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Tracer Experiments with Lithium Chloride to Evaluate the Hydrodynamics of Constructed Wetlands. Comparison of Alternative Analytical Methods

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Abstract. The characterization of water flow dynamics (hydrodynamics) through constructed wetlands is relevant for optimizing wastewater treatment. Although constructed wetlands consist of simple systems, the water flow is complex and irregular, therefore, the study of hydrodynamics requires the use of experimental technics such as tracer experiments. To evaluate the effects of the use of three different analytical methods to compute the concentration of lithium chloride on the main hydrodynamics parameters, tracer experiments were conducted in ten independent lab-scale constructed wetlands. The concentration of lithium chloride in the output flow of the wetlands was calculated by flame photometry, electrical conductivity using a calibration curve and electrical conductivity using the salt molar conductivity. The paired samples T-test or the non-parametric Wilcoxon's Signed-Ranks test were used to demonstrate that the computed hydraulic retention time and the number of tanks accordingly with the tanks-in-series model were not significantly affected by the selected analytical method.

INTRODUCTION

Constructed Wetlands (CWs) consist in an eco-friendly, affordable and sustainable technology for wastewater treatment. CWs' systems comprise three main components: (i) a basin or a retention structure; (ii) a granular soil media; (iii) macrophyte vegetation. The wastewater is treated by a combination of chemical and physical processes such as assimilation and bioconversion by plants and microbial community, precipitation, filtration and adsorption [1,2].

CWs behave as bioreactors and the treatment efficiency can be optimized using reaction and transport models. Kinetics and equilibrium models for chemical and transport phenomena interpretation are linked to system hydrodynamics, which describe the water flow through the CWs. However, the water path can be very complex due to particle size distribution and uniformities of the granular media packing, the development of biofilms and, particularly, the spread of the plants' roots. As a result, the water flow is usually modeled empirically using tracer experiments [3,4].

Tracer experiments are performed by the injection of a traceable compound in the CWs' inflow wastewater stream and measuring the time-evolution of the tracer concentration in the outflow stream. The monitored tracer concentration over time is used to compute the hydraulic retention time (HRT) and to evaluate the CW's hydrodynamics compared to the theoretical regimes well-mixing continuous stirred reactor or plug-flow reactor types [3,4].

Several substances can be used as tracers as long as they do not affect the CWs' performance, are conservative and can be analyzed by available methods. Examples of usable substances are salts, dyes, fluorescent or radioactive

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compounds [3,5]. Inorganic salts, such as sodium or lithium chloride, are cheaper materials and require simpler analytical methods than the referred alternatives. However, common salts may not be conservative as they can be assimilated by the CWs' biota or retained in the granular media by adsorption and precipitation phenomena.

The aim of the present work was to evaluate the use of lithium chloride as a conservative tracer for the hydrodynamics modelling of CWs and to compare three different analytical methods for the quantification of lithium chloride in the outflow stream. The HRT was obtained by numerical integration and the tanks-in-series (TIS) model was fitted to experimental data to obtain the number of equivalent tanks (N). N and HRT, computed from the three different sets of data resulting from the different analytical methods, were compared by paired T-test or by Wilcoxon Signed-Rank test when the compared pairs differences failed the Shapiro Wilk's normality test.

MATERIALS AND METHODS

The tracer experiments were conducted in lab-scale CWs prototypes, whose setup and operative conditions were described in previous works [6]. The experimental set up consisted in five sets of CWs in duplicate. Each set had a different combination of filling material, whose objective was to evaluate the reuse of waste solids as CW's filler. The CWs were operated in continuous mode with regular feed of wastewater. To conduct the tracer trials, a 40 g/l aqueous solution of lithium chloride was injected in the input stream of each CW. The tracer concentration in the outflow stream was quantified at regular time intervals by the three analytical methods.

Analytical methods for lithium chloride concentration evaluation

Method 1 consisted in the evaluation of lithium chloride concentration by flame photometry. Samples of water taken from the outflow stream of each CW were analyzed in a flame photometer (FP910, PG Instruments, UK). The lithium chloride concentration was computed using a calibration curve obtained from standards of known concentrations.

Method 2 consisted in the evaluation of lithium chloride concentration by measuring the electrical conductivity directly in the outflow stream with a multi-parameter meter with data logging capability (HI 98194, Hanna Instruments, US). The electrical conductivity of aqueous solutions depends in the concentration of ionic compounds. The lithium chloride concentration was computed using a calibration curve obtained from measuring the conductivity of standards of known concentrations. As all ionic compounds contribute to the measured electrical conductivity, a baseline was measured before and after the tracer experiments. The accuracy of this method depends strongly on the baseline exactness and precision.

Method 3 is a simplification of method 2. Instead of computing the lithium chloride concentration from a calibration curve, the concentration was computed using equation 1, where Λ_M is the measured electrical conductivity in the outflow streams, Λ_{BL} is the baseline electrical conductivity and Λ_{LiCl} is the molar conductivity of lithium chloride aqueous ions (Li^+ and Cl^-). A value of 114.97 m^2 S mol^{-1} was used for Λ_{LiCl} [7]. As for the method 2, the calculated concentrations depend strongly on baseline accuracy.

$$C = \frac{\Lambda_M - \Lambda_{BL}}{\Lambda_{LiCl}} \tag{1}$$

Numerical methods for CWs' hydrodynamics evaluation

The tracer conservation in each run (T) was evaluated from equation 2, where C_{in} and V_{in} are, respectively, the concentration and the volume of the injected solution, and C is the concentration of lithium chloride in the outflow streams measured in sample extracted at time t, using the analytical method 1. Q is the volumetric flowrate measured in the outflow stream for the corresponding time intervals.

$$T = 1 - \frac{\int_0^\infty QCdt}{C_{in}V_{in}} \tag{2}$$

The observed distribution of residence times was computed from the concentration of lithium chloride measured in the outflow streams over time by each one of the three analytical methods using equation 3.

$$f(t) = \frac{QC}{\int_0^\infty QCdt} \tag{3}$$

The hydraulic retention time (HRT, τ), which represents the mean residence time of tracer in the CWs, was computed from equation 4.

$$\tau = \int_0^{\infty} t f(t) dt \tag{4}$$

The tanks-in-series (TIS) model, which consists in the Gamma distribution (eq. 5), was fitted to experimental data by non-linear regression to compute the parameter N, which represents the observed number of equivalent tanks.

$$g(t) = \frac{N}{\tau\Gamma(N)}\left(\frac{Nt}{\tau}\right)^{N-1} exp\left(-\frac{Nt}{\tau}\right) \tag{5}$$

Numerical computations were performed using Microsoft Excel® 2016. The HRT and N obtained using the three different methods for the analysis of LiCl concentration were compared using IBM SPPS® version 25.

RESULTS AND DISCUSSION

Figure 1 presents an example of fitting the TIS model to the tracer data obtained by the three different methods. The complete results are presented in Table 1.

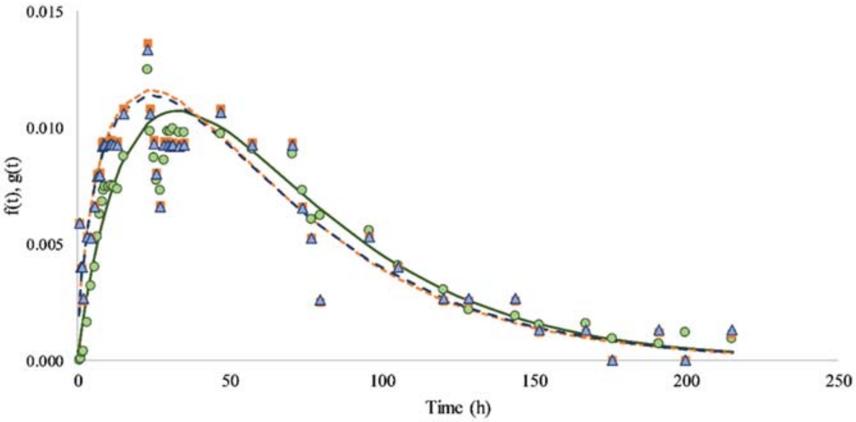

FIGURE 1. Examples of frequency data obtained for dataset 1 by the three analytical methods and respective fittings by the TIS model: Method 1 (● observed; —— fitted); Method 2 (■ observed; ------ fitted); Method 3 (▲ observed; – – – – fitted).

TABLE 1. Hydraulic residence time (τ), fitted number of tanks (N) and r^2 for the 10 experimental datasets by the three analytical methods.

CW (dataset)	**Tracer conservation (%)**	**Method 1**			**Method 2**			**Method 3**		
		τ (day)	**N (-)**	**r^2**	**τ (day)**	**N (-)**	**r^2**	**τ (day)**	**N (-)**	**r^2**
1	96%	68.4	1.93	0.909	62.5	1.62	0.827	63.7	1.61	0.810
2	96%	63.3	1.85	0.816	68.8	1.46	0.803	69.8	1.46	0.790
3	93%	72.4	1.96	0.935	59.4	2.01	0.908	61.0	1.97	0.908
4	96%	74.6	2.16	0.971	65.6	2.26	0.954	67.7	2.19	0.961
5	98%	35.1	2.68	0.876	35.2	2.81	0.849	35.9	2.75	0.849
6	97%	35.7	1.96	0.770	36.5	1.99	0.706	37.1	1.97	0.717
7	91%	75.1	2.23	0.926	73.1	2.51	0.956	74.2	2.44	0.956
8	89%	80.5	2.35	0.878	87.1	2.40	0.891	87.5	2.37	0.887
9	92%	18.8	0.74	0.871	19.5	0.73	0.872	17.1	0.81	0.907
10	97%	22.6	1.12	0.815	19.8	1.19	0.888	17.6	1.30	0.882

Tracer conservation according to Table 1 was always close to or higher than 90%, which is higher than the acceptable value of 80% to validate tracer results [3]. The data scattering observed in Figure 1 is typical and expectable in real and hydrodynamic complex systems like the CWs.

Table 2 presents the results of the statistical tests whose goal was evaluating the hypothesis that any method can be applied to obtain the experimental hydraulic retention time and the number of tanks accordingly with the TIS model. The methods were compared 2 by 2.

TABLE 2. Results of the statistical tests evaluating the significance of the differences between the three analytical methods.

Variable	Test	Method 2 – Method 1	Method 3 – Method 1	Method 3 – Method 2
N	Mean of the differences	0.0036	-0.0104	-0.0140
	95% C.I. of the mean	[-0.1400; 0.1472]	[-0.1497; 0.1289]	[-0.0571; 0.0292]
	Shapiro-Wilk test significance (Statistics)	0.065 (0.854)	0.029 (0.825)	0.070 (0.857)
	Paired t-test significance (Statistics)	0.956 (0.056)		0.483 (-0.732)
	Cohen’s d	0.019		0.244
	Wilcoxon test significance (Statistics)		0.432 (-0.866)	
	Matched-pairs rank correlation		0.309	
τ	Mean of the differences	-1.901	-1.505	0.397
	95% C.I. of the mean	[-6.261; 2.459]	[-5.637; 2.627]	[-0.682; 1.476]
	Shapiro-Wilk test significance (Statistics)	0.803 (0.962)	0.883 (0.969)	0.015 (0.802)
	Paired t-test significance (Statistics)	0.349 (-0.987)	0.431 (-0.825)	
	Cohen’s d	0.329	0.275	
	Wilcoxon test significance (Statistics)			0.432 (-0.866)
	Matched-pairs rank correlation			0.309

The 95% confidence intervals include the zero for all evaluated paired-differences between the analytical methods. The differences of the paired results for the number of tanks by Method 1 and Method 3 failed the Shapiro-Wilk test for normality. The same non-normality evidence was obtained from the paired results for the hydraulic residence time calculated by Method 2 and Method 3. The Wilcoxon non-parametric test was applied considering the non-normality issue. The results of both parametric and non-parametric tests show that the number of tanks and the hydraulic residence time do not differ significantly across the three implemented analytical methods.

CONCLUSIONS

Constructed wetlands hydrodynamics evaluation using tracer experiments with lithium chloride was not significantly affected by three different analytical methods for tracer quantification. Under the conditions tested, the hydraulic retention time and the number of tanks according to the tanks-in-series model did not differ significantly when the concentration of lithium chloride at outflow streams was quantified by flame photometry or by electrical conductivity. In addition, calculation of tracer concentration using the molar conductivity proved to be acceptable for constructed wetlands hydrodynamics characterization, which represents a fast and affordable experimental technic.

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