

# Accurate Description of Conservative Tracer Plumes Evolution by a Thermodynamic Function in Streams

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**Abstract-** An important environmental issue for theory and applications of quality of water models in natural flows is to know precisely how to evolve the solute plume in time and space. Transport theory is by definition the branch of water sciences that most information bear due to the several physical and chemical mechanisms involved at the same time. However, currently, state-of-the-art available models are unclear when addressing this subject. This drawback probably appears by the lack of understanding of real mechanism acting in the process. In this paper, the definition of a thermodynamic function that may help to reveal those mechanisms behind this process is discussed, and in this approach discharge may be involved as internal parameter. Applying the new equations it is presented here the experimental results in a large mountain river in Colombia.

**Keywords-** Mass Transport in Fluids; Tracer Dynamics

## I. INTRODUCTION

One of most critical problems of today's world is about water contamination, which demands for a lot of money and management resources from environmental authorities. At the same time, the design of new conceptual tools is crucial to understand the varied and complex questions that arrive in field. Despite the evident advances in computational tools applied to water sciences, especially in first years of this new century [1, 2], some major drawbacks remain in this theoretical frame. One of these is the lack of understanding of the significant mechanisms in solute plume formation, in terms of general physical principles that may give a coherent and integrated answer to several questions in this subject. Almost all up to date models use the concept of "dead zone" mechanism as main conceptual base to describe the dynamic of solute plumes in flows, however, this approach is analytically very complex [3, 4], making it very difficult to apply them in some cases. For this reason, it may be useful to develop a different theory, rather from Thermodynamics. This approach may take advantage of generality and a clear experimental meaning of this science, as is usually acknowledged.

### A. Formation of a Solute Plume in Flows: A Le Chatelier-Braun Mechanism

Since long time ago, it is well known the response mechanism of a chemical system to an external perturbation that breaks the equilibrium condition. This mechanism is named the Chatelier-Braun Principle [5, 6], which is stated as: "Any system in chemical equilibrium undergoes, as a result of a variation in one of the factors governing the equilibrium, a compensating change in a direction such that, had this change occurred alone it would have produced a variation of the factors considered in the opposite direction". This general principle may be used as well in the case of pouring a tracer in flow, in order to discover the evolution features of the resulting plume in Fig. 1.

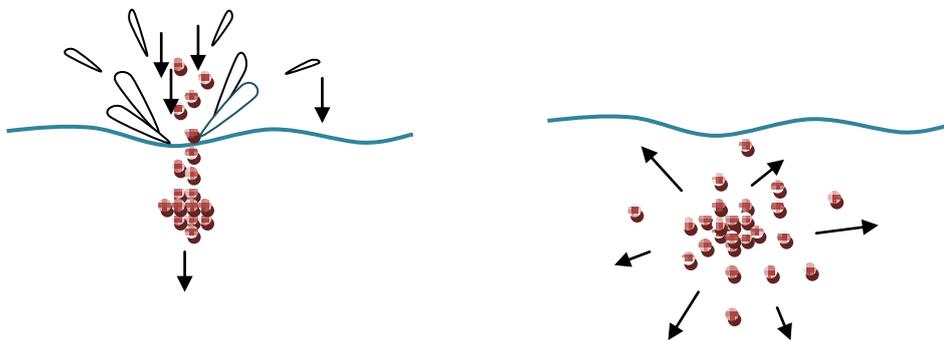


Fig. 1 Perturbation and response due to a tracer injection

In this case, when a conservative solute is injected suddenly in water, the factor that is varied is the mass concentration of the tracer, and then the reaction should be in the opposite direction. If the first process is understood as an increase of concentration in a small region, then the response has to be described as a decreasing mechanism of that factor. This picture means that a dynamic process follows a sudden injection of tracer, which last until equilibrium is recovered in a finite time.

This process may be described mathematically with the Gaussian curve that guides the process itself. To do this, it is enough looking the behaviour of inflection points of the curve (at 0.608 of peak), as currently is used to measure this kind of

movements [7] as shown in Fig. 2.

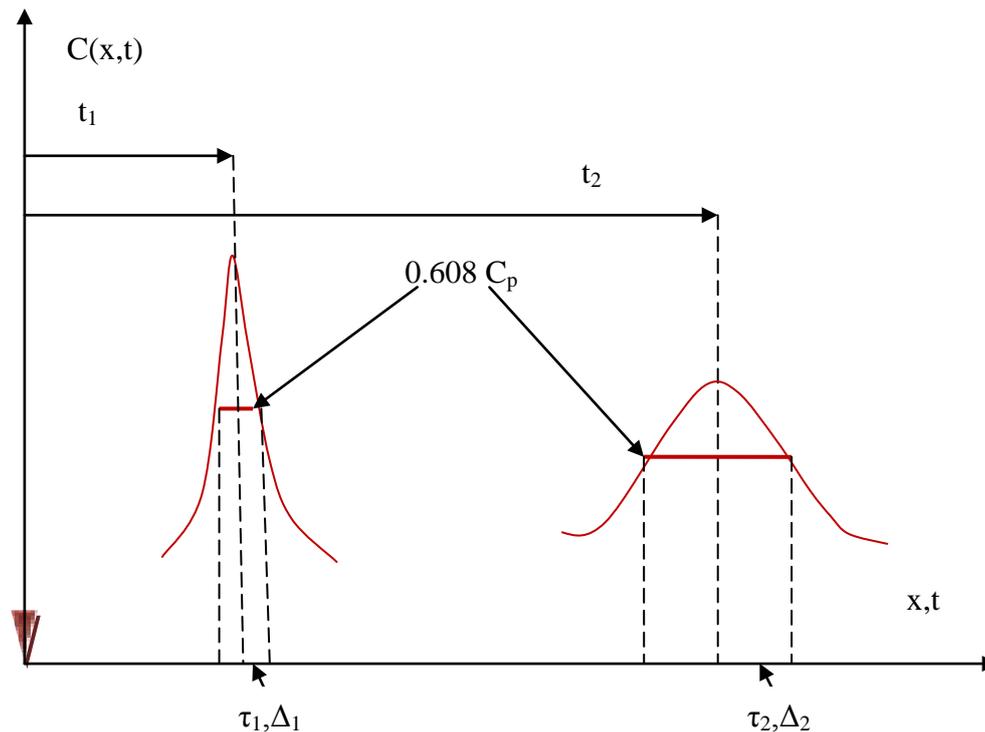


Fig. 2 Gaussian dynamics as reaction to tracer injection

Two important issues about this motion should be noted: 1) The time of tracer motion measured for each curve,  $\tau$ , is different from the travel time of peak,  $t$ , because this first time is an internal phase related with separation effects of tracer particles, while the second time,  $t$ , is an external phase related with elapsed time of fluid motion since injection instant (marked with a red arrow); 2) The related displacement of tracer particles is named as  $\Delta$ , and is proportional to square root of  $\tau$ , because essentially this is a Brownian motion [8]. As will be shown next, there is a relationship between these two times.

Then, it is possible to define a mono-dimensional tracer dispersion velocity,  $V_{disp}$ , involving a transport coefficient  $E$ , for each of the two curves as follows:

$$V_{disp}(t, x) = \frac{\Delta}{\tau} = \sqrt{\frac{2E}{\tau}} \tag{1}$$

This velocity clearly has a statistical nature, so we can see it as an average value. Regarding Eq. (1) as inverse of square root of time, it is clear that once the initial perturbation of equilibrium in the considered system is passed, the dispersion velocity will vanish as time increase, as required by Le Chatelier-Braun principle.

*B. Relationship between the External and Internal Phases in the Motion of a Tracer*

Now it is important to establish a relationship between  $t$  and  $\tau$ , in order to obtain operational equations for the tracer motion itself. If in Fig. 3 we consider that in a stream there is a sudden injection of certain mass of tracer in a point A, and if in a point B (downstream) there is an observer counting the tracer particles, then a question that may be asked is: how the observer in B may state a statistics of arriving tracer particles? If we consider that the detection of a tracer particle is a “rare” (uncommon) event, and also if this process is also a pure random one, then it may be modelled in time by a “Poisson’s probability distribution. It makes sense to relate the whole (external) time centred in the peak of tracer plume with the infinite addition of individual Brownian (internal) times of each particle in the spreading plume, using the Poisson’s distribution. This limit is justified as long as there are a very large number of atoms in each molecule-gram of solute.

$$t = \lim_{n \rightarrow \infty} \tau \left( 1 + a + \frac{a^2}{2!} + \frac{a^3}{3!} + \dots + \frac{a^n}{n!} \right) \tag{2}$$

On the other hand, the mean value,  $a \approx 1.54$ , of this distribution for the case of Brownian motion is well-known since the pioneering researches of T. Svedberg in early years of XX century [9]. Then,

$$t \approx \lim_{n \rightarrow \infty} \tau \left( 1 + 1.54 + \frac{1.54^2}{2!} + \frac{1.54^3}{3!} + \dots + \frac{1.54^n}{n!} \right) \approx 4.67\tau \tag{3}$$

This constant relationship is named as  $1/\beta$ :

$$\tau \approx \beta t \approx 0.2143 t. \tag{4}$$

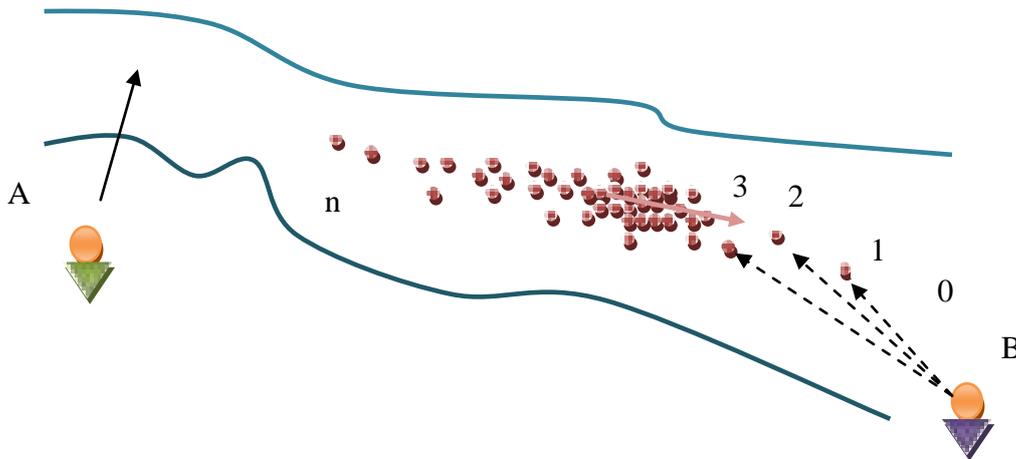


Fig. 3 A Poisson’s observer in B counting tracer particles

*C. A New Function to Describe a Solute Plume Evolution in Flows: a Fick’s Modified Equation*

Therefore, when a tracer (solute) is poured in a flow, there are two different velocities that should be observed in order to describe properly the physical situation: stream mean velocity and dispersion velocity. First velocity,  $U$ , characterizes the average advective one-direction motion of flow. Second one,  $V_{disp}$ , characterizes two-opposite direction motion of tracer plume (Fig. 4). If dispersion is mainly due to shear effect and if this depends on the advective mean motion (through the distribution of velocities created by the advection), it is reasonable to state that there is a cause-effect relationship between them. A way to find this link is defining a function as the module ratio of dispersion and advective mean velocities [10, 11].

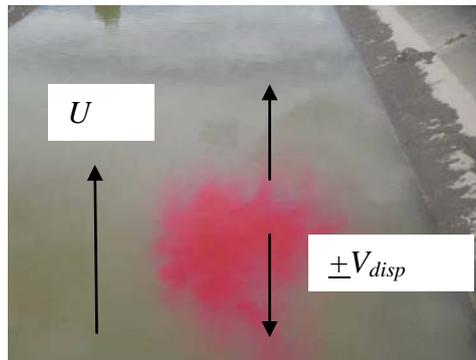


Fig. 4 Advective and dispersive velocities in a stream

Then,

$$\phi = \frac{V_{disp}}{U}. \tag{5}$$

Put Eqs. (1) and (5) together, it holds

$$U = \frac{1}{\phi} \sqrt{\frac{2E}{\tau}}. \tag{6}$$

This is a non-uniform flow velocity equation with the same squared-root structure with Chezy’s equation. The uniformity of flow condition is not necessary here because the linear impulse conservation principle is not used to derive it. Clearing the longitudinal dispersion coefficient,  $E$  from Eq. (6), it holds

$$E = \frac{\phi^2 U^2 \tau}{2}. \tag{7}$$

Considering the Fick’s classical definition for concentration of tracer,

$$C(x,t) = \frac{M}{A\sqrt{4\pi Et}} e^{-\frac{(x-Ut)^2}{4Et}} \quad (8)$$

Then, replacing value in (7) with A in (8) as cross section, we have a modified Fick's equation, with discharge  $Q=U*A$ ,

$$C(x,t) = \frac{M}{Q\phi t\sqrt{2\pi\beta}} e^{-\frac{(x-Ut)^2}{2\beta\phi^2 U_x^2 t^2}} \quad (9)$$

At the measuring point, it is possible to calculate discharge by means of the following equation. Here,  $C_p$  is the peak concentration at this point.

$$Q = \frac{M}{C_p \phi t \sqrt{2\pi\beta}} \quad (10)$$

#### D. Related Parameters and Nature of Function

Looking at denominator of exponential argument in classical Fick's Eq. (9), it should be remembered that although this equation is a time function, the dimension of standard deviation is space. Hence, in one dimension,

$$\sigma_x = \sqrt{2Et} \quad (11)$$

and the standard deviation as time function is

$$\sigma_t = \frac{\sigma_x}{U} \quad (12)$$

Combining the equations we stated

$$\tau = \frac{\sigma_t \sqrt{\beta}}{\phi} \quad (13)$$

Equation (13) is important because it allows calculating dynamic parameters of dispersion by means of time measurements on Gaussian curves (Fig. 5). Finally, the thermodynamic nature of model arises again when we study the nature of function and found that is a Pfaffian function, which may be integrated as follows [12],

$$\oint_c d\phi = 0 \quad (14)$$

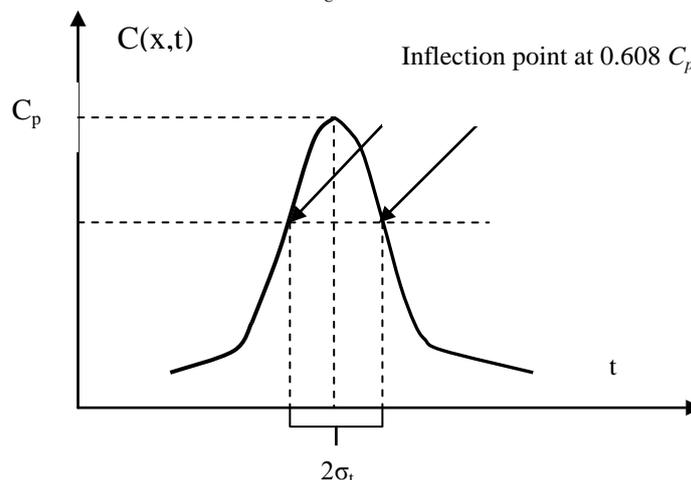


Fig. 5 Key points to make calculations

Hence,  $\phi$  is a special kind of function that does not depend on path, i.e. it is a state function. This function is sensible to loss of freedom degrees in evolution of that system. This is a very important feature for Eq. (14) because it reflects a critical concept in water quality studies known as "Complete mixing" condition. This condition occurs when tracer covers all cross section of flow, i.e. the lateral diffusion vanishes, losing a thermodynamic restriction.

#### E. Availability of Tracer Mass in Plume Evolution Measured by $\phi$ Function

When a sudden conservative tracer pouring in a turbulent flow occurs, this substance is spreading in a greater volume, mainly due to shear effect in a velocity distribution. In this motion, tracer mass is not immediately available but is rather a

progressive coupling phenomenon because the “internal” time,  $\tau$ , actually measures how much tracer mass is observed in a time  $t$ . To see this process, we observe several cases.

1) *Earlier Instant of Pouring*

This first case corresponds to more extreme accessible sight of experimenter, looking to the plume evolution. It corresponds to an ideal, very near observation on tracer, almost in injection site. In this theoretical case the elapsed time is  $t=\sigma t$ . (Fig. 6).

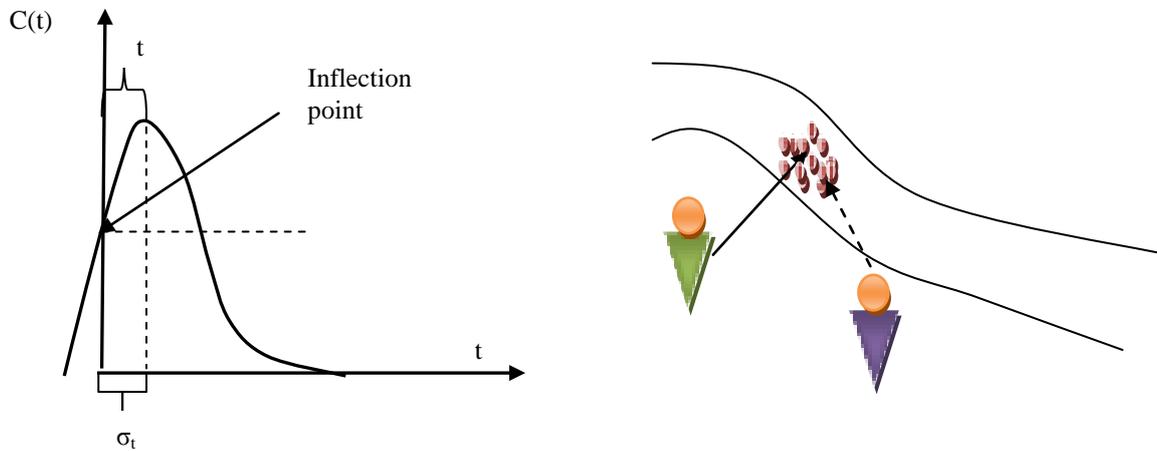


Fig. 6 Observation at very near the injection site

In this ideal case, we will have

$$\tau = \beta t = \frac{t\sqrt{\beta}}{\phi} \tag{15}$$

Clearing  $\Phi$ ,

$$\phi = \frac{\sqrt{\beta}}{\beta} \approx 2.16. \tag{16}$$

Now, accepting that in current Gaussian theory, 95% of tracer mass takes  $4\sigma t$  of time as independent variable, we may think that in earlier stages of solute cloud evolution in a turbulent flow, the “available mass” of tracer for discharge calculation is only  $1/4$  of total ( $\sigma t/4\sigma t$ ), when  $\phi=2.16$ .

2) *Observation Instant at  $t=2\sigma t$*

For this case, it holds that  $t=2\sigma t$  as in Figure 7.

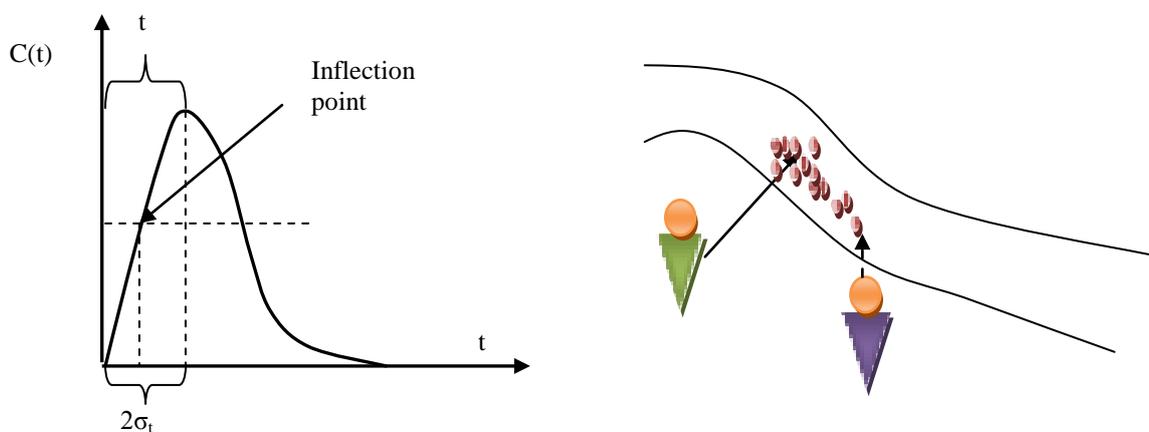


Fig. 7 Close observation from injection site

The first particles of tracer appear at  $t=0$ . The proper calculations for this case are

$$\tau = \beta t = \frac{\left(\frac{t}{2}\right)\sqrt{\beta}}{\phi} \tag{17}$$

Clearing  $\Phi$ ,

$$\phi = \frac{\sqrt{\beta}}{2\beta} = 1.08. \tag{18}$$

This means that for this case, the available mass is only one half of the nominal (whole) value,  $M$ , since it is only observed a time  $2\sigma t$ , when  $\Phi=1.08$ .

3) *Observation Instant at Effective Distance for “Complete Mixing” Condition*

An approximate, commonly referred concept when a physical condition is reached, in a statistical sense, is the “effective value” of the parameter, which corresponds to the observed value multiplied by  $\sqrt{2}$  [13]. In this case, we are using “reference” value as the 95% of Gaussian mass distribution corresponding to  $4\sigma t$  in time. Then, the effective value for this measure is  $\sqrt{2} \cdot 4\sigma t \approx 5.66 \sigma t$ . At this moment, the observer “see” all tracer mass as “available” (Fig. 8).

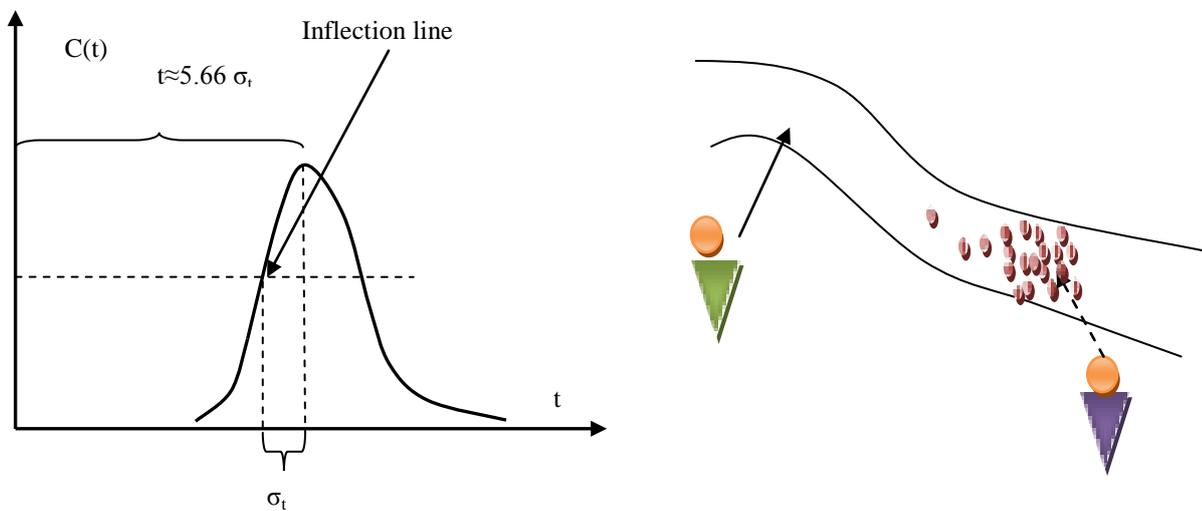


Fig. 8 Tracer observation in “complete mixing” condition

Then, in this case, corresponding to “Complete mixing” condition, it holds

$$\tau = \beta t = \frac{\left(\frac{t}{4\sqrt{2}}\right)\sqrt{\beta}}{\phi} \tag{19}$$

Clearing  $\Phi$ , which in this case is  $\phi_o$ ,

$$\phi_o = \frac{\sqrt{\beta}}{4\beta\sqrt{2}} \approx 0.38. \tag{20}$$

This is a very important result because it gives us a general and accurate procedure to know the “Mixing Distance” for a tracer, when it fills uniformly the cross section. The account of all tracer mass by an observer leads to the well-know relationship of “mass conservation” for discharge calculation, using “area under concentration curve” between  $t_1$  and  $t_2$  [14],

$$Q = \frac{M}{\int_{t_1}^{t_2} c(t)dt} \tag{21}$$

As the authors have shown in [15, 16], the “ergodic principle” may be applied in this case to allow defining a method to know how and when to apply this method. This principle was used first time by L. Boltzmann, who says that in equilibrium, macroscopic averages of a certain function measured with diverse arguments, will tend toward the same value if the function is evaluated with only one argument several times. For the case of a conservative tracer spreading on cross section of flow, when the “Complete mixing” condition is reached the following equation is valid, if approximate transverse equilibrium is

considered in wide direction,

$$\frac{M}{Q \times t} \approx 0.441 \times C_p. \quad (22)$$

In the case of a very large stream, if not enough mass of tracer is injected, a detectable peak concentration,  $C_p$ , cannot be measured and the criterion cannot be applied.

## II. ADVANTAGES OF THE NEW APPROACH

As was pointed out, the new approach brings together thermodynamics and tracer dynamics, allowing handling in a very compact and elegant form the several stages of tracer plume developments. According to this approach, it is necessary to wait a certain time to observe the entire “available” injected tracer mass, which occurs until “Mixing length” is already reached. This is measured by a guiding function  $\phi(X)$ , which tells us how each stage of process is evolving. This sort of description, well-known as “black box” system, typical of Thermodynamics, gives us theories free from contradictions, and presents if “structural” models are used, as in the case of “Dead zone” procedures. In this latter case there are unclear issues derived from a wrong and incomplete interpretation of interaction forces for “trapped” tracer particles in peripheral, low velocity zones of flow.

As was stated, the calculation of this function is very easy from time information of Gaussian tracer curve. One way to verify the accuracy of the procedure is to determine the distance at which  $\phi \approx 0.38$  and then apply “ergodic principle” of Eq. (22), as is explained in the next chapter.

## III. APPLICATION OF THE THEORY TO A LARGE MOUNTAIN RIVER IN COLOMBIA

The scientific team of authors performed several experiments in southern Colombia testing their method, especially in Rio Pance, a city near Cali. Some pictures of the stream are shown in Fig. 9. It also presents the special hardware-software tool named “Inirida Deep Flow”, which takes measurements of two tracers at the same time (Rhodamine WT and common Salt) in real time fashion.



Fig. 9 Views of stream and instrumentation

The instruments include a hand computer, a digital interface and a conductivity probe that has integrated a temperature sensor to correct the concentration value, according to a routine. The operation of equipment is fully graphical as will be shown in subsequent photos. The calibration of measurement procedure is as follows: A. - First the conductivity itself was calibrated by means of standard international norms. For this case, facilities of main environmental agency (CVC) in Cali. B were used. The fluorescence (Rhodamine WT) was calibrated against proprietary standard (Turner Designs, USA). Additionally the device was tested against current meter measurements.

### A. Procedure to Test the New Equations

In the presented experiment, for two pouring, 6.0 and 9.0 Kg of common salt were used as tracer, at a distance of 400 m. The chosen stream is a large mountain river of 20 m in width. The result of first pouring is shown in Fig. 10. The discharge is calculated by two methods: A. Classical method using conservation of mass principle by means of Eq. (21) as is shown in (b) photo, and B. the proposed Eq. (10), and the results are presented in Table 1 and Fig. 10(d) (with  $Q$ = “Caudal” in Spanish). Usually, the two values of  $Q$  and  $Q_a$  are very close, indicating that the device is properly calibrated. Photo (a) in Fig. 10 corresponds to experimental curve with theoretical modulation using Eq. (9). Photo (c) shows  $\phi$  value, which is very near “critical” value of 0.38, then it is reasonable to accept “Complete mixing” condition for tracer in cross section of flow. The second pouring is shown in Fig. 11. This pouring shows the same kind of information as in Fig. 10 but for the second experiment.

**B. Experimental Results**

In Figs. 10 and 11 are the screens of instrument shown with the experimental results.

*1) Numerical Results*

Table 1 shows numerical information from IDF instrument for the two pouring.

TABLE 1 NUMERICAL INFORMATION OF EXPERIMENTS

Distance, X (M)	Mass, M (K)	Mean Velocity Ux (M/s)	$\Phi$	Discharge, Q (M3/s)	Discharge, Qa (area under curve) M3/s	Peak Concentration Cp (Mgr/l)	Peak time to (S)
400	6.020	0.803	0.396	10.8	10.6	2.16	498
400	9.060	0.742	0.374	10.1	9.7	3.88	539
Mean value	-----	0.780	0.39	10.5	10.2	-----	-----

Results of the first pouring are shown in Fig. 10.

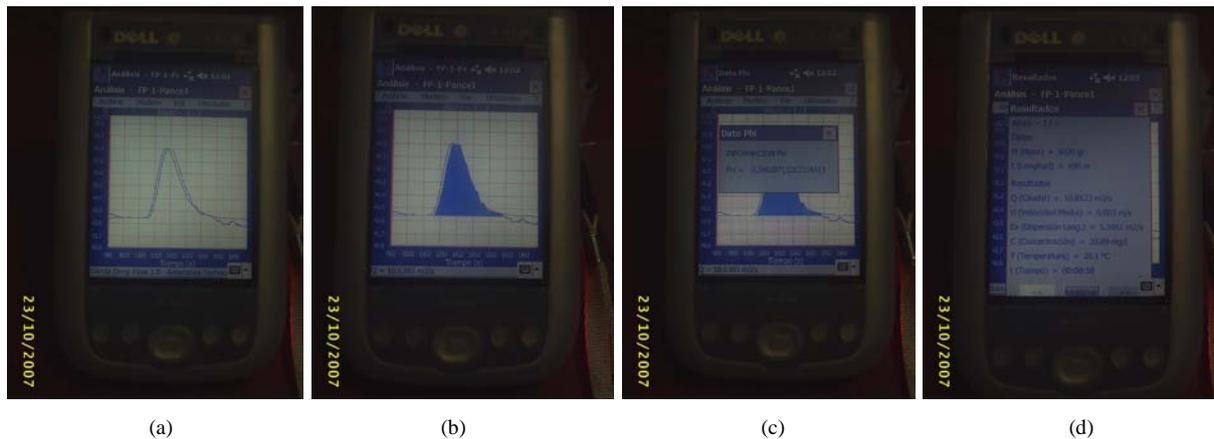


Fig. 10 Screens for first salt pouring

Results of the second pouring are shown in Fig. 11.

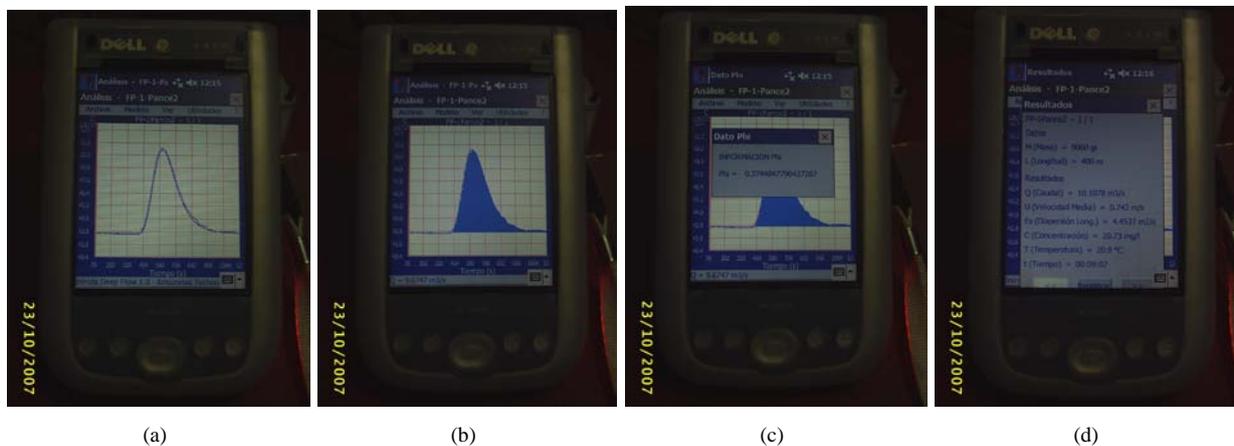


Fig. 11 Screens for second salt pouring

*2) Data Analysis*

*a) First Pouring:*

It has  $\Phi = 0.396$ , a figure near “Complete mixing” condition (approximation of 4%), and the “Mixing distance” is approximately 400 m. This fact is verified by application of Eq. (22) regarding ergodic principle for transverse equilibrium, with data in Table 1.

$$\frac{M}{Q \times t_o} = \frac{6020000}{10800 \times 498} = 1.1 \text{ mgr/l}$$

$$0.441 \times C_p = 0.441 \times 2.16 = 0.95 \text{ mgr/l}$$

In this case, the approximation is 16%.

b) *Second Pouring:*

It has  $\Phi=0.374$ , indicating that “Complete mixing” condition is reached (approximation of 2%), and the “Mixing distance” is 400 m. This fact is also verified by application of Eq. (22), with data shown in Table 1.

$$\frac{M}{Q \times t_0} = \frac{9060000}{10110 \times 539} = 1.66 \text{ mgr/l}$$

$$0.441 \times C_p = 0.441 \times 2.16 = 1.71 \text{ mgr/l}$$

In this case the approximation is 3%.

These results are in good agreement with the presented theory, indicating that  $\phi(X)$  represents accurately the instant in which the tracer fills almost all the cross section, at least with statistical significance. In this way, testing a particular consequence of theory is possible to show that the models proposed are correct, as least in the margin of experimental errors in tracer pouring.

#### IV. CONCLUSIONS

1. A theory was developed to interpret the role of a thermodynamic function  $\phi(X)$  that guides the evolution mechanisms of conservative tracer plumes in streams. This function appears as a coefficient in a definition of mean velocity of flow that links hydraulics with dispersive transport.

2. The aim of this article was to discuss the application of a procedure that does not depend on “structural” concepts about the evolution of tracers, as current theories lead to very complex, difficult to test relationships trying to put the evolution stages as function of “dead zones”.

3. The main focus is on the existence of a state function that guides all related processes. One of its properties is to indicate when the tracer has reached the transversal diffusion along all cross section of flow. In this way, it is easy to understand the several stages of solute evolution in turbulent flows.

4. Two pouring experiments were performed with 6 and 9 Kg of common salt as tracer, in a large mountain river at 400 m of distance in Colombia. In this experiment a function of  $\Phi \approx 0.39$  in average was found, i.e. very near to “Complete mixing” condition of tracer in cross section. The Inirida Deep Flow (IDF) was used as measuring instrument. This is a hardware-software tool, operating in “real time” fashion. This instrument was calibrated following international procedures to get proper metrological specifications. It is remarked that in this field journey the discharge was measured by two independent methods: the conservation of mass principle (area under tracer curve),  $Q_a$ , and a modified Fick’s equation, which includes discharge as inner parameter,  $Q$ . The approximation of these two values was a satisfactory 3%.

5. Applying the ergodic principle relationship to these two pouring experiments, the average approximation was 9%, an acceptable figure regarding the usual statistical dispersion for this kind of experiments of limited number of trials. This fact and the close approximation of  $Q$  and  $Q_a$  allow accepting the validity of theoretical arguments presented here. In this case, the Pance River had a peak concentration,  $C_p$ , large enough to apply ergodic formula. In case of very large rivers, a test of detectability of this parameter would be required. It would happen that tracer mass injected cannot produce a detectable level at measurement point.

6. This approach gives a coherent description of tracer plume evolution allowing highlighting of the main aspects of development in time and space. This issue is important when specialists want to apply quality water modulations.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] J. L. Martin and S. C. McCutcheon, *Hydrodynamics and Transport for Quality Modeling*, Lewis Publishers, Boca Raton, 1999.
- [2] S. C. Chapra, *Surface water quality modeling*, Waveland, LandGrove, 2003.
- [3] P. M. Davis, T. C. Atkinson and T. M. L. “1. Longitudinal dispersion in natural channels; 2. The role of shear flow dispersion and dead zones in the River Severn, UK,” *Hydrology and Earth systems Sciences*, vol. 4(3), pp. 355-371, 2000.

- [4] A. J. Constain and R. Lemos, "Una ecuación de la velocidad media del flujo en régimen no uniforme, su relación con el fenómeno de dispersión como función del tiempo y su aplicación a los estudios de calidad de aguas," *Revista Ingeniería Civil* No. 164, Madrid, CEDEX, pp. 114-135, 2011.
- [5] I. Prigogine and D. Kondepudi, *Modern Thermodynamics*, John Wiley & sons, Chichester, 1999
- [6] A. Constain, "Definición y análisis de una función de evolución de solutos dispersivos en flujos naturales," *Revista DYNA*, Medellín, vol. 79(175), 2012.
- [7] I. Bronshtein and K. Semediaev, "*Mathematics Manual*," Mir Publisher, Moscow, 1973
- [8] A. Einstein, "*Investigations on theory of Brownian movement*," Dover Publishers, N.Y. 1955
- [9] R. Von Mises, "*Probability, statistics and Truth*," Dover Publications, New York. 1957.
- [10] A. Constain, "A thermodynamic view of tracer plume evolution: complete mixing condition evaluation," *EPI*, vol. 50, 2013
- [11] A. Constain, R. Lemos and O. F. Agredo, "Applications of a non-uniform Flow velocity equation in streams," *River Flow Proceedings*, vol. 1, pp. 135-142, 2002.
- [12] L. Pogliani and M. N. Berberan-Santos, "Constantin Carathéodory and the axiomatic thermodynamics," *Journal of Mathematical Chemistry*, vol. 28(1-3), 2000.
- [13] L. D. Landau, A. J. Akhiezer and E. M. Lifshitz, "General Physics, Mechanics and Molecular Physics," Pergamon Press, 1967.
- [14] F. A. Kilpatrick and E. D. Coob, *Measurement of Discharge Using Tracers*, USGS, Book 3, Chapter A16, Washington, 1985.
- [15] A. Constain, "Verificación del principio ergódico para un proceso de dispersión en flujos," *Aqua-LAC, UNESCO*, vol. 4(1), pp. 19-29, Mar. 2012
- [16] A. Constain and D. Mesa, "Nuevos métodos para la modelación de la calidad del agua usando trazadores," *Jornadas Internacionales del agua*, 2013