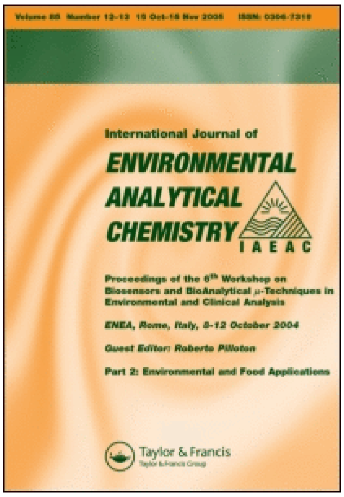

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Hydraulic parameters and statistical residence time distribution moments correlations-a lysimeter study for pesticides mitigation

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Hydraulic parameters and statistical residence time distribution moments correlations – a lysimeter study for pesticides mitigation

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A lysimeter consisting of small tanks containing filtering solid mass is used to better understand and optimise constructed wetlands. The residence time distribution (RTD) representing the characteristics of a lysimeter is an essential tool for evaluating the hydraulic efficiency for optimal constituent removal. The moments of RTD function are used to determine the performance of a lysimeter, but the calculation process can be complicated. In this study, we focus on the correlations of some key experimental hydraulic parameters including the moments of RTD function. The tracer solution of sodium chloride was injected into the lysimeter to investigate hydraulic parameters affecting RTD characteristics. Tracer distribution at the outlet was measured and recorded using a conductometer with varying flow rates and different outlet heights during five independent experiments. Results indicate that the RTD moments and other hydraulic parameters which can be directly calculated or observed are strongly correlated. Understanding such results will help in the design and management of lysimeter and will facilitate further lab or field studies.

Keywords: correlation; constructed wetland; lysimeter; RTD moments; tracer experiment

1. Introduction

Constructed wetlands are utilised for treating wastewaters from domestic and industrial sources. The residence time distribution (RTD) is widely used in the design and management of constructed wetlands [1]. In this study, RTD moments are used to characterise the lysimeter's hydraulic behaviour. A pulse of a non-reactive chemical tracer dissolved into a lysimeter inlet is used to measure the RTD. Ideally, a lysimeter exhibits plug flow, in which water and the tracers run uniformly and without dispersion from inlet to outlet. If a tracer pulse is added to an ideal lysimeter inlet, all of the tracers will exit at the same time defined as the residence time. But in constructed wetland, no similar circumstances prevail; there is neither a plug flow nor a complete mixing. A practical flow has different flow path lengths, flow velocities, and mechanisms of diffusion and mixing, causing a distribution of residence times, an RTD [1]. When a tracer pulse is introduced into a non-ideal lysimeter, the outflow tracer concentration is a RTD reflecting the

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dispersive nature of the lysimeter. The effects of these non-ideal flow patterns on pollutant reduction can be important. Fast-moving water parcels interact weakly with the sediments and leave the lysimeter with little chemical and biological reaction; slow-moving parcels have a stronger interaction, and yield a greater reaction. These two parcels form a flow with the intermediate reaction with the microorganism in the sediments for diminishing the pollutants. RTD analysis has been developed to more accurately improve the lysimeter model, leading to a better management and design.

In order to study treatment potentialities to mitigate non-point source pesticide pollution in constructed wetland systems, the European LIFE ENVIRONMENT Project Artwet (LIFE 06 ENV/F/000133) will implement mitigation solutions at six demonstration and experimental sites (http://www.artwet.fr/artwet/). The project includes the construction of lysimeters at Colmar, France. The aim of the prototype installation is to develop a process of treatment of surface waters contaminated by pesticides. The principle of remediation is based on association of microorganisms, plants and sand within a vertical flow sand filter.

Previous studies on vertical or horizontal flow constructed wetland have been consisted on tracer experiments in order to estimate the RTD [2–6]. But the correlations among the hydraulic parameters concerning RTD analysis have not been effectively studied, especially in a lysimeter. This study proceeded in a range of hydraulic conditions that affect RTD stability. By performing tracer studies during hydraulic manipulation of a lysimeter with different flow rates and outlet heights for five experiments, this study explores the correlations between the important hydraulic parameters which influence the characteristics of an RTD.

1.1 *Important hydraulic parameters*

A raw RTD can be measured by adding a pulse of tracer into the system and then measuring the tracer concentration at the outlet as a function of time. Monitoring the system outlet for the tracer concentration, $C(t)$, allows the concentration to be plotted as a function of time, t, where t is the elapsed time since the tracer injection (Figure 1). The residence time distribution function, commonly represented by $E(t)$, is:

$$E(t) = \frac{C(t) \cdot Q(t)}{M} \tag{1}$$

where $Q(s)$ is the flow rate of the system, M is the total mass of tracer injected in the lysimeter. Although tracer degradation is avoided, some loss of tracer is inevitable. In this study, the mass M into Equation (1) is substituted by M_{out}:

$$M_{\text{out}} = \int_0^{\infty} Q(t) \cdot C(t) \cdot \mathrm{d}t \tag{2}$$

where M_{out} is the amount of tracer to exit the lysimeter.

The ratio of the exit mass, M_{out}, to the added mass, M_{in}, was calculated to determine the tracer recovery. The inevitable tracer losses are neglected here so that $M_{\text{out}} \cong M_{\text{in}}$.

When using functions such as $E(s)$ to compare RTDs, qualitative comparisons are obtained by plotting the curves together, and quantitative comparisons are made with statistical measurements. Such measurements include the mode, the zeroth and first moments about the origin, and the second, third and fourth moments about the mean [7].

The mode is the time to the peak concentration, the peak time. For example, in a perfectly stirred system, the mode is zero, and in a plug flow system, the mode is the nominal detention time. By defining V_{sys} as the volume of fluid in the system, the Q_{sys} as the system volumetric flow rate, the nominal detention time is:

$$\tau = \frac{V_{sys}}{Q_{sys}} \tag{3}$$

The moments of the normalised RTD functions $M_i(E)$, $(i = 0, 1, 2, 3, 4)$ for zeroth, first, second, third and fourth order are well known and briefly described in [8].

The zeroth moment about the origin is the integral of the RTD function. For steady-flow systems, the zeroth moments of the functions $E(t)$, is equivalent to the fraction of the tracer recovered mass. According to Equations (1) and (2), $M_0(E)$ is always unity. The first moment, $M_1(E)$, about the origin is the centre of balance of the function or the centroid of the RTD, also known as the mean residence time. The second moment about the mean is the variance which provides a measure of the spread of the curve. The third and fourth moments about the mean characterise the asymmetry and the flattening of the curve.

The minimum travel time was also calculated as a characteristic of the RTD that identifies short-circuiting. The minimum travel time was defined as the shortest time of travel from the inlet to the outlet, determined by the fastest flow paths through the wetland. Theoretically, this is the elapsed time between the introduction of tracer at the inlet and the detection of tracer at the outlet.

The definition of the concentration of tracer at the inlet is introduced for further calculation. The concentration of the tracer at the inlet is the concentration of the tracer in the water above the filtering solid mass (Figure 1),
where

- Q, flow rate of the system;
- C_i, background noise;
- C_0, concentration of the solution of tracer;
- V_0, volume of the solution of tracer;
- V_1, volume of the water above the filtering solid mass;

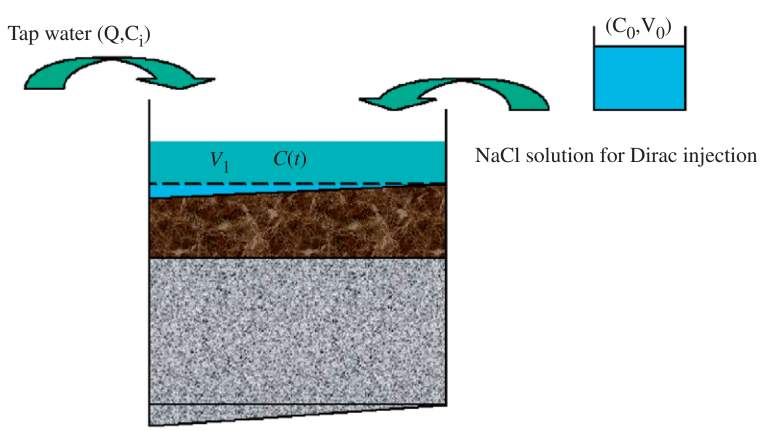

Figure 1. Protocol of the tracer injection.

$C(t)$, concentration of tracer at the inlet;
m, total masse of the tracer in the water;
V_t, total volume $= V_1 + V_0$;
C_{init}, initial concentration in the water;
$C_e(t)$, real concentration at the inlet.

$$\frac{\mathrm{d}m}{\mathrm{d}t} = -Q \times (C(t) - C_i) \tag{4}$$

$$m = V_t \times C(t) \tag{5}$$

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \frac{\mathrm{d}(V_t \times C(t))}{\mathrm{d}t} = C(t) \times \frac{\mathrm{d}V_t}{\mathrm{d}t} + V_t \times \frac{\mathrm{d}C(t)}{\mathrm{d}t} \tag{6}$$

in a steady state system,

$$\frac{\mathrm{d}V_t}{\mathrm{d}t} = 0,$$

according to Equations (4) and (6)

$$C(t) = K \times \exp\left(-\frac{Q}{V_t} \times t\right) + C_i \tag{7}$$

$$C(t = 0) = C_{\text{init}} \quad \text{hence } K = C_{\text{init}} - C_i \tag{8}$$

$$C_{\text{init}} = \frac{M_t}{V_t} = \frac{V_1 \times C_i + V_0 \times C_0}{V_1 + V_0} \tag{9}$$

using Equation (8), Equation (7) becomes:

$$C(t) = \left[(C_{\text{init}} - C_i) \times \exp\left(-\frac{Q}{V_t} \times t\right)\right] + C_i \tag{10}$$

By taking away the background concentration, so the real tracer concentration at the inlet is:

$$C(e) = C(t) - C_i$$

$$C_e(t) = (C_{\text{init}} - C_i) \times \exp\left(-\frac{Q}{V_t} \times t\right) \tag{11}$$

With the knowledge of the concentration of the tracer at the inlet, the definitions of time of homogenisation and capacity of storage, which are two important hydraulic parameters for characterising the performance of the lysimeter, can be introduced in this study. Time of homogenisation is the moment when the tracer's concentration at the inlet equals the tracer's concentration at the outlet. Theoretically, the concentration of the tracer at the outlet has the maximum value at this moment because of the feeding water which continuously dilutes the fluid. The capacity of storage is the maximum mass of pollutants captured in the filter, which is the difference in the concentrations at the inlet and the outlet of the filter. The time of homogenisation is also the moment when the

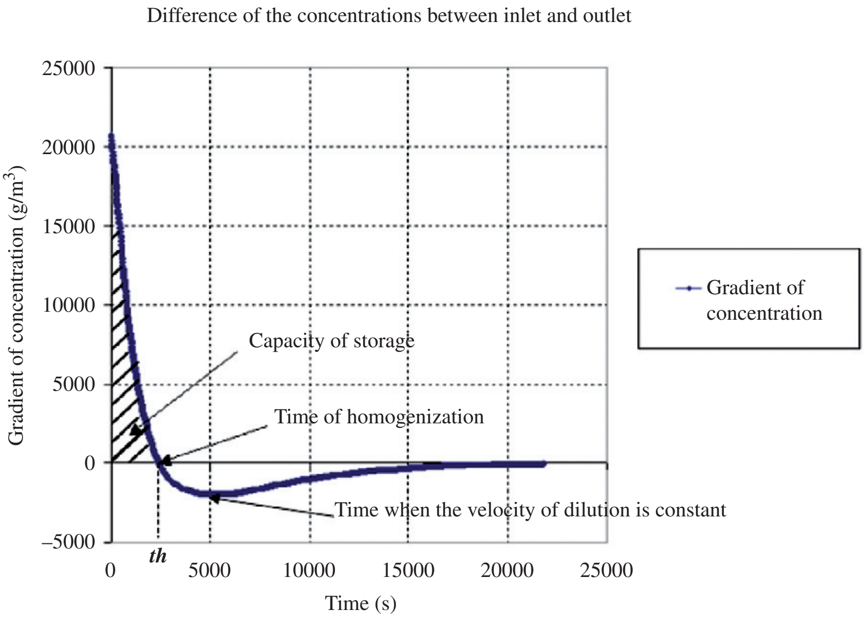

Figure 2. Three parameters presented in the curve of the difference of tracer's concentration between inlet and outlet of the filtering solid mass.

capacity of storage is reached. The time when the velocity of dilution is constant is the moment when the gradient of concentration reaches its minimal value (Figure 2).

1.2 *Purpose of study*

Series of tracer experiments were run in a lysimeter to elucidate two purposes. First, the experiments will help determine the correlations between the different hydraulic parameters, especially the relation between the moments of RTD function and other hydraulic parameters. Second, they will permit distinguishing the useful and strong correlations to facilitate further research by estimating the parameters according to the strong correlations without any further tracer experiment.

2. Experimental

2.1 *Site description*

This study was performed during the summer of 2008 in a pilot plant device at Colmar, Alsace, in France. This device consists of 12 tanks (Figure 3) – lysimeters in outdoor conditions made out of the high-density polyethylene (HDPE) avoiding any adsorption of organic or mineral pesticides because of our targets pollutants including glyphosate and diuron. They were filled with three layers: a mixture layer in the top, sand (0–4 mm; 80%) – sediment (< 8 µm; 20%); an intermediate layer of gravel (4–8 mm) in the middle; a layer of gravel (10–14 mm) in the bottom (Figure 4(a)). The lysimeter had an inlet structure that discharged water from a fire hydrant. Flow rate was controlled by the valves on

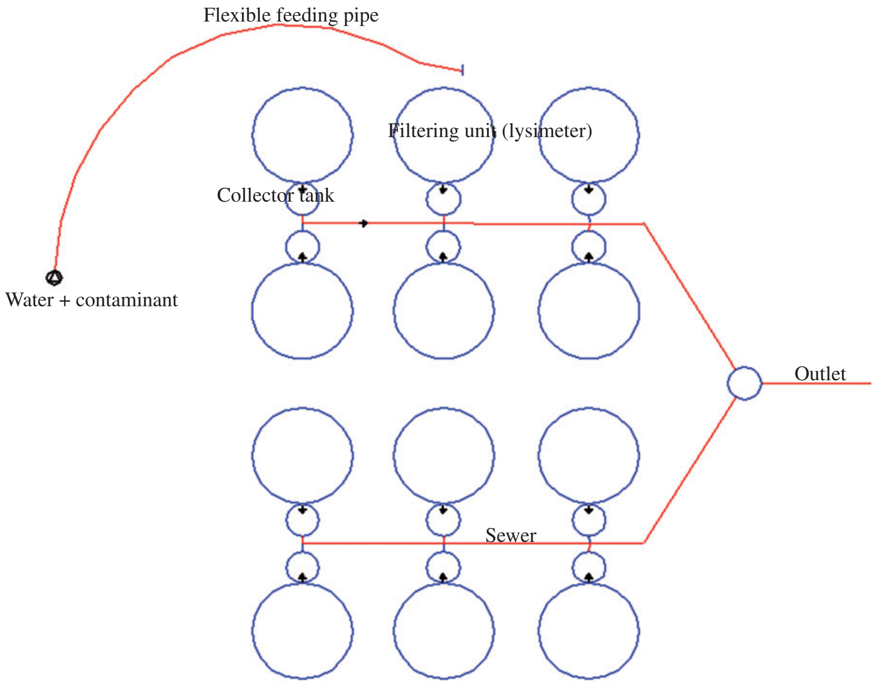

Figure 3. Description of the site.

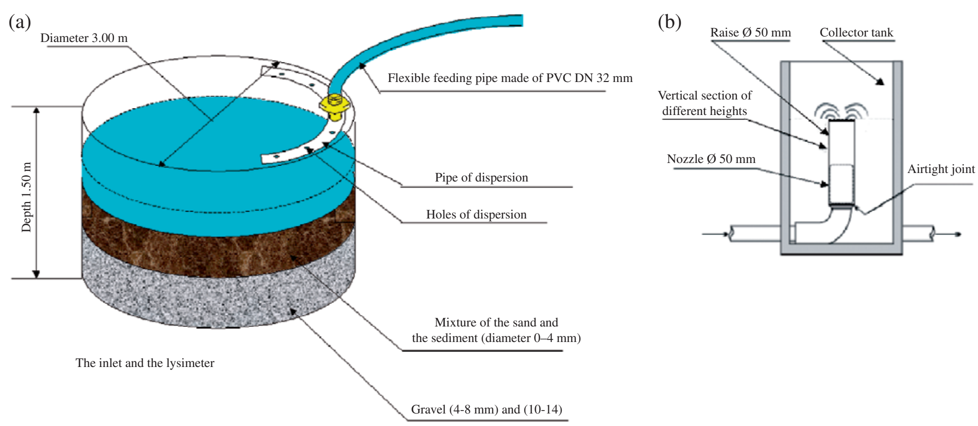

Figure 4. Description of the lysimeter. (a) The inlet and the different layers. (b) The outlet.

the fire hydrant. At the outlet, four different heights were prepared for five independent experiments and were used to control the height of the outlet (Figure 4(b)).

To determine the volume of fluid of the lysimeter for different experiments, the water level in the lysimeter was surveyed. With the dimension data of the lysimeter, the porosity of the filter layers and the survey result, the volume of fluid of the lysimeter was simply calculated.

Table 1. Experimental settings for the five tracer experiments, showing the flow rate and the outlet heights for each tracer experiment.

	Flow rate ($L\,min^{-1}$)	Outlet heights (m)
Experiment 1	34.99	0.66
Experiment 2	16.00	0.78
Experiment 3	8.50	0.70
Experiment 4	13.00	0.66
Experiment 5	12.00	0.78

2.2 *Materials*

The outlet to the lysimeter was monitored by a TetraCon®325 probe (range from $1\,\mu S\,cm^{-1}$ to $500\,mS\,cm^{-1}$) connected to a conductometer MultiLine P4 capable of monitoring automatically the conductivities with a 5 s interval and recording the data in a connected laptop computer.

Sodium chloride (NaCl) was chosen as the tracer, not only because of the simple utilisation with existing instrumentation, but also because of its common use as an inorganic tracer in wetland and lysimeter studies [9]. Besides, NaCl has nearly no adsorption and degradation in the systems regardless of the retention time.

2.3 *Protocol*

To concurrently test the effects of different outlet heights and different flow rates on the RTD, five experiments were performed over a period of four weeks (Table 1). With the valve on the fire hydrant, the flow rates were easily maintained precisely during the experiments and the outlet heights were controlled by different vertical pipes.

Before each tracer experiment, the water flow was allowed to flush the lysimeter until the steady state system was reached. NaCl was added in approximate proportion to the lysimeter volume considering the duration of the injection and the limit of the linear relation between the concentration and the electric conductivity of NaCl : $150\,g\,L^{-1}$ for each experiment. NaCl was added to the inlet by instantly (between 15 and 24 s) pouring 40 L of a mixture of NaCl. At the outlet, the MultiLine P4 equipped with TetraCon®325 probe and the laptop computer monitored the concentration at 5 s intervals. The result of the main hydraulic parameters are shown in Table 2.

3. Results and discussion

3.1 *Statistical study*

Considering that the calculation of the mean residence time is a calculation of integration, if a strong correlation exists between the mean residence time of the lysimeter and other parameters, this correlation would obviously help facilitate future research. The linear correlations were computed between mean residence time and each of other parameters. The strong correlations ($0.90 \le |r| \le 1.00$) were chosen and presented in Table 3. Where the correlation coefficients (r) varying from 0.92 (for the mean residence time and time of homogenisation) to 0.97 (for the mean residence time and the minimum travel time) are strongly advised for further studies using this type of lysimeter. The correlations listed in

Table 2. Result of the important hydraulic parameters of the lysimeter.

	Nominal retention time (s)	Peak time (s)	Minimum travel time (s)	Time of homogenisation (s)	The time when the velocity of dilution is constant (s)	Capacity of storage (g)	Mean residence time $M_1(E)$	Variance $M_2(E)$	Asymmetry $M_3(E)$	Flattening $M_4(E)$
Experiment 1	2785.63	455	180	1270	2735	1098.6	2588.7	3.48E + 06	5.00E + 09	3.61E + 13
Experiment 2	9272.8	2850	345	3215	6995	5022	6368.7	1.64E + 07	6.08E + 10	9.5E + 14
Experiment 3	13,465	3600	470	5000	9890	2667.9	7817.4	2.29E + 07	9.68E + 10	1.96E + 15
Experiment 4	7499.76	2455	355	2400	5180	3956.9	5885.6	1.55E + 07	6.38E + 10	9.06E + 14
Experiment 5	12,363.8	3750	645	4535	9610	3652.5	9558.3	3.79E + 07	2.22E + 11	4.88E + 15

Table 3. Strong correlation between mean residence time and the other hydraulic parameters.

	Y ($M_1(E)$)	X	r	r^2
1	$Y=0.69X$	Nominal detention time	0.94	0.89
2	$Y=2.37X$	Peak time	0.97	0.94
3	$Y=15.96X$	Minimum travel time	0.97	0.95
4	$Y=1.90X$	Time of homogenisation	0.92	0.84
5	$Y=0.92X$	The time when the velocity of dilution is constant	0.94	0.89
6	$Y=3.10^{-4}X$	Variance $M_2(E)$	0.97	0.94
7	$Y=3.10^{-8}X$	Asymmetry $M_3(E)$	0.91	0.83

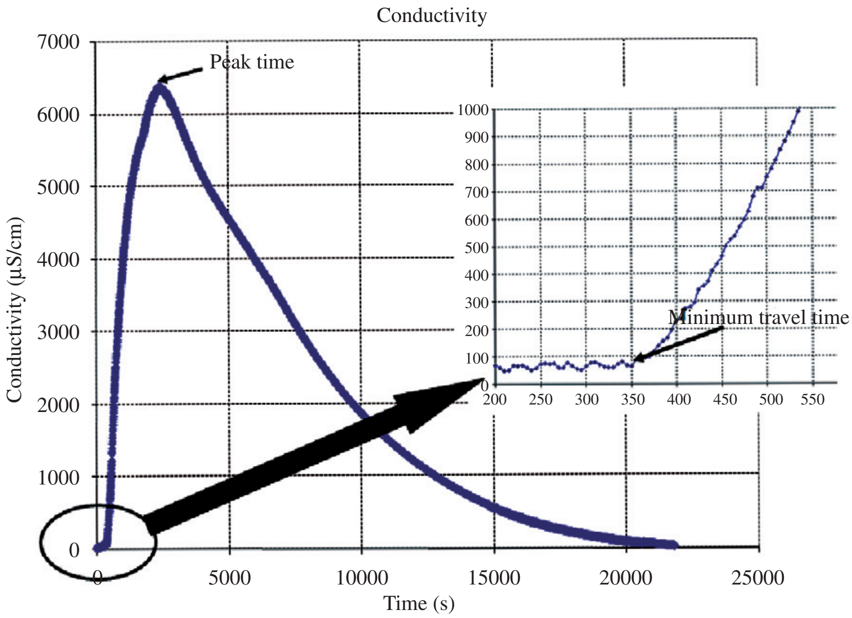

Figure 5. Peak time and minimum travel time in an experiment.

Table 3 are reliable enough for estimating the mean residence time of the lysimeter (Y) with the corresponding equations presented in the first column.

The result also indicates that there are different kinds of correlation in Table 3 according to the different nature of the explicative variable. Peak time, minimum travel time, time of homogenisation and the time when the velocity of dilution is constant (Figure 2) can easily be directly read on a breakthrough curve (Figure 5). The nominal detention time can be calculated as mentioned (Equation (3)). The moments of the RTD function as Variance $M_2(E)$ and Asymmetry $M_3(E)$ are not straightforwardly computed but directly linked with the mean residence time (Table 3). Consequently, the first five correlations are recommended for use in the future as the mean residence time calculation

Table 4. Strong correlation between the other hydraulic parameters.

	Y	X	r	r^2
1	Nominal detention time	Peak time	0.9759	0.9523
2	Nominal detention time	Time of homogenisation	0.9890	0.9781
3	Nominal detention time	The time when the velocity of dilution is constant	0.9917	0.9834
4	Peak time	Time of homogenisation	0.9372	0.8784
5	Peak time	The time when the velocity of dilution is constant	0.9566	0.9150
6	Time of homogenisation	The time when the velocity of dilution is constant	0.9958	0.9917
7	Minimum travel time	Variance $M_2(E)$	0.9964	0.9929
8	Minimum travel time	Asymmetry $M_3(E)$	0.9746	0.9498
9	Minimum travel time	Flattening $M_4(E)$	0.9592	0.9200
10	Variance $M_2(E)$	Asymmetry $M_3(E)$	0.9847	0.9697
11	Variance $M_2(E)$	Flattening $M_4(E)$	0.9694	0.9397
12	Asymmetry $M_3(E)$	Flattening $M_4(E)$	0.9948	0.9896

whereas the estimation of the other moments of the RTD function can be resolved by using the other linear correlations (Tables 3 and 4).

Other parameters were positively related to each other as well as to the mean residence time. The strong correlations ($0.90 \leq |r| \leq 1.00$) are presented in Table 4 and the coefficient of correlation r varies between 0.94 (represented by the correlation between peak time and time of homogenisation) and 0.99 (represented by the correlation between minimum travel time and variance $M_2(E)$).

From Table 4, it appears that we can categorise. Generally, for these experiments, there are three kinds of correlation among the parameters:

Correlation between theoretical parameter and experimental hydraulic parameter (lines 1 to 3; Table 4)

For instance, the nominal detention time on one hand and the peak time, the time of homogenisation and the time when the velocity of dilution is constant on the other hand are well correlated ($|r| > 0.97$). That means that for such a lysimeter, the knowledge of nominal detention time allows the deduction of certain significant hydraulic parameters.

Correlation between experimental hydraulic parameters and the RTD statistical moments (lines 7 to 9; Table 4)

The $M_2(E)$, $M_3(E)$ and $M_4(E)$ which respectively measures the average spread of the breakthrough curves relative to the mean breakthrough time, its asymmetry and its flattening are highly correlated with the minimum travel time. Consequently, the beginning of a tracer experiment would provide the values of the statistical moments.

Cross-correlation: first between experimental hydraulic parameters (lines 4 to 6; Table 4) and secondly between the RTD statistical moments (lines 10 to 12; Table 4)

As certain field conditions experiments are very long, these correlations could be used when not enough experimental data was available.

3.2 *RTD sensitivity to the flow rate and the outlet heights*

The results of this study indicate that the RTD of the lysimeter is sensitive to changes in different outlet heights and the flow rate. If this result is typical of lysimeters in general, then it shows that a change in outlet height by an average factor of 1.19 (10 cm), and a change in flow rate by a factor of 1.88 are enough to elicit a significant change in RTD characteristics. Therefore, if lysimeter management or hydraulic factors cause the outlet height and the flow rate change of a similar magnitude, more than one RTD will be needed for an appropriate hydraulic characterisation and care should be taken in interpreting an RTD during large volumetric fluctuations.

Werner and Kadlec [1] acknowledged that volumetric fluctuations were problematic in their procedure. Determining V_{sys}, the average system volume, a step necessary for normalisation, is not straightforward under large volumetric fluctuations. In this study, the lysimeter is relatively small compared to the other lysimeters or even small wetlands and the experiments proceeded without the natural events that could be a variable element. Consequently, the V_{sys} is constant during the procedure.

Although this study demonstrates the effect of the flow rate and the outlet height on the RTD, the limits must be considered under which this observation is made. The limits may change considerably with a variation of the dimension of the lysimeter and the natural flow rates may vary by magnitudes greater than those tested in the experiment. The outlet height remained stable within the range tested in this study. It is therefore expected that flow rate effects on the RTD may play a greater role under naturally pulsed conditions. In this study, not enough experiments were run to test the limits or test this conjecture under the natural conditions.

4. Conclusion

Linear correlations between several hydraulic parameters were studied for five different sets of experiment in a lysimeter. There are strong correlations between mean residence time $M_1(E)$ and other parameters. Especially the relation between the mean residence time and the time when the velocity of dilution is constant correlated by the equation $Y = 0.9191X$ means that this time could approximate the mean residence time $M_1(E)$. Generally, for these experiments, there are three kinds of correlation among the parameters: first the correlation between theoretical parameter and experimental hydraulic parameter; secondly, the correlation between experimental hydraulic parameters and the RTD statistical moments; and finally, several cross-correlation between experimental hydraulic parameters on one hand and between the RTD statistical moments on the other hand.

Consequently, all the moments of RTD function which represent the characteristics of the RTD can be estimated by other hydraulic parameters which are easily calculated or directly obtained, which makes further studies within such a type of lysimeter more efficient using the same approach and correlations mentioned in this paper.

The universality of the result needs to be examined by proceeding with other experiments in other lysimeters and by changing the dimension of the lysimeter as well as the relation between these correlations and the dimension of the lysimeter. Also, the result can facilitate the design and the management of the lysimeter, even the wetland.

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