

**Published in: Sinkholes and the Engineering and Environmental Impacts on Karst, Ed. B.F. Beck, Geotechnical Special Publication No. 122, American Society of Civil Engineers, p. 287-295.**

## **EMPIRICAL DETERMINATION OF TRACER MASS FOR SINK TO SPRING TESTS IN KARST**

Stephen R.H. Worthington<sup>1</sup> and C. Christopher Smart<sup>2</sup>

**ABSTRACT:** A large number of equations have been proposed for determining the quantity of tracer needed for a successful groundwater trace in carbonate rocks. Surprisingly, there is a lack of empirical evaluation of these equations in the literature. Data from 203 quantitative tracer tests were used to statistically evaluate the equations. The pertinent variables in these equations include input discharge, spring discharge, distance, velocity, mass of tracer injected, peak tracer concentration recovered, and time from injection to peak recovery. The tests included a wide range of spring discharges (0.002-47 m<sup>3</sup>/s), distances (30 m - 30 km) and mass of dye used (2 mg - 50 tonnes). Two regression equations gave excellent fits to the tracer test data set. Peak tracer concentration is usually chosen to be in the sub-visual range, but depends upon methods of sampling and of analysis. Use of these equations gives a high probability of successful sub-visual detection of dye in water or charcoal samples, and thus addresses one of the major problems of tracer testing.

### **INTRODUCTION**

Tracer testing is an invaluable, commonly-used, and well-established technique in carbonate aquifers for determining flow direction and transport parameters. These tests have often shown that there is rapid groundwater flow over long distances. For instance, the first long-distance quantitative trace in 1877 showed that flow from river losses in the upper Danube took only two days to flow 12 km to the Aach Spring, which feeds the River Rhine (Käss, 1998, p. 5). Quinlan (1986) estimated that more than 90% of a total of some 1300 tracer tests in the USA had been in carbonate aquifers, and that almost all of these were between sinking streams and springs.

<sup>1</sup> Principal Hydrogeologist, Worthington Groundwater, 55 Mayfair Avenue, Dundas, Ontario, L9H 3K9, Canada, sw@worthingtongroundwater.com

<sup>2</sup> Associate Professor, Dept. of Geography, University of Western Ontario, London, Ontario, N6A 5C2, Canada

One of the critical issues in planning a tracer test is in determining what mass of tracer to inject, and a number of empirical equations have been developed. Field (2003) documented 33 such equations, but concluded that “no means is available by which one equation may be reasonably selected over the others” (Field, 2003, p. 1). In this paper we show that these equations can indeed be tested, and we develop two empirically-based equations which provide excellent predictability over a wide range of conditions.

### **DATA SET AND EQUATIONS EVALUATED**

The equations in the literature used for the estimation of the mass of tracer for a sink to spring test almost all take one of six general forms:

$$M = a (LQC)^b \tag{1}$$

$$M = a (TQC)^b \tag{2}$$

$$M = a (LC)^b \tag{3}$$

$$M = a (QC)^b \tag{4}$$

$$M = a (qC)^b \tag{5}$$

$$M = a (LQC/q)^b \tag{6}$$

where  $M$  is the mass of tracer injected,  $a$  is an empirical coefficient,  $b$  is an exponent which is unity in most cases,  $Q$  is discharge at the spring or springs where the tracer emerges,  $q$  is the discharge at the tracer input point,  $L$  is distance between input and output points,  $T$  is travel time, and  $C$  is peak tracer concentration at the spring.

Continuous flow is important at the injection point so that the tracer is carried into the main conduit flow network in the aquifer. However, discharge at the injection point is seldom measured during tracer tests, and does not appear to be an important variable in determining the mass of tracer needed, so we did not test Equations 5 and 6. We assembled data from a large number of published sinking stream to spring tracer tests where the variables  $M$ ,  $Q$ ,  $L$ ,  $T$ , and  $C$  were available. Some tracer tests resulted in tracer recovery at more than one spring, and in these cases the discharge-weighted mean peak tracer concentration was calculated.

The initial data set of about fifty traces had a rather narrow range in most parameters, with a range in tracer mass of three orders of magnitude. This range was extended upwards by including some tracer tests from the literature where very large masses had been injected, with the maximum for fluorescent dye being 250 kg and

the maximum for salt being 50 tonnes. We extended the range downwards by conducting a number of low-mass tracer tests in Ontario.

The final data set has a range of tracer mass that exceeds ten orders of magnitude, from 2.7 mg to 50 tonnes, and comprises 203 traces. This includes 32 tests in the high-relief setting of the Canadian Rocky Mountains and 54 tests in the low-relief setting of Ontario which were conducted by ourselves (Smart, 1983, 1988a, 1988b; Worthington, 1991). Other major sources of tracer data were Smart (1981), Mull et al. (1988), Behrens et al. (1992), Crispim (1995), and Gospodarič and Habič (1976).

The tracers used in these tests were either fluorescent dyes or salt. More than half of the tests used the fluorescent dye uranine (sodium fluorescein, Colour Index Acid Yellow 73). This dye offers the advantages of very low toxicity and very high detectability. It is approved by the U.S. Food and Drug Administration for use in drugs and cosmetics and has a detection limit in the range 1 - 5  $\mu\text{g}/\text{m}^3$  on a spectrofluorometer. The second most commonly used dye was Rhodamine WT (Colour Index Acid Red 388), which has a detection limit of about 5  $\mu\text{g}/\text{m}^3$  on a filter fluorometer. Sodium chloride was the most commonly used salt tracer, though potassium chloride was also used. Salt traces require far larger quantities than fluorescent dyes since detection limits and groundwater background levels of sodium, potassium, and chloride are several orders of magnitude higher than for the most sensitive dyes. Figure 1 shows the mass of salt or dye used in the analyzed tracer tests.

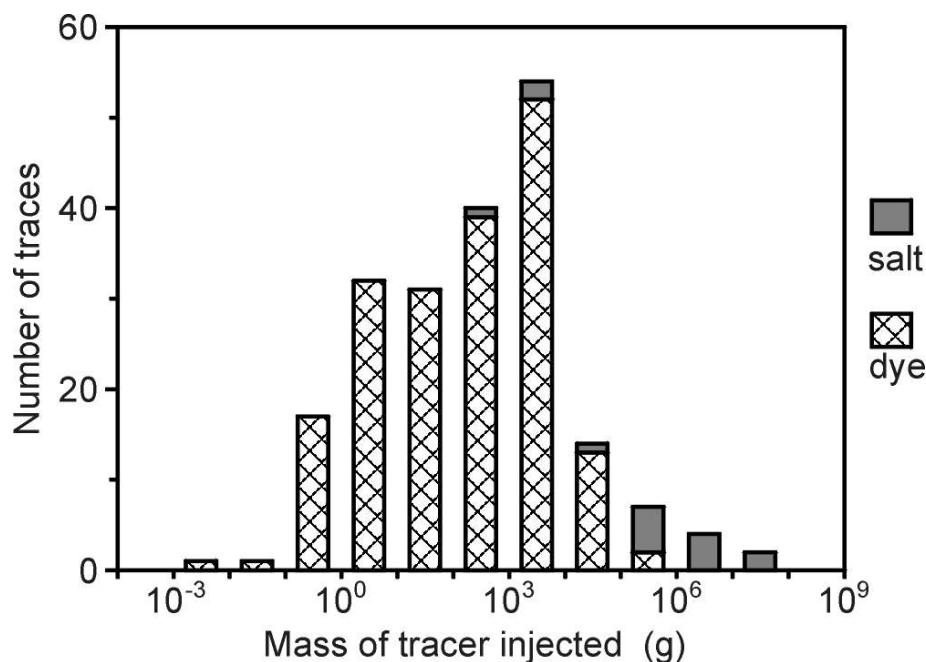
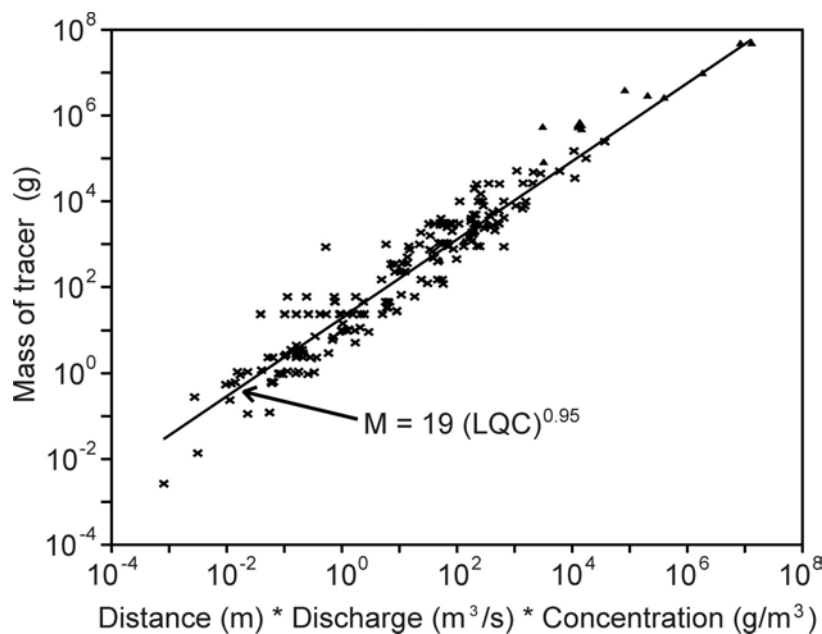


FIG. 1 Mass of tracer used in the data set of 203 tracer tests

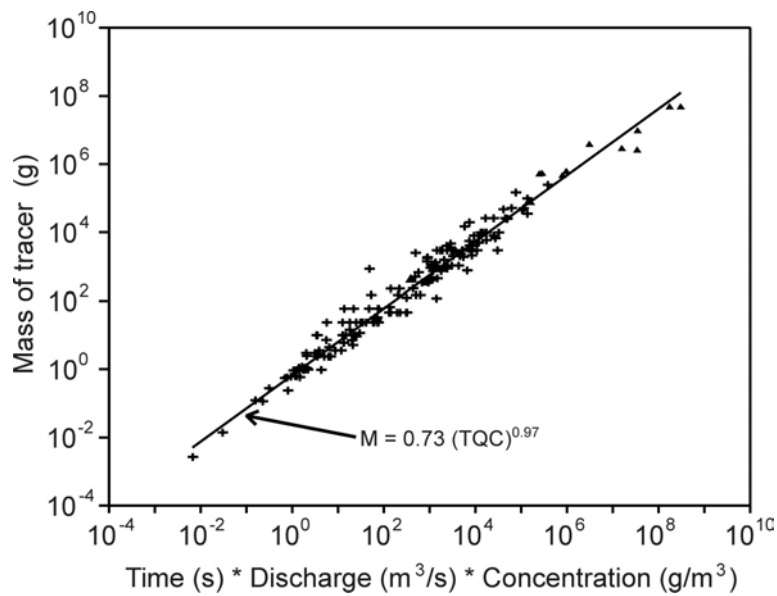
Tracer recovery in 185 of the 203 tests was more than 20 % of the mass injected, and these medium- and high-recovery tests were subject to regression analysis to determine which of the equations best fitted the data. Low recovery often occurred in two situations: (1) where the tracer flowed to a number of distributary springs that were not all were monitored for the tracer, and (2) where the tracer testing took place under low-flow conditions. Thus the median tracer velocity of the low-recovery tests (0.011 m/s) was substantially slower than the median velocity of the complete data set (0.036 m/s).

## RESULTS

Initial regression analysis was performed separately for traces using uranine, Rhodamine WT, and salt. However, no significant differences in results were found, so all tracer data were therefore analyzed together. Linear regression of the log-transformed data yielded results of the form  $y = a x^b$ . Values for  $a$ ,  $b$ , and the coefficient of determination ( $r^2$ ) are given in Table 1. All four equations are close to being linear (where  $b=1$ ). Equations 1 and 2 have excellent fits to the data ( $r^2=0.93$  and  $0.97$ , respectively), and these are shown in Figures 2 and 3, respectively. Equations 3 and 4 have much poorer fits to the data.



**FIG 2. Correlation of mass with traced distance, spring discharge, and peak tracer concentration for dye traces (x) and salt traces (▲)**



**FIG. 3 Correlation of mass with travel time, spring discharge and peak tracer concentration**

**Table 1. Empirical results using the data set of 185 traces**

Equation	Variable	a	b	r <sup>2</sup>	Reference
1	LQC	19	0.95	0.93	Martel, 1913
2	TQC	0.73	0.97	0.97	Dole, 1906
3	LC	5.1	1.08	0.67	Parriaux et al., 1988
4	QC	40000	1.09	0.72	Haas, 1959

Note: Units used are g, m, s

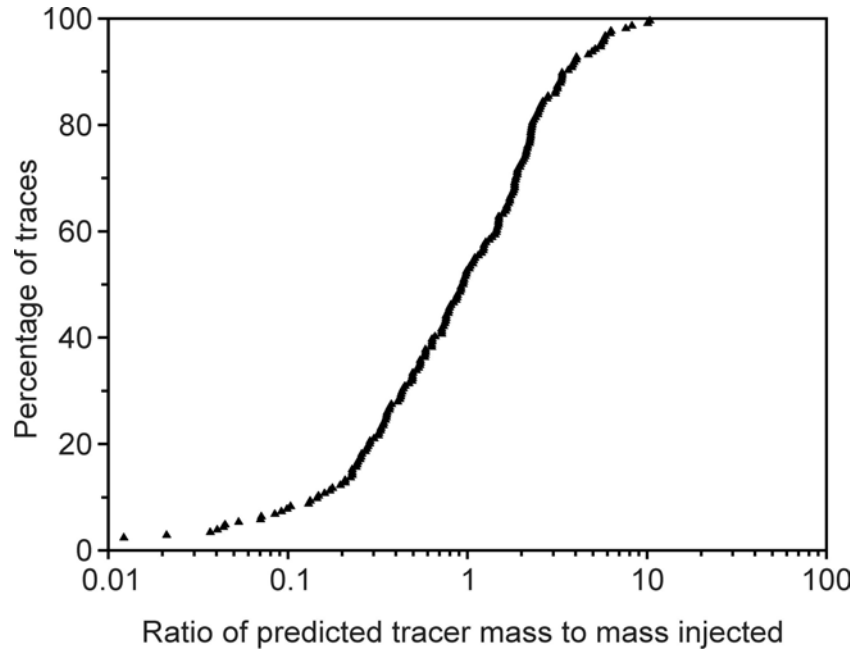
## DISCUSSION

Groundwater velocity is not accurately known in most situations where tracer testing is planned. Consequently, Equation 2 has limited applicability, even though it is the most accurate equation. Equation 1 only requires the measurement of spring discharge and the distance between tracer injection and tracer recovery point, and thus is more useful.

The effectiveness of Equation 1 can be evaluated by calculating the ratio R between the mass of dye predicted from Equation 1 for a given peak tracer concentration and the mass of dye used for each of the 203 tracer tests, by using the equation

$$R = 19.3 (LQC)^{0.95} / M \quad (7)$$

Results are shown in Figure 4. The accuracy of Equation 1 in predicting peak tracer concentration can be estimated from Figure 4. More than 60% of the traces have peak concentrations that are within a factor of three of unity, the latter representing a perfect prediction. The maximum ratio of 10.4 is significant because this means that the maximum tracer concentration is unlikely to be more than a factor of ten times greater than indicated by Equation 1.



**FIG. 4 Ratio of predicted to injected tracer mass for Equation 1**

Equation 1 was first proposed by Martel (1913) for the dye uranine, in the form

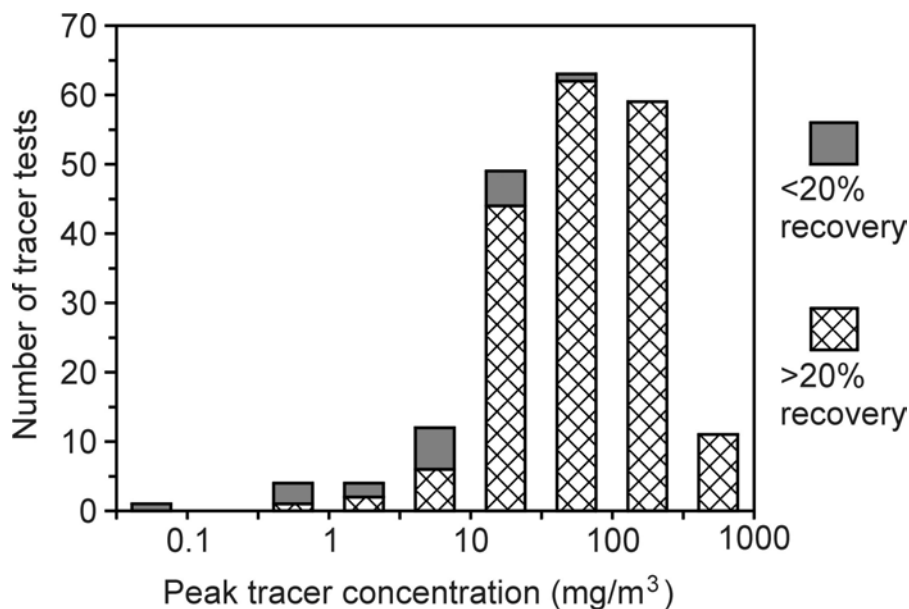
$$M = L Q \quad (8)$$

The accuracy of Equation 8 can be evaluated by determining

$$C_M = C L Q / M \quad (9)$$

for each of the 203 tracer tests in the data set, where  $C_M$  is the peak tracer concentration using the Martel Equation (Eq. 8). The detection limit for uranine is about  $30 \text{ mg/m}^3$  with the naked eye, or about  $0.1 \text{ mg/m}^3$  with a fluoroscope, which was the most sophisticated measuring instrument at the time (Dole, 1906). Results are shown in Figure 5. Only one of the tracer tests evaluated would clearly have been

undetected using the Martel Equation and early Twentieth Century detection techniques, and most would have just been detectable to the naked eye, which was the method used at the time. Thus the Martel Equation provided an excellent estimator of tracer mass needed using early Twentieth Century techniques.



**FIG. 5 Predicted peak concentration for 203 tracer tests using the Martel Equation**

The 203 tracer tests analyzed above all involved analysis using water samples. An alternative method for dye tracing is to use activated carbon which accumulates the dye and is often left in the spring flow for periods of days or weeks. Bauer (1967) showed that there is a linear correlation between dye concentration in water and in activated carbon, so that Equations 1 and 2 are applicable for dyes traces with either sampling method.

Modern detection techniques for dyes employ filter fluorometers or spectro-fluorometers, and these instruments have detection limits as low as a few parts per trillion ( $\mu\text{g}/\text{m}^3$ ). Consequently, much smaller masses of dye may be employed than with older detection techniques. The target peak concentration is best determined after measurement of the background fluorescence at the sample points over a period of time because background fluorescence may vary considerably in space and time (Smart and Karunaratne, 2001). Salt traces are easy to conduct since the conductivity of the water is readily measured in real time using an electrical conductivity probe, but the method suffers from high background variability.

Field (2003) has recently developed a method for predicting the mass of tracer needed for tracing. His method involves using the advection - dispersion equation, and requires an estimate of groundwater velocity or of the area of the conduit cross-section. Neither of these parameters can be reliably estimated a priori, and a wide range of velocities have been measured in conduits (Worthington et al., 2000). Thus the method of Field (2003) suffers from the same problems as does Equation 2 above in that its usefulness is conditional on having already conducted a tracer test.

## CONCLUSIONS

Martel (1913) developed an effective equation for visual detection of dyes in groundwater tracer tests in carbonate aquifers. Two new equations,  $M = 19 (LQC)^{0.95}$  and  $M = 0.73 (TQC)^{0.97}$ , have been developed by regression analysis using a data set of 185 tracer tests. These equations facilitate accurate estimation of the mass of tracer needed for sink-to-spring tracer tests in carbonates under a wide range of conditions.

## REFERENCES

- Bauer, F. (1967) "Erfahrungen beim Uraninnachweis mit Aktivkohle" *Steierische Beiträge zur Hydrogeologie*, 18/19, 169-178.
- Behrens, H., Benischke, R., Bricelj, M., Harum, T., Käss, W., Kosi, G., Leditzky, H.P., Leibundgut, Ch., Maloszewski, P., Maurin, N., Rajner, V., Rank, D., Reichart, B., Stadler, H., Stichler, W., Trimborn, P., Zojer, H., and Zupan, M. (1992). "Investigations with natural and artificial tracers in the karst aquifer of the Lurbach system (Peggau-Tanneben-Semriach, Austria)." *Steierische Beiträge zur Hydrogeologie*, 43, 9-158.
- Crispim, J.A. (1995). "Dinâmica cársica e implicações ambientais nas depressões de alvados e minde", Unpublished Ph.D. thesis, University of Lisbon, 394 p.
- Dole, R.B. (1906). "Use of fluorescein in the study of underground waters", in *Underground-water papers, 1906*, Fuller, M.L., Ed. U.S. Geological Survey Water-Supply Paper 160, 73-85.
- Field, M.S. (2003). "A review of some tracer-test design equations for tracer-mass estimation and sample-collection frequency", *Environmental Geology*, DOI 10.1007/s00254-002-0708-7.
- Gospodarič, R., and Habič, P. (1976). "Underground water tracing investigations in Slovenia, 1972-1975". Inst. Karst Research, Ljubljana, 312 p.
- Haas, J.L. Jr. (1959). "Evaluation of ground water tracing methods used in speleology", *Bulletin of the National Speleological Society*, 21, 67-76.
- Käss, W. (1998). *Tracer technique in geohydrology*, Balkema, Rotterdam, 581 p.
- Martel, E.-A. (1913). "Sur les expériences de fluorescéine à grandes distances". *Comptes Rendus de l'Académie de Sciences*, 157, 1102-1104.

- Mull, D.S., Liebermann, T.D., Smoot, J.L., and Woosley, L.H. (1988). *Application of dye-tracing techniques for determining solute transport characteristics of ground water in karst terranes*, U.S. Environmental Protection Agency, EPA 904/6-88-001.
- Parriaux, A., Liskay, M., Müller, I., and della Valle, G. (1988). *Guide pratique pour l'usage des traceurs artificiels en hydrogéologie*, Swiss Geological Society, Hydrogeological Group, 48 p.
- Quinlan, J.F. (1986). "Discussion of "Ground water tracers", by Davis et al. (1985), with emphasis on dye tracing, especially in karst terrains." *Ground Water*, 24, 253-259; 396-399.
- Smart, C.C. (1983). "The hydrology of the Castleguard karst, Columbia Icefields, Alberta, Canada". *Arctic and Alpine Research*, 15, 471-486.
- Smart, C.C. (1988a). "Quantitative tracing of the Maligne karst system, Alberta, Canada". *J. Hydrol.*, 98, 185-204.
- Smart, C.C. (1988b). "Artificial tracer techniques for the determination of the structure of conduit aquifers". *Ground Water*, 26, 445-453.
- Smart, C.C., and Karunaratne, K.C. (2001). "Characterisation of fluorescence background in dye tracing". *Environmental Geology*, 42, 492-498.
- Smart, P.L. (1981). "Variation of conduit flow velocities with discharge in the Longwood to Cheddar Rising system, Mendip Hills". *Proc. 8th Internat. Congr. Speleology*, Bowling Green, Kentucky, B.F. Beck, Ed.. National Speleological Society, Huntsville, Alabama, 333-335.
- Worthington, S.R.H. (1991). "Karst hydrogeology of the Canadian Rocky Mountains". Unpublished Ph.D. thesis, McMaster University, 380 p.
- Worthington, S.R.H., Davies, G.J., and Ford, D.C. (2000). "Matrix, fracture and channel components of storage and flow in a Paleozoic limestone aquifer". *Groundwater flow and contaminant transport in carbonate aquifers*, C.M. Wicks and I.D. Sasowsky, Eds., Balkema, Rotterdam, 113-128.