taken successively from the left bank, the right bank and the centre of the river, to ensure that the tracer was properly mixed (Goodell & Steppuhn, 1973; Wilson *et al*., 1973; Bauwens *et al*., 1982; Masson *et al*., 1987; Elder *et al*., 1990; Okunishi *et al*., 1992; Dutillet, 1993). For each flow measurement, a sample of the injection solution was also taken. During the series of experiments, different injection flow values (between 0.012 and 0.029 L s^{-1}) were tested. Different injection solution concentrations, varying between 5.1 and 54.0 g L^{-1} were also tested.

In order to validate the results of the E110 tracer method, statistical comparison of the flow measurements was done using two tests (ANOVA and a comparison of the rating curves). A principal component analysis (PCA) was performed on the different variables needed in a flow measurement.

Comparison of the two simultaneous flow measurement types

The first test is an analysis of variance of 17 flow measurements comparing the mechanical and chemical techniques simultaneously used. It shows that the flows recorded do not significantly differ between the two methods at a 95% confidence limit.

The second test is the comparison of the two rating curves (Neuilly, 1998). The two rating curves, one from 15 mechanical flow measurements, the other from 17 chemical dilution flow measurements are shown in Fig. 3. The difference in the number of measurements of each type is due to the fact that, on 19 July 1996, three chemical dilution measurements were performed while there was only one mechanical measurement.

The instantaneous flows measured between 1996 and 1999 are within the range of a minimum of 57.2–63.0 L s^{-1} and a maximum of 3579–3630 L s^{-1}. Both rating curves can be described by a second-order polynomial.

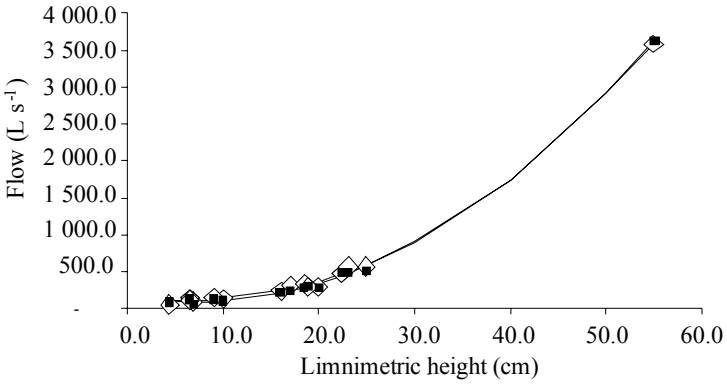

Fig. 3 Rating curves obtained by the two methods: mechanical (◇) and chemical (■) dilution.

For the chemical dilution method:

$$Q(\text{L s}^{-1}) = 1.498H_{(\text{cm})}{}^2 - 20.49H_{(\text{cm})} - 172.93 \qquad r^2 = 0.998 \qquad (2)$$

For the mechanical method:

$$Q(\text{L s}^{-1}) = 1.573H_{(\text{cm})}{}^2 - 23.82H_{(\text{cm})} - 180.3 \qquad r^2 = 0.998 \qquad (3)$$

The calibrations allow us to obtain two rating curves in such a way that the sum of the residuals square is equal to Q_1 (with ν_1 degrees of freedom) for the first curve and Q_2 (with ν_2 degrees of freedom) for the second curve. The variance, identical for both curves according to the ANOVA, is estimated by:

$$s^2 = Q_1 + Q_2 / \nu_1 + \nu_2 \qquad (4)$$

Combination of all flow measurements ($N = 32$) leads to a single common rating curve of the same mathematical form as the two individual rating curves:

$$Q(\text{L s}^{-1}) = 1.535H_{(\text{cm})}{}^2 - 22.15H_{(\text{cm})} - 176.6 \qquad r^2 = 0.998 \qquad (5)$$

The statistical analysis of these three rating curves derives variables that can be subjected to a Snedecor test. The results imply that the two curves cannot be distinguished at a 95% confidence interval level. Finally, we have done some tests on the variability of the chemical dilution method by repeating the procedure at a certain water level, on the same day in stable flow conditions, leaving enough time between each measurement for the complete flushing of the tracer. This was confirmed by the blanks sampled before each measurement. This test was conducted six times at six different water levels and it shows an average dispersion of 5% of the flow measured by the chemical dilution method (3.8% if one excludes the operations on 10 March 1997). The comparison of the uncertainties of the discharge for both methods shows that the uncertainties are roughly equivalent over the range of conditions studied (Table 2).

Table 2 Comparison of the measurement errors of the mechanical and chemical dilution methods.

Deciles	Flow limit (L s^{-1})	Standard deviation (%): Chemical dilution method	Mechanical method
D10	95	18.7	15.5
D50	459	14.2	15.6
D90	864	12.9	7.4

Statistical analysis of the chemical dilution flow measurements

Various concentrations and injection rates of the marker were used during the flow measurements and at different river discharges. The number of variables thus studied allows a PCA which

reduces the number of variables and establishes the correlations between them. The variables included in this analysis were:

INJ injection rate;
CM concentration of the marker in the original marker solution;
CR average concentration of E110 in the 10 to 12 samples taken at each flow measurement;
CVR standard deviation of the concentrations in the previous samples;
LE water level as measured at the river gauge;
DT discharge as established by the rating curve based on mechanical flow measurements;
DC discharge as established by the chemical dilution method; and
ECART percentage difference between DT and DC.

The analysis has identified three principal components that explain 76% of the variance; this is presented graphically in Fig. 4.

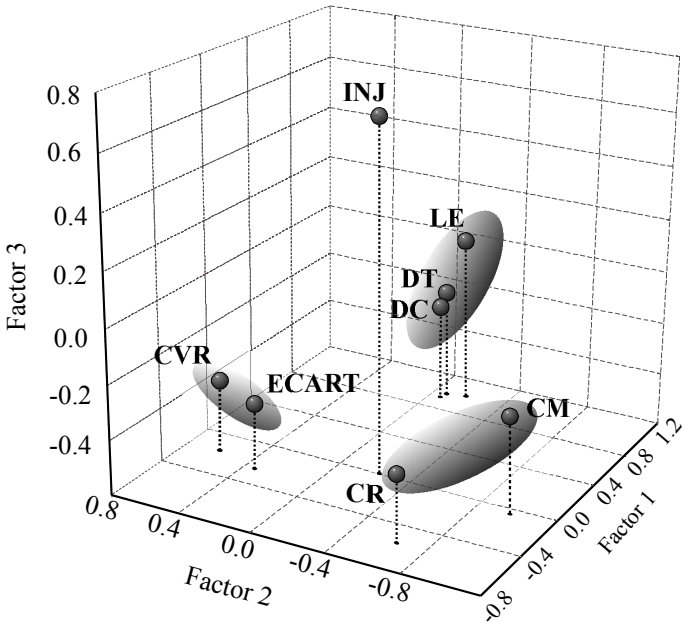

Fig. 4 Principal component analysis of injection variables.

The injection rate is independent of the other variables and has seemingly no influence. The graph shows three main clusters:

(a) DC, DT and LE are obviously (and fortunately) strongly correlated;
(b) CVR and ECART are also strongly correlated, which implies that the differences in the results obtained using the two methods correlate with the dispersion of the different values of the E110 concentrations in the samples. In the 39 chemical dilution measurements performed, the mean variance coefficient of the 8–12 samples in each is 5.1% (minimum 0.5%, maximum 26.7%); and
(c) CR and CM are inversely correlated to CVR and ECART, which implies that, when the concentration of the tracer is low in the river, the difference between the results using the two methods increases.

The main source of uncertainties seems to be the variance between the concentrations of the different samples from a single flow measurement (Masson *et al.*, 1987) but these differences may have two sources: problems of the tracer's dilution and timing of the sampling. The precision of the chemical dilution flow measurements can be calculated according to the equations established

by André (1964), Masson *et al.* (1987) and Audinet (1995):

$$X_q^2 = \left(\frac{S_q}{q}\right)^2 + \left(\frac{\mathrm{SD}}{D}\right)^2 \quad (6)$$

where X_q is the standard deviation of the river discharge; S_q is the standard deviation of the injection rate; q is the injection rate (in L s^{-1}); SD is the standard deviation of the dilution; and D is the dilution factor between the concentration of the original dye solution and the average concentration in the samples.

The analysis of the contribution of the two terms of equation (6) for the chemical dilution method shows that the dispersion of the concentration values in the different samples for a single measurement is highly variable (from 9 to 92%) but not correlated with the streamflow. The average contribution to the total uncertainty is 50%, which confirms the strong correlation between CVR and ECART in the PCA.

CONCLUSIONS

The results of this study can be used to improve the accuracy of flow measurements in torrential rivers. The low adsorption of the colorant E110 on suspended matter and sediment, and its low sensitivity to photochemical degradation have confirmed its high potential as a tracer. The spectrophotometric approach to the measurement of concentration of E110, coupled with a rigorous statistical analysis, confirms that the method is sensitive and permits time gains. Using E110 as a tracer compound has many advantages: it is quite insensitive to interferences, its precision is comparable to that of a classical mechanical method, it has a low toxicity and low visual impact (over the range of concentrations used in this study), and has a low detection limit (20 μg L^{-1}) in spite of interfering components. The method is relatively simple to use and can be realized by two operators. As the equipment is neither too heavy, nor too large it can even be used below ground. Moreover, using a field spectrophotometer, the results can be obtained *in situ*.

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