

Basic Theory and Simulation Tools

A thermodynamic view of tracer plume evolution: Complete mixing condition evaluation

A. Constain^a

Amazonas Technologies Inc. Parquesoft, Cali, Colombia

Abstract. One of most controversial issues of modern tracer theory is the “complete mixing condition” because of its importance in evolution of hazardous solutes in natural flows. This condition named also as “Mixing length” measures the distance from pouring point when tracer particles have spread uniformly on cross section of stream. The point is that until now there is no rational, complete and easy to use formula to calculate it. Rather, this condition is evaluated mostly by means of empirical relationships; among them Ruthven’s is one of current usage. Also there are statistical methods that applied by software packages allow to characterize this condition. However a new focus on this issue is important, because is necessary to tie together, generality, easiness and accuracy. This paper puts on discussion a thermodynamics method to understand when a tracer is in this remarkable condition. Herein it is developed the conditions when this method may be applied. It is shown also how the resulting formula is convergent with Ruthven’s equation. An experimental demonstration is presented.

1. INTRODUCTION

The fact that most of real human level processes are *all* irreversible gives a special character to those physical events: Thermodynamics allow describing them in a simple and comprehensive way with a surprisingly small degree on details of process. [1] This is especially true for a key totally irreversible phenomenon as Diffusion of solutes in water flowing. Then is possible to use some thermodynamics concepts to develop a useful approach to calculation of the so-called “Complete mixing condition” in which tracer has spread in all cross section of flow.

2. STREAM MEAN VELOCITY AND DIFFUSION VELOCITY OF A TRACER

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 diffusion velocity. First one, U , characterizes the average advective one-direction motion of flow. Second one, V_{diff} , characterizes two-direction macroscopic motion of tracer plume. Figure 1.

There is a significant difference among them. Advective stream velocity is a parameter which module value may be repeated several times, whereas it is dependent upon hydraulic condition of considered trench. Diffusive velocity of plume tracer however cannot repeat in module value because is a characteristic of irreversible diffusion process. When the chemical equilibrium is broken due to pouring, a specific mechanism should appear to restore it accord with *Le Chatelier* principle [2], so diffusion velocity is the way in which the tracer tends to spread toward equilibrium as last stage.

Then U velocity is not a state function while V_{diff} has this nature.

However, there is a certain relationship among them. An increase of advective velocity should lead generally to

^a e-mail: alfredo.constain@amazonastech.com

an increase of dissipative factors (by means of turbulence generated by roughness) and then to a different pattern of diffusion velocity, then it is possible to define a state function, Φ , in the following way [3,4]:

$$\phi = \frac{V_{diff}}{U}. \quad (1)$$

It is interesting to develop a specific definition of this function. First one may define a characteristic displacement of diffusion (one variance), Δ using the Brownian one-dimension model, with τ corresponding characteristic time and E the Longitudinal dispersion coefficient.

$$\Delta = \sqrt{2E\tau}. \quad (2)$$

As Nobel Prize winner I. Prigogine [5] had pointed out extensively studying Poincare’s chaotic processes, this model is more general than usually is taken because not only free (thermal) independent molecular motions are Brownian but also potentially (dependent) molecular motions evolve (transmitting disorder) with same law. Now, V_{diff} may be defined as:

$$V_{diff} = \frac{\Delta}{\tau}. \quad (3)$$

Hence:

$$U = \frac{1}{\phi} \sqrt{\frac{2E}{\tau}}. \quad (4)$$

Clearing Φ function in this equation and putting it as differential superposition expression:

$$d\phi = \left(\frac{\partial \phi}{\partial E} \right) dE + \left(\frac{\partial \phi}{\partial U} \right) dU. \quad (5)$$

Using Eq. (4) it is easy to verify that $d\Phi$ is an exact differential accordingly with following equation:

$$\left(\frac{\partial \left(\frac{\partial \phi}{\partial U} \right)}{\partial E} \right) = \left(\frac{\partial \left(\frac{\partial \phi}{\partial E} \right)}{\partial U} \right). \quad (6)$$

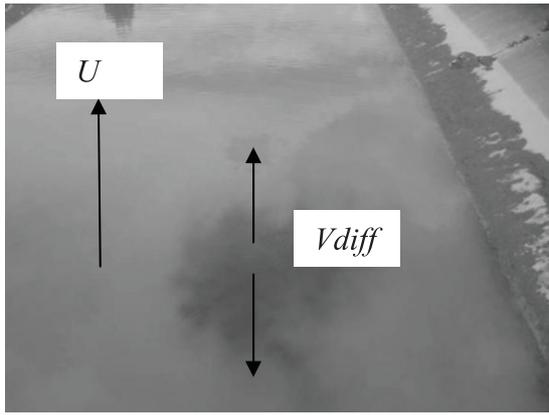


Figure 1. Advective and diffusive velocities in a stream.

And then:

$$\oint_C d\phi = 0. \tag{7}$$

That is, Φ is a state function as was defined before, and it describes thermodynamic evolution of plume from dissipation point of view in the same way that Chezy's coefficient, C , characterizes friction effect in uniform flow regime, as function of energy line slope, S , and hydraulic radio, R .

$$U = C\sqrt{RS}. \tag{8}$$

Here it is interesting to see how the two equations for mean velocity of flow have same structure, following Occam's principle in the sense that Nature does not multiply entities describing same thing.

3. AN APPROACH TO IRREVERSIBLE EVOLUTION OF TRACER PLUME IN FLOW

When a closed system (which don't interchange mass with its environment) evolves with temperature and pressure constant there is a function that describes thermodynamic evolution of the system: Gibbs potential, G [6].

This function represents the part of enthalpy, ΔHo (formation heat in Hess's scheme) that can be converted in work and then its curve defines the evolution of available energy within system in such way that its decrement $-\Delta H = \Delta Ho$ indicates how initial energy, ΔH is spent until equilibrium is reached. Figure 2.

Loss of available energy in an irreversible process is related with the increase of entropy (second thermodynamic principle) and then with the way in which the system loss free degrees, regarding the statistical approach to this subject. So, the curve of decreasing G reflects when a key event appears in plume evolution, as for example when tracer has spread along all cross section of flow, ie: the well-mixing condition.

There is a consideration regarding practical calculation of Gibbs potential in this case: it is not easy to do in the case of tracer evolution. So it seems more easy to use $\Phi(X)$ function which presents the same thermodynamic properties that G but is more specific. [7]. Figure 3.

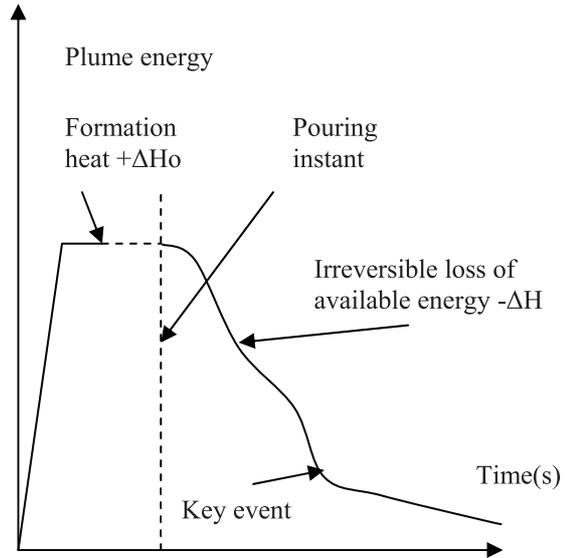


Figure 2. Tracer plume Energy evolution in flow.

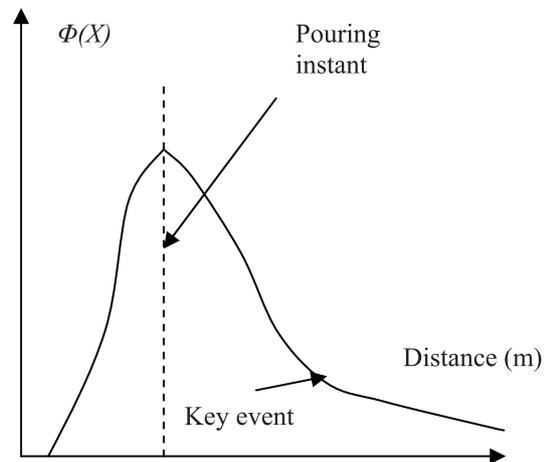


Figure 3. Specific function describing tracer evolution.

In this case, to know when a tracer has reached the *complete mixing condition* is enough to know when the $\Phi(X)$ function takes a specific value [8].

4. A SPECIFIC VALUE FOR $\Phi(X)$ FUNCTION IN "COMPLETE MIXING CONDITION" FOR EVOLUTION OF TRACER PLUME IN FLOW

When tracer plume reaches well-mixing condition it means also that lateral diffusion vanishes also completely. So, chemical equilibrium is reached in Y axis. Figure 4.

If the system is isobaric and isothermal also, then there is thermodynamic equilibrium in this axis. If this condition holds, then also processes in this coordinate are stationary. Hence here is possible to apply the well know *ergodic principle* to the system. This principle has several versions whereas is one of most fertile in physics. One of them very useful to the faced problem is presented in the following way [9]: For a steady random variable, $Y(x)$, the mean value is constant, then the outcomes for different argument values: $Y(x_1), Y(x_2) \dots, Y(Xn)$

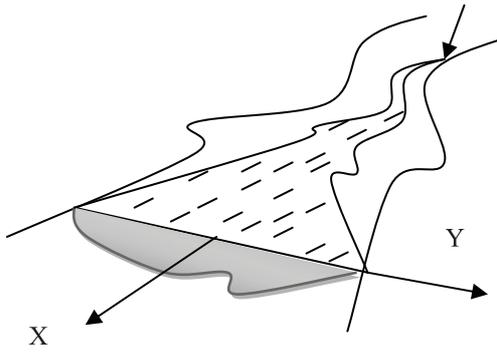


Figure 4. Complete mixing condition for tracer in flow.

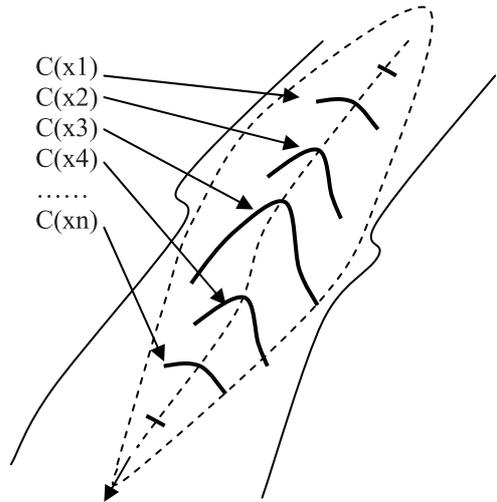


Figure 5. Concentration distribution based in first set.

and the outcomes for different functions with the same argument: $Y1(x), Y2(x) \dots, Yn(x)$ are equivalent, leading for the same mean value.

This principle means that when tracer has reached *well-mixed condition* there are two different concentrations that are convergent, being useful to know the key value for $\Phi(X)$ function in Mixing Length, Φ_o .

To apply this approach is convenient to define first set of concentration along all volume of tracer where concentrations are peak values for different X coordinate. Figure 5. Second set may be defined conveniently as different concentrations (function of Y coordinate) in a specific distance, X_o , where is the peak value. Figure 6.

If we extent the calculation to a infinite number of values for two sets, it states as follows:

$$\bar{C}_x = \lim_{n \rightarrow \infty} \frac{\sum C_p(x_n)}{n} \quad (9)$$

and

$$\bar{C}_y = \frac{1}{y_{lim}} \int_0^{y_{lim}} C(y) dy. \quad (10)$$

It is easy to see that firsts mean concentration along all plume is:

$$\bar{C}_x \approx \frac{M}{Q \times t_o}. \quad (11)$$

Here M is the tracer mass poured in injection point (considering conservative solute), Q the discharge of flow

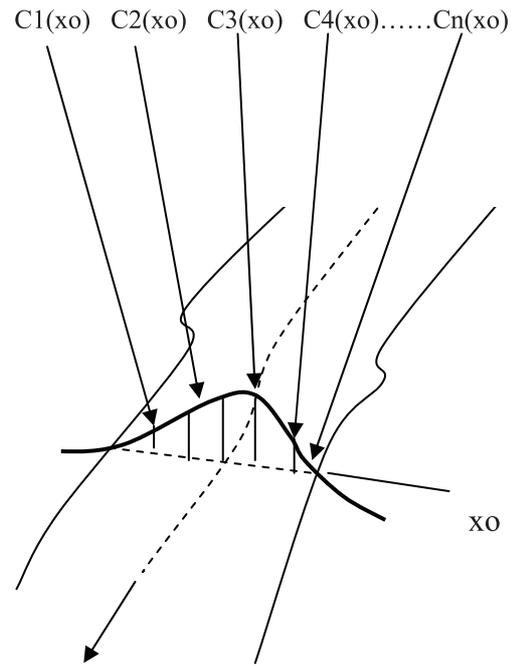


Figure 6. Concentration distribution based in second set.

and t_o be the time spent from injection point to Mixing length.

For second mean concentration is necessary to use *error function* to integrating the expression. Here y_{lim} is a characteristic value of transverse coordinate related to inflection points of Gaussian bell form.

$$\bar{C}_y \approx 0.441 \times C_{po}. \quad (12)$$

Here C_{po} is peak concentration value in X_o , the Mixing Length. Hence, using ergodic principle:

$$\bar{C}_y \approx \bar{C}_x. \quad (13)$$

This means that:

$$\frac{M}{Q \times t_o} \approx 0.441 \times C_{po}. \quad (14)$$

Now, to relating this expression with $\Phi(X_o)$ it is necessary to use a modified Fick's equation presented by author in a companion paper.

$$C(x, t) = \frac{M}{Q \times \phi \times t \times \sqrt{2\pi\beta}} e^{-\frac{(X-Ut)^2}{2\beta\phi^2 U^2 t^2}}. \quad (15)$$

Here $\beta \approx 0.215$ from Poisson's analysis of plume evolution. Then, peak value for well-mixed condition is:

$$C_{po} \approx \frac{M}{Q \times \phi_o \times t_o \times 1.16}. \quad (16)$$

Replacing Eq. (16) in Eq. (14) it states:

$$\phi_o \approx \frac{0.441}{1.16} \approx 0.38. \quad (17)$$

This result means that, in every case, tracer plume spreads along cross section of flow when Φ takes the approximate value 0.38.

5. A COMPARISON OF DEVELOPED SPECIFIC VALUE OF $\Phi(X)$ FUNCTION FOR “COMPLETE MIXING CONDITION” AND RUTHVEN’S RELATIONSHIP

In a science field, when a new formula is developed one of first requirements is that its results being convergent with well accepted formulas. Then new approach should be compared with a well established relationship. Unfortunately due to huge spread of semi empirical formulas about tracer theory, there is not a unique, wide accepted one. However, an approximate definition for Mixing Length due to Ruthven has been very used along the years with satisfactory results:

$$X_o \geq 0.075 \frac{U \times W^2}{\varepsilon_y} \tag{18}$$

Here W is the mean transverse distance (wide) of flow and ε_y the transverse diffusion coefficient. Now, this equation is for a centerline injection; for an injection at the side of stream width has to be multiply by two and coefficient should be multiplied by 4, remaining:

$$X_{so} \geq 0.3 \frac{U \times W^2}{\varepsilon_y} \tag{19}$$

To analyze the issue is necessary to write concentration distribution in transverse coordinate as follows.

$$C(y, t) = C_y = \frac{M}{Qt\phi 1.16} e^{-\frac{(y)^2}{4\varepsilon_y t}} \tag{20}$$

It should be noted that we use C_p value as is defined in Eq. (15) due to continuity principle between longitudinal and transversal functions. Now, clearing the value for transverse diffusion coefficient and reordering factors:

$$\varepsilon_y = \frac{1}{Ln \left(\frac{\left(\frac{M}{Qt\phi} \right)}{C_y \times \phi \times 1.16} \right)} \times \frac{y^2}{4t} \tag{21}$$

For well-mixed condition in which there is thermodynamic equilibrium in Y axis, tracer concentration value may be replaced by more probable value which in turn is the mean value, accord with Darwin-Fowler principle in statistical mechanics [10].

$$C_y \approx \bar{C}_y \approx 0.441 C_{po} \tag{22}$$

Then

$$\varepsilon_y = \frac{1}{Ln \left(\frac{(0.441 C_p)}{0.441 \times C_p \times \phi_o \times 1.16} \right)} \times \frac{W^2}{4t} \tag{23}$$

Hence:

$$\varepsilon_y = \frac{1}{Ln \left(\frac{1}{0.38 \times 1.16} \right)} \times \frac{W^2}{4t} \tag{24}$$

And, replacing time by key distance divided by velocity

$$\varepsilon_y \approx 1.22 \times \frac{U \times W^2}{4X_o} \tag{25}$$

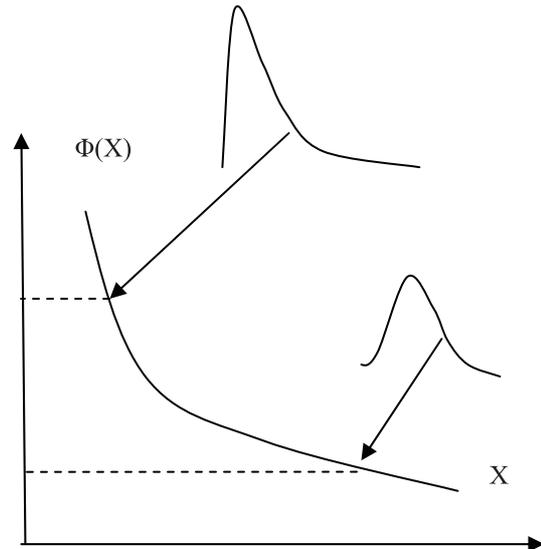


Figure 7. $\Phi(X)$ function as measure of skewness of tracer curve.

Finally:

$$X_o \approx 0.305 \times \frac{U \times W^2}{\varepsilon_y} \tag{26}$$

This result is very close to Ruthven’s equation for side injection.

6. SOME CONSIDERATION ABOUT FUNCTION $\Phi(X)$

Beside the thermodynamic considerations discussed in this article about $\Phi(X)$ there are some characteristics of this function that deserve our attention. First, if is accepted that skewness of tracer curves in real life is due to a kinematic composition (Galilean transformation) between one-direction mean flow velocity and two-direction diffusion velocity, then ratio of these two kind of velocities is a measure of the observed skewness. Figure 7.

Upper curve shows a higher degree of skewness corresponding to a higher value of $\Phi(X)$ function. Lower curve by the other hand has a lower degree of skewness, corresponding to a lower value of function. Second, experimental values of $\Phi(X)$ have been encountered as high as 0.8 and low as 0.15 in tracer measurements done by author. Third, always is used decreasing edge of function curve. In practice never has been used other zone of curve. Figure 8. For theoretical reasons it seems that this function never goes to unity value, and never have been observed such value.

To measure this function, author’s special hardware-software tool has been developed, named INIRIDA DEEP FLOW (IDF). Beside this routine, the package that operates in real time fashion, offers also a filter function to clean experimental curve and a discharge calculation routine based on conservation of mass principle. Figure 9. In this Figure it is shown a set of screens of this tool with those mentioned aspects. Upper photo shows cleaned experimental curve with theoretical modelation on it. Middle photo shows a particular calculation of $\Phi(X)$

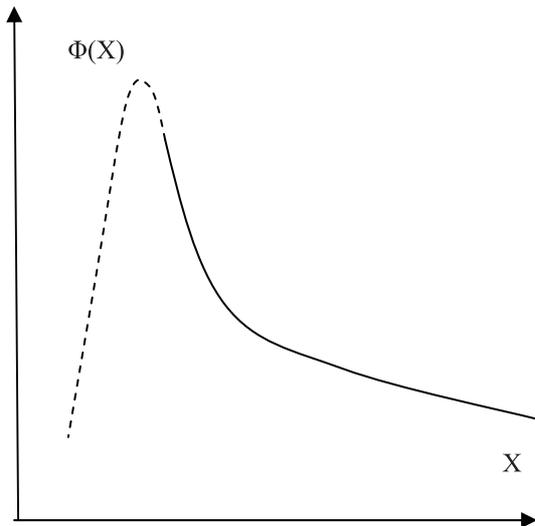


Figure 8. Used zone of $\Phi(X)$ curve in practice.

function with a value of 0.74 meaning that tracer curve is in the so called “convective” period in which there is a significant lateral diffusion yet. There is also a warning label in Spanish indicating that key value $\Phi \approx 0.38$ is not reached yet and that injection distance has to be enlarged. Lower photo shows the result of discharge calculation using “area under curve” procedure.

The set of screens have been taken in an experiment done at 10 m far from injection point, using common salt as tracer. Measurement task is shown in Figure 10.

This is a small stream of 0.042 m³/s of discharge and a mean flow velocity of 0.11 m/s. Here it was taken the following $\Phi(X)$ curve for twelve pouring experiments in a trench of 120 m. with a mean width W of 1.5 m. Figure 11.

In this curve is easy to see that well-mixed condition for tracer plume is about 72 m distance in which $\Phi(X) \approx 0.38$ as key value.

7. AN EXPERIMENTAL APPLICATION OF “COMPLETE MIXING CONDITION” BY MEANS OF $\Phi(X) = 0.38$ RELATIONSHIP

Author’s research team had worked several field journeys between 2005 and 2009 to test ergodic principle applied to tracer plume evolution using IDF tool [11]. As a representative example of these verifications following is shown experiment at $X = 70$ m for journey in the small stream documented before. Figure 12.

Selection of this particular result is obvious because mixing length is supposed about 72 m and then in this case the numerical values may be applied to verify theoretical conjectures.

First photo shows experimental curve and its modelation with Fick’s modified equation of Eq. (15) adding background concentration value. Second photo shows discharge calculation using mass conservation principle. Tracer mass was 200 grams of NaCl ionic tracer.

Data for this particular experiment is in Table 1.

It should be noted in data of this Table that discharge calculated using Fick’s modified equation, Q , and mass

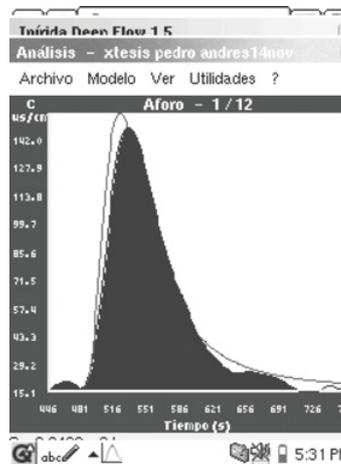
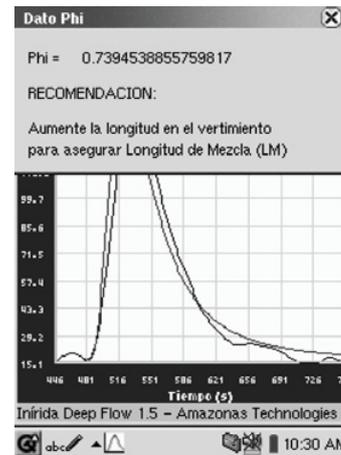
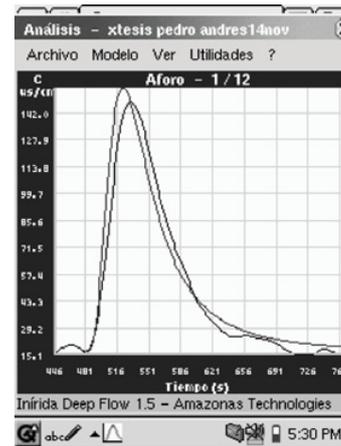


Figure 9. IDF screens shown filter, modelation and calculation routines.

conservation principle, Qa , are very close numerically with a relative error less than 1%.

Now, the ergodic principle applied to concentrations of tracer pouring at well-mixed distance says that:

$$\frac{M}{Q \times t_o} \approx 0.441 \times C_{po}. \quad (27)$$

Replacing numeric values:

$$\frac{200g}{45l/s \times 583.3} \approx 0.441 \times 16.9mgr/l. \quad (28)$$



Figure 10. Experimental usage of hardware-software IDF tool in a small stream.

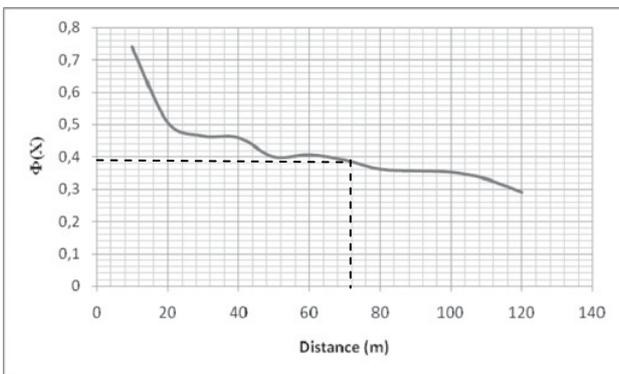


Figure 11. $\Phi(X)$ curve for a 12 tracer pouring experiments.

Table 1. Data for experiment No.7.

Data	Value
Xo	70 m
Cpo	16.9 mgr/l
U	0.120 m/s
Q	0.0450 m ³ /s
Qa	0.0443 m ³ /s
to	583.3 s
Φ_o	0.39
W	1.5 m

Left equation member is 7.62 mgr/l while right member is 7.45 mgr/l, or in other words: key concentrations differs one to each other in a relative error less than 3%. This means that for $X \approx 70$ m. There is well-mixed condition for tracer in considered flow. This event occurs at $\Phi \approx 0.38$ as was stated in theoretical developments.

Finally, using this condition one may calculate the transverse diffusion Coefficient for this reach.

$$\varepsilon_y \approx 0.305 \times \frac{U \times W^2}{X_o} \approx 1.14 \times 10^{-3} (m^2/s). \quad (29)$$

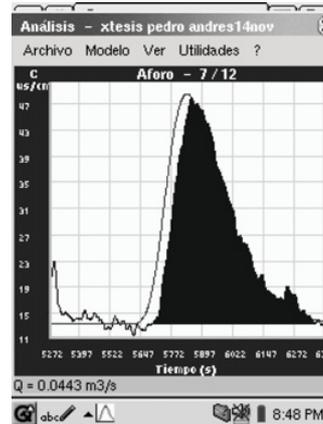
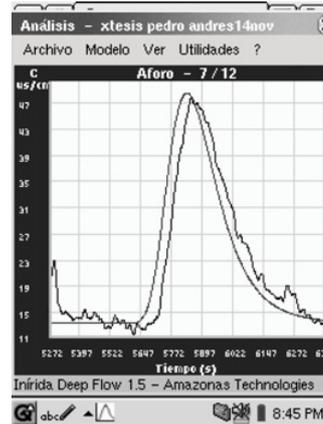


Figure 12. IDF screens shown filter, modelation and calculation routines for $X = 70$ m. Near Mixing Length distance.

8. REMARKS AND CONCLUSIONS

1. It is possible to define a general and useful formulation of tracer plume evolution in an isothermal and isobaric flow by means of Gibbs function. This function describes how is spent the formation energy of solute in a turbulent environment toward the equilibrium. More restricted but easier to use is a special state function, $\Phi(X)$, which is related with a mean velocity equation. When there is the so called “well-mixed condition” (tracer spread on all cross section of flow) this function has the value 0.38.
2. This approach is convergent with classical ones, as for example Ruthven empirical equation. Using the condition $\Phi_0 \approx 0.38$ for Mixing Length, X_0 , may be calculated the Transverse diffusion Coefficient.
3. Current methods usually limit two different stages in tracer evolution: “Convective” period in which there is significative transverse diffusion and “Diffusive” period in which only is longitudinal dispersion. First period occurs in earlier moments of plume transport and currently is supposed that tracer curves are much skewed, lacking a formal representation in Gaussian form. Within the theory presented by author, it is assumed that this kind of asymmetry is not a real but a virtual effect, which allow accepting this kind of curves like Gaussian in every moment.
4. Theory presented by author converges close to Ruthven’s equation.
5. This methodology allowing to do solute fate studies since the very early moment of evolution, avoiding a major drawback in state of the art methods.

Author has been supported in his researches by Colombian government small companies’ agency (FOMIPYME), by

Universidad de la Salle and by Dr. Edgard Holguin, Universidad de los Andes (Bogota, Colombia) former researcher. Also Amazonas Technologies company in Cali. Colombia.

References

- [1] R. Meyer, *Introduction to mathematical fluid dynamics*. Dover publications, New York (1982)
- [2] I. Prigogine, and D. Kondepudi. *Modern Thermodynamics*. John Wiley & Sons. New York (1998)
- [3] A. Constain. Svedber’s number playing a main role in diffusion processes. (to be published) (2011)
- [4] A. Constain. Is storage mechanism in Dead Zone model violating second principle? (to be published) (2011)
- [5] I. Prigogine. *El fin de las certidumbres*. Taurus, Bns As (1997)
- [6] M.W. Zemansky. *Heat and thermodynamics*. Mc Grw-Hill, New York (1967)
- [7] A. Constain, A. Carvajal and J. Carvajal. Accurate measurement of discharge using Rhodamine WT. IAHR Intl. Congress, Vancouver (2009)
- [8] A. Constain, O. Agredo and J. Carvajal. Applications of a new mean flow velocity equation in streams. River Flow, Lovaine la neuve (2002)
- [9] V.S. Pugachev. *Introduction to Probability theory*. Nauka Editors, Moscow (1973)
- [10] H.J. Morowitz. *Entropy for biologist: An introduction to thermodynamics*. Academic Press, New York (1971)
- [11] Fomipyme project final report (internal circulation). Bogota, Colombia (2009)