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Wastewater treatment in wetlands: Theoretical and practical aspects

Conducting hydraulic tracer studies of constructed wetlands: a practical guide

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Abstract

This paper reviews and summarises the theory and techniques used when conducting hydraulic tracer tests in treatment wetlands, with particular attention paid to the practical issues to be considered during the planning and implementation phases. Typically, a single-shot impulse of tracer is introduced at the inlet and the concentration tracked at the outlet or other internal point in order to uncover information about the hydraulic characteristics of the wetland. The following aspects are discussed: the range of commonly used tracer substances, the mass of tracer to be added, and planning of the sampling regime. A range of graphical and statistical tools are described for interpreting the data from a tracer study, with example data from an impulse tracer study used to demonstrate the required computational procedures. It is recommended that a standardised approach be adopted for presenting tracer study data in order to allow the direct comparison of data from different wetland systems.

Key words: impulse tracer study, mixing, plug flow, residence time distribution, tracers.

1. Introduction

The treatment performance and efficiency of chemical reactions within constructed wetlands are greatly affected by hydraulic characteristics, such as residence time, mixing, and short-circuiting. The main method by which wetland scientists and engineers gain information about these hydraulic processes is through the use of inert tracers which provide a means of tracking the movement of water through a wetland. The theory and practice behind hydraulic investigations have predominantly evolved out of the field of chemical reaction engineering. While numerous wetland tracer studies have been reported in the literature to date, limited detail is typically provided regarding the experimental and analytical procedures. Additionally, the literature is riddled with various engineering based calculations and equations for graphically and statistically processing and summarising the data from a tracer study. Consequently, setting out to conduct a wetland tracer study can be a daunting task for the uninitiated and those with a limited background in engineering or mathematics. Thus, the aim of this paper is to provide a comprehensive overview of the fundamental theoretical background and practical issues to be considered when conducting hydraulic tracer studies in constructed wetlands, with a view to providing a user-friendly guide for those without a background in chemical engineering.

2. Background on hydraulic theory and wetlands

The removal of pollutants within a constructed wetland occurs through a diverse range of interactions between the sediments, substrate, micro-organisms, litter, plants, the atmosphere and the wastewater as it moves through the system. The nature and dynamics of water movement through the wetland can have a significant influence on the efficiency and extent of these interactions. Many of the important biogeochemical reactions rely on contact time between wastewater constituents and micro-organisms and/or substrate, while wastewater velocity can be an important determining factor for other pollutant removal processes, such as sedimentation. Any short-circuiting or dead zones that occur within a wetland will consequently have an effect on contact time and flow velocities, and therefore impact on treatment efficiency.

The length of time that water spends within a wetland is defined as the Hydraulic Residence Time (HRT), also referred to as the detention time or retention time. The nominal (or theoretical) HRT (nHRT) is defined as:

$$nHRT = V/Q \qquad (1)$$

where, V is the wetland water volume (m^3) and Q is the volumetric flow rate (m^3 day^{-1}), ideally taken to be the average of the inflow and outflow rates. The actual residence time of water within the wetland may be shorter than the nHRT due to the occurrence of dead zones, or in some cases longer due to inaccuracies in flow rate and/or wetland volume measurements. Climatic effects, such as rainfall and evapotranspiration can also cause the actual residence time in a wetland to vary dynamically over time. Furthermore, due to various degrees of mixing, dispersion and hydraulic inefficiencies, wetlands tend to be characterised by having a range, or distribution, of residence times (Werner, Kadlec 2000). That is, parcels of water that enter a wetland at time zero do not all leave simultaneously after one nHRT, but will leave the wetland after varying lengths of time, both shorter and longer than the nHRT. This distribution of times that various fractions of water spend in a wetland is termed the residence time distribution (RTD).

Levenspiel (1972) and Fogler (1992) provide comprehensive overviews of the important theory regarding RTDs and hydraulics in chemical reactors, much of which has formed the basis for the majority of constructed wetland hydraulic analyses conducted to date. A good review of RTD theory, with specific reference to constructed wetlands, has been provided by Kadlec and Knight (1996). These texts are a recommended starting point for anyone wanting to learn more about hydrodynamics and mixing in chemical reactors, including constructed wetlands. A summary of the important fundamental elements of this theory is provided here.

Ideal Flow, Non-ideal Flow and the Residence Time Distribution

Based on the degree of mixing, there are two ideal types of steady-state flow reactors that sit at opposite ends of the spectrum. At one end there is the ideal plug-flow reactor in which the pattern of flow is characterised by the fact that wastewater flows through the reactor without any elements of water mixing or diffusing along the direction of the flow path. In this way, all parcels of water spend the same amount of time in the system. Under steady-state flow conditions a plug flow reactor (PFR) therefore has a single residence time (equal to the nHRT), which is represented by a distribution equal to a Dirac delta function (Fig. 1a). Much of the constructed wetland design literature has assumed this type of ideal flow (for example: United States Environmental Protection Agency 1988; Water Pollution Control Federation 1990; Reed *et al.* 1995). However, as will be discussed later, this presumption of plug flow has repeatedly been shown to be incorrect (Kadlec 1994; Kadlec 2000; Werner, Kadlec 2000).

At the opposite extreme to the PFR is the ideal continuously stirred tank reactor (CSTR), in which the wastewater is uniformly mixed throughout the entire reactor. In such a completely mixed reactor, any fluid entering the reactor becomes instantaneously mixed with the contents of the reactor, while the fluid exiting the CSTR has the same composition as the fluid within the reactor (Levenspiel 1972). In this way, all parcels of wastewater have equal probability of leaving the wetland at a given moment. Under steady-state flow conditions a CSTR experiences a range of residence times, and an exponential decay curve characterises the distribution of residence times in the reactor (Fig. 1b).

In actuality, flow through a constructed wetland is typically non-ideal, characterised by intermediate degrees of mixing and a distribution of residence times lying somewhere between the plug flow and completely mixed scenarios (Bowmer 1987; Bavor *et al.* 1988; Kadlec 1994; Kadlec 2000;. Werner, Kadlec 2000). Broadly speaking, there are two main processes that can contribute to the distribution of residence times (or degree of non-ideality) observed in constructed wetlands: velocity profiles and mixing. Importantly, the distribution of residence times may not necessarily be caused by mixing processes, but may result solely from vertically stratified or horizontally distributed differences in flow velocities (Kadlec 2000).

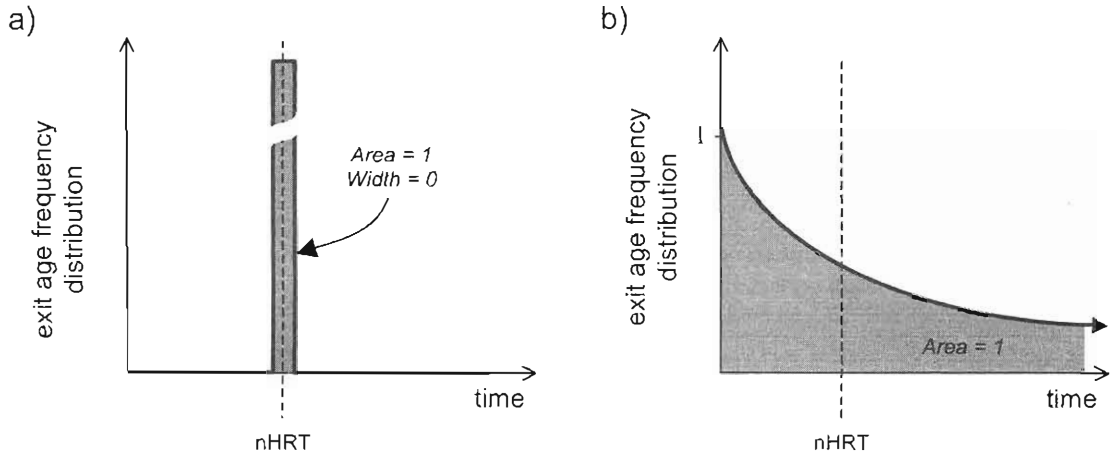

Fig. 1. Frequency distribution of fluid exit age in an ideal plug flow reactor (PFR a) and continuously stirred tank reactor (CSTR b).

Vertical velocity profiles can develop as a result of fluid shear phenomena. In free water surface (FWS) wetlands, vertical and horizontal variations in water velocity can be caused by spatial patterns in topography and vegetation density. In addition, water moves more slowly through the litter layer, and more rapidly in surface waters in unobstructed channels (Kadlec, Knight 1996). In subsurface flow constructed wetlands (SSF-CWs), velocity profiles can result from spatial variability in substrate permeability, root biomass and accumulated clogging solids. An extreme case of this is surfacing of flow and resultant short-circuiting of wastewater above the substrate surface due to hydraulic overloading. The design and effectiveness of inlet and outlet structures, and the shape and bathymetry of the wetland can also be important (Persson *et al.* 1999). Wetlands with single-point inlet and outlet configurations are prone to short-circuiting as water follows the shortest flow path between the inlet and outlet. Ideally, the inflow should be uniformly distributed across the entire inlet cross-sectional surface area, while the outflow is collected across the entire outlet width of the wetland. Although irregular wetland shapes may be more aesthetically appealing, they are generally hydraulically less efficient and prone to the development of dead-zones and back-waters when compared to rectangular shaped wetlands. Ultimately, all of these variations in flow velocities cause some cohorts of water to move quickly to the wetland outlet, while others are delayed and arrive after much longer travel times (Werner, Kadlec 1996). The net effect is transit time dispersion observed at the wetland outlet, as typified by a bell-shaped RTD.

The distribution in wetland residence times can also be caused by vertical and lateral mixing. Small scale mixing may be induced by turbulence as water flows around submerged macrophyte stems and clumps (FWS), or substrate particles and roots (SSF). In FWS wetlands the action of wind driven waves can be significant (Werner, Kadlec 1996). Large scale recirculation occurs when wind drives surface waters to one side of the wetland, resulting in compensatory return currents in deeper water. Bioturbation caused by animals or over-zealous wetland scientists can also have an influence on mixing.

Implications of Non-ideal Flow for wetland treatment

The degree of non-ideal flow can have important implications for the efficiency of treatment in constructed wetlands. On one hand, fast moving parcels of water spend less time in the wetland and experience limited interactions with sediment, substrate and biota, ultimately leaving the wetland with limited chemical alteration (Fisher 1990; Werner, Kadlec 1996). These parcels of water can be considered to have experienced short-circuiting with regards to the nHRT. The impact of these high speed flow paths becomes more important as the design removal-efficiency of the wetland is increased (Kadlec, Knight 1996). On the other hand, slow moving parcels of water spend longer in the wetland and therefore have increased opportunity for interaction and chemical treatment. This results in varying levels of treatment which, when blended at the outlet, produces the overall level of observed treatment (Werner, Kadlec 2000). Except for the case of zero order kinetics (with incomplete reaction), such non-ideal flow tends to result in poorer pollutant reduction performance in comparison to the ideal plug-flow situation (Levenspiel 1972; Mecklenburgh 1974; Werner, Kadlec 2000).

Although well-known techniques are available to calculate the effect of the RTD on pollutant removal performance (Kadlec, Knight 1996; based on Levenspiel 1972), these have rarely been used in treatment wetland data analysis or design. Instead, the steady, constant flow variant of the first-order plug-flow model has been force-fitted in data analysis, and accepted as 'conservative' in design. It has been previously recognized that non-ideal mixing can cause large errors in rate constant estimation and performance prediction (Kadlec *et al.* 1993). For example, Dahab *et al.* (2000) reported that the use of plug flow model calibrations resulted in an over-estimation of the treatment performance of their pilot scale wetland system in Nebraska. Importantly, if the hydraulic efficiency of the wetland being designed is less than that of the wetlands in the data set that generated the rate constants, as indicated by more mixing or short-circuiting, then corrections for the degree of non-ideality should be applied in design (Kadlec, Knight 1996, Kadlec 2000). Particular dangers exist when scaling-up and using data collected from more readily optimised pilot-scale systems to design large operational systems for which the factors that contribute to non-ideal flow can be inherently more difficult to control. Thus, the distribution of residence times in a constructed wetland is a very important factor governing the level of treatment achieved and should be taken into consideration when deriving reaction rate constants for the purpose of design.

The use of hydraulic tracers to approximate the RTD

The extent to which non-ideal flow exists in a given wetland is indicated by the RTD. However, because of the difficulty in knowing how long individual molecules of water have spent in a wetland, the RTD is typically inferred by studying the behaviour of a soluble, inert tracer on passage through the wetland. The tracer is assumed to follow the same flow pattern as the parcel of water with which it entered the wetland, and should therefore give a reasonable reflection of the hydraulic RTD. The resultant tracer RTD can then be used to elucidate the actual wetland water volume that is involved in treatment (hydraulic efficiency), as well as the degree of apparent mixing and deviation from ideal flow (Werner, Kadlec 1996). The RTD can be most simply parameterized with either a tanks-in-series (TIS) or plug flow with dispersion (PFD) model and used with a rate equation to more accurately predict outlet pollutant concentrations (Kadlec, Knight 1996; Kadlec 2000). More complicated models have been applied (Martinez, Wise 2003; Keefe *et al*, 2004), but these are not easily calibrated or used in design.

The two simplest approaches to conducting a tracer study are to introduce either a step or impulse input of tracer at the wetland inlet, and measure the tracer concentration over time at the outlet. Figure 2 displays typical tracer input and response curves following step and impulse additions of tracer to ideal and non-ideal plug flow and complete mix reactors. The same information can be gained through step and impulse approaches. However, the vast majority of constructed wetland tracer studies conducted to date have used the impulse addition technique. This is predominantly because it requires far less tracer than a step input and is therefore much less costly, particularly for large scale wetland systems. Consequently, this paper focuses on the techniques relevant to the impulse input approach. Impulse tracer additions to constructed wetlands typically result in positively skewed bell-shaped exit distributions, with some tracer exiting at short times, and some exiting at longer times.

Other information to be gained through the use of hydraulic tracers in wetlands

While hydraulic tracers have typically been used to derive information about the RTD and hydraulic efficiency of constructed wetlands, they can also be used as an experimental tool to uncover useful information about the internal hydrodynamics of constructed wetlands and to evaluate the effect of different design variables on flow processes. For example, Serra *et al.* (2004) used tracers to model the effect of emergent vegetation on lateral diffusion within FWS wetlands. Garcia *et al.* (2004) examined the effect of aspect ratio and substrate grain size on hydrodynamics in a parallel set of SSF wetlands, and reported that aspect ratio has an influence on the shape of the RTD.

Hydraulic tracers can also be used to gain information regarding the internal flow paths within a treatment wetland system. The presence of preferential flow paths and dead zones can be identified through the introduction of a tracer at the inlet followed by spatial monitoring of tracer concentrations throughout the wetland. The tracer is likely to be detected in preferential flow paths before it arrives in low-flow areas or dead zones within the wetland. The tracer is also likely to remain in back-waters and low-flow zones for longer periods of time when compared to preferential flow channels. Spatial tracer monitoring can be conducted along longitudinal, lateral and vertical profiles within a wetland to gain an insight into the distribution of flow velocities, preferential flow paths and mixing characteristics as wastewater moves through the system (e.g. Fisher 1990; Kadlec *et al.* 1993; Netter 1994; King *et al.* 1997; Rash, Liehr 1999; Grismer *et al.* 2001). A number of studies have used this technique in SSF wetlands to identify preferential flow across the bot-

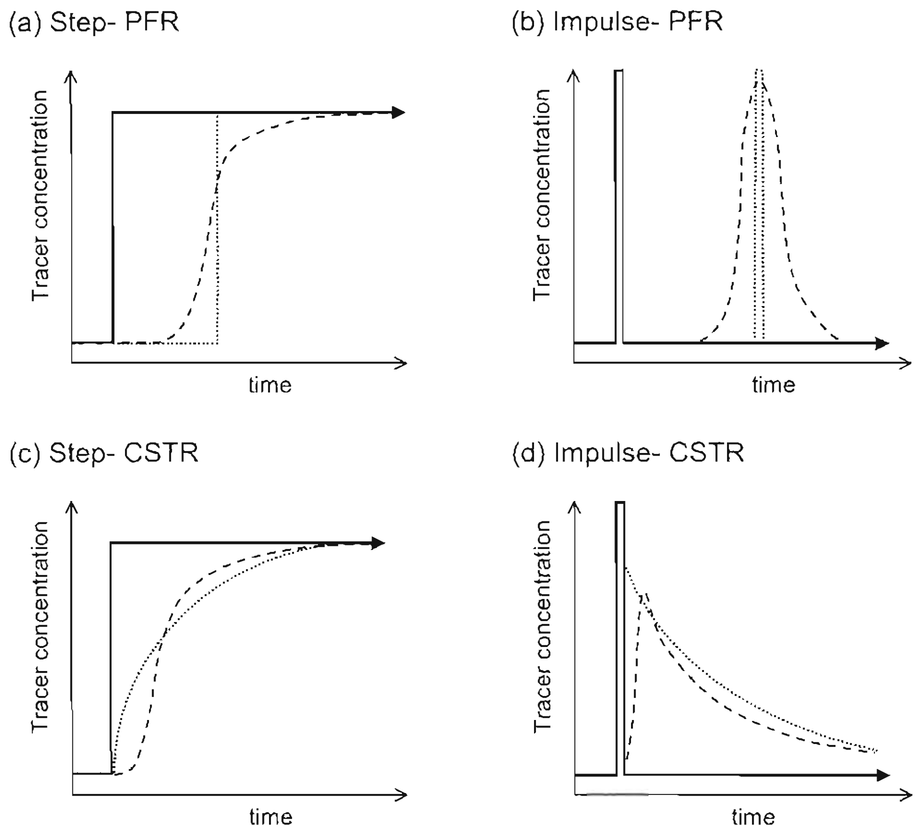

Fig. 2. Tracer response curves for ideal (dotted) and non-ideal (dashed) plug flow (a and b) and complete mix (c and d) reactors following step and impulse additions of a tracer at the inlet (solid line).

tom and therefore below the root zone (e.g. Drizo *et al.* 2000; Garcia *et al.* 2003). Such studies can be used to gain an indication of the influence of inlet and outlet configurations (such as vertical location of distribution pipes) on wetland flow paths. Headley *et al.* (2005) injected an impulse of tracer at the mid-depth of a SSF-CW and monitored its progress at different depths downstream and demonstrated the occurrence of substantial vertical mixing as water progressed through the system. Clearly, there is great opportunity for improving our understanding of flow dynamics and optimising treatment wetland design through the execution of carefully thought out tracer studies.

3. Practical issues to consider when conducting a tracer study

A range of practical issues need to be considered when planning to conduct a hydraulic tracer study. These include the type and quantity of tracer to use, the method of introducing the tracer into the wetland, sampling approaches and data requirements.

Types of hydraulic tracers and their strengths and weaknesses

A range of tracers have been used for hydraulic analysis of constructed wetlands. Essentially any substance can be used as a hydraulic tracer, providing that it is highly soluble in water (representative), does not react with wastewater and wetland constituents (inert and conservative), occurs in low background levels within the wetland, is relatively easy and inexpensive to analyse, has low toxicity, and does not influence the flow pattern in a significant way (Taylor *et al.* 1990; Whitmer *et al.* 2000). One of the most important tests of a tracer's reliability is the recovery percentage. Consequently, the tracer mass recovery rate should always be reported in the results of a tracer study. It is generally considered acceptable if at least 80% of the mass of tracer added as an impulse at the inlet is recovered at the outlet.

The three most popular choices for a tracer for use in constructed wetlands have been the cation lithium, the anion bromide, and fluorescent dyes. Dyes have advantages of low detection limits, zero natural background and low relative cost. However, they are susceptible to a variety of environmental influences which can affect their stability and detection (Kasnavia *et al.* 1999; Sabatini 2000). One of the most suitable dyes is rhodamine WT, because it exhibits the fewest matrix artefacts. Dissolved solids have no effect below about 600 g m^{-3} and pH has no effect above pH=6, although the level of fluorescence is temperature sensitive, changing about 2% per degree Celsius (Smart, Laidlaw 1977). Rhodamine WT is, however susceptible to biodegradation, photolysis and adsorption onto organic solids, detritus and some plastics (Smart, Laidlaw 1977; Lin *et al.* 2003; Dierburg, DeBusk 2005). The use of a sorbing tracer can distort the tracer response curve and lead to errors in calculating hydraulic characteristics. An irreversibly sorbing tracer like rhodamine WT may cause the peak time to be shorter than it really is, while a reversibly sorbing tracer will cause a flattening of the RTD and an unrepresentative extension of the tail. Dierburg and DeBusk (2005) reported that the recovery of rhodamine WT declined as the initial concentration of the impulse was reduced. Due to the above characteristics, it is recommended that rhodamine WT is only applied at moderate to high initial concentrations, in short term tests (nHRT less than about one week) and within environments that are not highly organic. Samples should be collected in glass bottles and kept in the dark prior to analysis to prevent photo-degradation. Rhodamine WT is typically measured using fluorescence spectrophotometry with an excitation wavelength of 558 nm and an emission wavelength of 580 nm (Smart, Laidlaw 1977; Simi, Mitchell 1999).

A range of other dyes may be potentially suitable as tracers in wetlands. de Nardi *et al.* (1999) evaluated the effect of six different dye tracers (bromophenol blue, dextran blue, eosin Y, mordant violet, rhodamine WT and bromocresol green) on the shape of RTD curves and hydrodynamic parameters in a horizontal packed bed anaerobic reactor. They concluded that dye properties can have a very significant influence over the shape of RTDs and apparent degree of mixing due to differences in the effective diffusivity of the various dyes into the porous media used. These authors reported that dextran blue gave the most reliable results. Other dyes that have been used with varying degrees of success include eriochrome acid red (Bowmer 1987), uranine and eosine (Netter, Bischofsberger 1990; Netter 1994), and naphthionate (Ammann *et al.* 2003).

Bromide and lithium are the most extensively used ionic tracers, mainly due to their relatively low cost and ease of analysis. They are typically added as solutions of sodium or potassium bromide, or lithium chloride and have yielded reliable results in numerous wetland studies (Bowmer 1987; Netter 1994; Tanner, Sukias 1997; King *et al.* 1997; Drizo *et al.* 2000; Rash, Liehr 1999; Grismer *et al.* 2001; Lin *et al.* 2003; Garcia *et al.* 2004; Smith *et al.* 2005). Lithium and bromide are not susceptible to degradation, but are capable of being taken up by wetland plants and other organisms (Chao 1966; Jemison, Fox 1991; Kung 1990; Owens *et al.* 1985; Schnabel *et al.* 1995; Whitmer *et al.* 2000). Background concentrations of lithium are typically very low, but bromide may be present in natural waters at concentrations well above detection. Although relatively inexpensive, very large quantities of ionic tracers can be required to achieve a significant peak and detection above background levels in large wetland systems, thereby making them most suitable for small to moderate sized wetlands. Bromide is typically analysed through ion chromatography, although less reliable portable probes are available and can be used in the field. Lithium can be measured using atomic absorption spectrometry or inductively coupled plasma-optical emission spectrometry (ICPOES).

Chazarenc *et al.* (2003) used high concentrations (67 000 g m^{-3}) of sodium chloride solution as a tracer in a horizontal SSF-CW, and measured conductivity in order to derive RTDs. They reported tracer recovery rates exceeding 78% from eight individual tracer studies. Sodium chloride can represent a relatively inexpensive option that can be easily monitored and logged in the field using electrical conductivity probes. However, high salt concentrations may have a negative effect on biota and treatment within the system. Furthermore, the high concentrations required to cause a significant spike in conductivity measurements above background wastewater concentrations can result in substantial density effects, with the heavy tracer impulse preferentially sinking to the bottom of the wetland and providing unrepresentative results. This process was confirmed by Chazarenc *et al.* (2003) and Schmid *et al.* (2004).

Radioactive tracers, such as tritium, have very good tracer properties and may be suitable for use in constructed wetlands. However, the use of radioactive substances in wetlands is often precluded by strict regulations and specific analytical requirements. Conservative biotracers, such as coliphage MS2, and the bacteriophage of Enterobacter cloacae show promise for use as hydraulic tracers, particularly where there are concerns regarding the toxicity of the various chemical tracers (Hodgson *et al.* 2003).

Determining the quantity of tracer to add

When conducting an impulse tracer test, a relatively concentrated, small volume of tracer solution (the 'impulse') is made up typically by mixing the tracer material (either in powdered form or as a stock solution) with clean water or a representative sample of the wetland water from the point where the tracer will be added to the wetland (usually the inlet). The concentration of tracer in the impulse that is added should be based on the observed or expected dilution factor of the wetland being tested, detection limits of the analytical techniques employed, the background concentration of the tracer in the wetland system, and fluid density properties of the impulse relative to the ambient water in the wetland.

After dilution during the introduction of the tracer impulse into the influent stream, the concentration should be higher than the detection limits of analytical instruments used and background concentrations within the wetland (Ammann *et al.* 2003). One of the first steps in conducting a tracer study should therefore be to determine the background tracer concentration in the wetland. This is of particular importance where repeated tracer studies are being conducted on the one system. Investigators should be certain that tracer from previous studies has been flushed from the wetland before beginning the next (Werner, Kadlec 2000). As a general rule, Keller and Bays (2001) suggest that the quantity of tracer added, if assumed to mix uniformly throughout the volume of the wetland, should be sufficient to achieve an average concentration at least 10 to 20 times the background concentration. Given that wetlands typically do not behave as CSTRs, this should result in a peak exit concentration significantly higher than 10 to 20 times the background. More complex calculations can be made of the anticipated level of dispersion and mixing of the tracer impulse as it moves through the wetland in order to estimate the likely peak concentration at the outlet that will result from a given inlet concentration.

Counter to the above requirements, the tracer concentration should not be so high as to cause a density effect when introduced into the wetland. At excessively high concentrations, the density of the tracer impulse may be substantially higher than that of the ambient wastewater in the wetland to which it is added, causing the tracer to sink to the bottom of the wetland. This can cause the flow of the tracer through the wetland to be retarded as it slowly creeps along the bottom and stagnates in depressions. Consequently, density stratification can lead to a significant distortion in the RTD (Schmid *et al.* 2004). Density effects will be particularly troublesome where flow velocities are low and flow is well within in the laminar range. Preliminary laboratory tests can be conducted to identify the tracer concentration at which density induced stratification becomes significant, as evidenced by the tracer settling to the bottom of a vessel. At the very least, it is recommended that the density of the tracer impulse should be within 1% of the density of the ambient wastewater in the wetland in order to minimise the risk of density effects. This may be achieved by diluting the impulse tracer mass within a large enough volume of water before it is added to the wetland, or prolonging the "impulse" duration, provided that the duration does not exceed a few percent of the nominal detention time.

Care must be taken when measuring or weighing out the quantity of tracer to be used, particularly if in powdered form. Reagent grade chemicals with known purity levels should be used. In order to minimise errors, powdered tracer salts, such as lithium chloride or sodium bromide should be predried in an oven prior to weighing in order to drive off any moisture that has been absorbed.

Adding the tracer impulse to the wetland

Prior to tracer addition, the wetland system should be evaluated to make sure that the conditions during the study period are representative of normal operating conditions. It is generally desirable to conduct the tracer study during a period of little or no rainfall, as excessive rainfall can complicate and confound the interpretation of the results. One obvious exception to this is when a tracer study is being conducted to evaluate the hydrodynamics of a stormwater treatment wetland during a runoff event, which will require the investigator to be prepared and ready to act as soon as a rainfall event begins.

The method in which the tracer is added to the wetland will depend on the system in question and the objectives of the tracer study. For an impulse input, the tracer should be added to the inflowing water over a relatively short period of time. Because the tracer is being used to represent the typical flow of water through the wetland, it should be added in a manner which is consistent with the normal delivery of water to the wetland (Keller, Bays 2001). For example, if water is normally pumped into the wetland inlet, then the tracer should be introduced during a pumping episode, either into the feed line at a location close to the point of discharge or at the point where the pumped influent enters the wetland. For gravity flow systems with a single inflow point, the tracer impulse should be added at the point where the influent enters the wetland in a way that does not cause a substantial increase in the typical influent flow rate. For systems with inlet distribution weirs or spreader pipes, the tracer impulse should be introduced at a point upstream so that it is distributed into the wetland in the same manner as the influent wastewater. Introducing the tracer in this way can provide a means of evaluating the efficiency of inlet distribution structures. Alternatively, flow weighted impulses can be simultaneously introduced at each discharge point along the distribution system. However, this approach can be logistically challenging.

Often, the tracer solution will have a density which is somewhat greater than the water in the wetland. Thus, it is preferable to introduce the tracer into a zone where there is some turbulence to prevent the tracer sinking to the bottom of the wetland. The inlet zones of most treatment wetlands will typically satisfy this requirement. If the tracer impulse is added to a quiescent or stagnant zone, density effects may cause the tracer to sink to the bottom and then slowly bleed into the wetland (Keller, Bays 2001). As discussed previously, this will result in an erroneous distortion of the RTD. In this regard, it is also important to carefully consider the tracer delivery rate. The likelihood of density effects will be increased if the impulse is dumped into the wetland in one hit.

Small wetlands will typically require relatively small tracer impulse volumes which can be added by manually pouring the solution into the appropriate point. For larger wetlands, requiring large volume impulses, a pump may be needed to adequately control the delivery of the solution to the wetland.

Sampling frequency and duration

Tracer studies can be a time and labour intensive endeavour, resulting in the generation of a large number of samples. Clearly, a well thought out and efficient sampling strategy can save a lot of time and money by avoiding the collection and analysis of unnecessary samples. However, if too few samples are collected, the entire exercise can be fruitless.

Closure of the tracer mass balance is a prerequisite to a good tracer test, as it is required for the accurate calculation of hydraulic parameters such as mean residence time (Kadlec 1994). This requires sampling for a long enough period, and at a suitable frequency, to adequately describe the tracer response curve. Thus, an estimate of the likely RTD of the wetland should be made based on nominal parameters in order to design a sampling regime. Important aspects of the RTD to be considered when determining sampling frequency are the steeply rising limb of the peak concentration profile, and the long, declining tail. However, wetland tracer responses often defy expectations, and a fair degree of buffering and flexibility should be incorporated into any sampling regime. It is often practical to collect and store more samples than anticipated to be needed, because lithium and bromide do not degrade. These "supplementary" samples can then be analysed retro-actively to fill in data gaps if they are deemed to be necessary based on analysis of the primary sample set. The ability to analyse samples in the field or immediately after collection will take much of the guess work out of determining the sampling frequency and duration. For example, the concentration of Rhodamine WT can be relatively simply measured and logged in situ using a portable fluorometer providing instantaneous feedback on the status and progress of the tracer through the wetland without the need for laboratory analyses. Thus, when used in conjunction with other more reliable tracers (such as bromide or lithium), in situ measurements of Rhodamine WT can enable an adaptive sampling approach to be taken with reasonable efficiency.

Ideally, sampling should begin immediately prior to injecting the tracer impulse in order to identify the background concentration at the time of the tracer study. The greatest sampling frequency is required at times when the concentration is changing most rapidly (that is around the time of the peak in concentration). The rise typically begins at 10 – 30% of the nHRT. The peak will typically, although not always, occur at 50 – 90% of the nHRT. Following the expected peak in tracer concentration, the sampling frequency can be progressively decreased. To adequately capture the declining tail of the RTD sampling is typically required for an extended period. Examination of tracer responses from the numerous available experiments indicates that the impulse response is typically complete after four nHRTs. In general, care should be taken not to allow too much volume to exit without being sampled. Otherwise, a spike or dip in the concentration could be partially or even completely missed, particularly at high flow rates (Werner, Kadlec 2000).

As a rule of thumb, 30 – 40 sample points are normally adequate to define the response curve. Sampling frequency and interval can be determined either based on flow or time. Note, that these will both give the same sample frequency where the flow is continuous and steady (generally only in experimental systems). However, in situations where the flow rate is somewhat variable (the majority of cases), flow-weighted sampling will generally be the best way to ensure that accurate sampling of the tracer response curve is achieved. In any case, it is necessary to record both the time of sampling, and volume of water that has passed through the sample point since the tracer impulse was added, as these will be required in interpreting the tracer response data. Ideally, accurate measurements of the flow rate entering and exiting the wetland should be continuously logged over the duration of the tracer study.

The use of automatic samplers can greatly increase the number of samples that can be collected, while reducing the labour requirement involved. In some cases, the use of an automatic sampler may be the only practical way of collecting the number of samples required. Automatic samplers can be configured to collect samples at regular time intervals. Alternatively, many modern automatic samplers have the capability of being connected to a flow measuring device, allowing the collection of samples on a flow weighted basis as well as the logging of flow rates.

It is important to obtain a reasonably accurate measurement (or estimation) of the wetland water volume. An inaccurate measurement, or incomplete knowledge, of the wetland volume can lead to a distortion of normalised RTDs and resultant calculation of tracer recovery and mean HRT (Werner, Kadlec 2000). An accurate understanding of the changes in wetland volume over time will be particularly important in cases where flow and water volume are non-steady, such as with wetlands receiving event driven runoff such as stormwater. The estimated volume also forms the basis for computation of the hydraulic efficiency of the wetland.

4. Data processing and analysis

Once the tracer samples have been collected and analysed, the next step is to process and interpret the data using computational tools. The type of data manipulation used will be somewhat dependent on the wetland in question, data availability and the purpose of the tracer study. An overview of the fundamentals is presented here.

Graphing the tracer response curve

A tracer response curve is produced by graphing the tracer concentration on the y-axis versus time since tracer addition on the x-axis. This can be thought of as a "raw RTD" curve (Holland *et al.* 2004). Figure 3 is a raw RTD curve resulting from the introduction of an impulse containing 40g of bromide (as sodium bromide) to the inlet of a 4 m^2 pilot SSF-CW at Alstonville in New South Wales, Australia in 2001.

Often, the "tail" of the measured exit concentration distribution is poorly defined, either because sampling was terminated too soon or the final baseline did not return to the initial background concentration. Under these circumstances, the tail may be estimated as an exponentially decreasing function approaching a background concentration (usually slightly above zero), extrapolated from the data points past the second inflection of the response (Nauman, Buffham 1983).

Normalisation of the RTD curve

The scale of the axes in a raw RTD curve is affected by the tracer mass added, wetland volume and flow rate, making it difficult to compare raw RTD curves from different systems or from the same system under different experimental or operational conditions (Werner, Kadlec 1996; Holland *et al.* 2004). Consequently, it is preferable to normalise the RTD curve, by converting both axes into dimensionless forms. A range of possible normalisation options exist, as reviewed by Werner and Kadlec (1996). Normalising the y-axis generally involves dividing the measured concentration by an appropriate function to eliminate the units of concentration. The x-axis is often normalised by representing it in terms of the number of nHRTs that have passed since tracer addition. For steady flow systems, such a normalisation can be achieved by calculating the dimensionless RTD function, $C'(\theta)$:

$$C'(\theta) = \frac{C(t) \cdot V_{sys}}{M_{out}} \qquad (2)$$

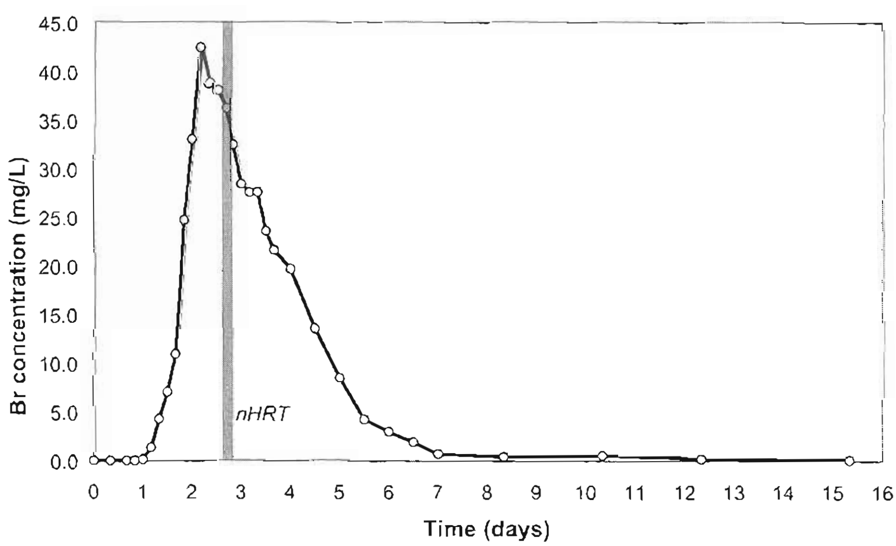

Fig. 3. Tracer response curve ("Raw RTD") for a bromide impulse added to a 4 m^2 SSF-CW in Alstonville, Australia in 2001. The grey bar represents the nHRT.

where $C(t)$ is the exit tracer concentration at time t since tracer addition (days), V_{sys} is the mean water volume of the wetland system during the tracer study (m^3), M_{out} is the total mass of tracer recovered (g), which should be close to the mass added, and θ is the dimensionless time:

$$\theta = \frac{t}{\tau} \tag{3}$$

in which τ is the tracer detention time (often referred to as the "tracer HRT" or "mean HRT"):

$$\tau = \frac{\int_0^\infty tC(t)dt}{\int_0^\infty C(t)dt} \tag{4}$$

Hence, $C'(\theta)$ defines the fraction of tracer, $C'(\theta)d\theta$, that spends θ HRT's in the wetland.

As highlighted by Werner and Kadlec (1996), RTD normalisation procedures, such as $C'(\theta)$, have been developed for steady-flow systems, and have limited applicability for non-steady systems where the flow rate varies dynamically over time. In such situations, the shape of the tracer response curve can be strongly influenced by the pattern of flow rates that occur after tracer injection, distorting the actual effect of mixing or dispersion with which we are more interested. To overcome this, Werner and Kadlec propose a normalising procedure which effectively eliminates time from the x-axis. Instead of time, the tracer progress is presented as a function of the proportion of wetland volume that has flowed through the system. This normalisation enables tracer study data from both steady and non-steady flow situations to be easily analysed and directly compared. The normalised concentration, C', is portrayed as a function of the dimensionless flow weighted time, ϕ, and results in the dimensionless "flow-weighted-time RTD function", $C'(\phi)$:

$$C'(\phi) = \frac{C(t)\,V_{sys}}{M_{out}} \tag{5}$$

where the dimensionless flow weighted time, ϕ, is equivalent to the number of nHRTs and is defined as:

$$\phi = \frac{V_{out}}{V_{sys}} \tag{6}$$

in which V_{out} is the cumulative volume of water that has exited the wetland since tracer addition (m^3).

If the volume of water contained in the wetland varies over time, then some form of average volume needs to be determined for V_{sys}. To do this, the exit volumetric flow rate and the system volume (often inferred via water depth measurements) need to be measured as a function of time during the tracer study. System volumes experienced when most of the tracer is still in the wetland should be given more weight than system volumes experienced when less tracer is present (Werner, Kadlec 1996). The tracer "mass averaged volume", V_m, achieves this:

$$V_m = \frac{\int_0^\infty (M_{out} - m_{out})V_t(t)dt}{\int_0^\infty (M_{out} - m_{out})dt} \tag{7}$$

in which m_{out} is the mass of tracer that has exited the wetland between time 0 and t, and $V_t(t)$ is the time average volume:

$$V_t(t) = \frac{\int_0^t V(t)\,dt}{t - 0} \tag{8}$$

In order to facilitate the universal comparison of tracer data from wetlands with different flow regimes, it is recommended that the dimensionless RTD function, $C'(\phi)$, be adopted as the standardised approach for the representation of wetland tracer study data.

Table I displays the data used to create Figure 3 and provides an example of the analyses required to generate the flow-weighted dimensionless RTD curve for this tracer test (Fig. 4), as well as other RTD parameters.

Because the Alstonville SSF-CW was operated under essentially steady-flow conditions during the tracer study, the shape and position of the curves in Figures 3 and 4 remain virtually identical. However, it is worth noting that wetlands experiencing variable or pulsed flow will display raw RTD and dimensionless RTD ($C'(\theta)$) curves that are somewhat distorted with regard to the x-axis when compared to the dimensionless flow-weighted-time RTD curves ($C'(\phi)$). This distortion, which $C'(\phi)$ essentially corrects for, can cause complications when it comes to evaluating aspects of the wetland hydraulics such as mixing and dispersion. A review of these issues and the various approaches for determining RTD functions is provided by Werner and Kadlec (1996).

Calculating statistical parameters to describe the RTD

It is often desirable to reduce the data from a tracer study down to a few parameters which summarise and describe the wetland RTD. Some of the more commonly used statistics are described here.

Tracer mass recovery

As mentioned previously, the tracer mass recovery provides an important quality check of the reliability of tracer study data. Table I demonstrates the process by which the mass of

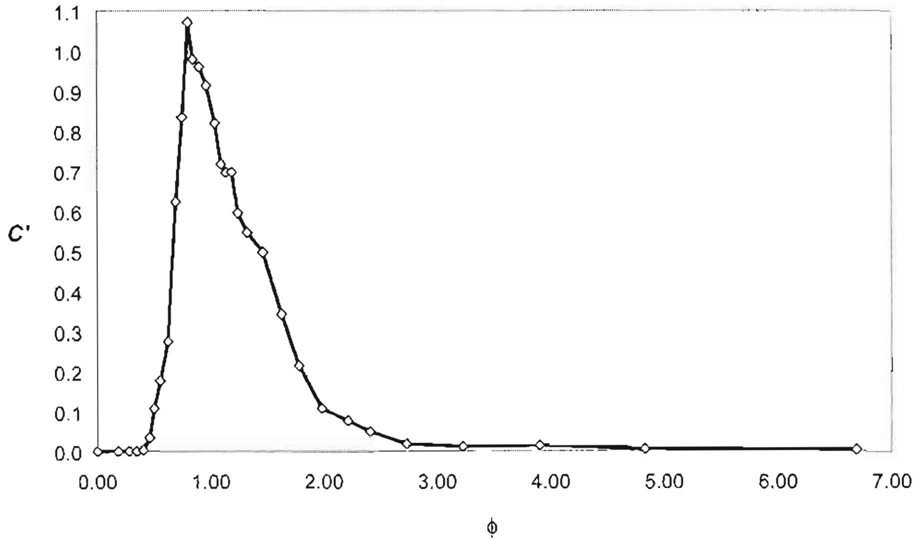

Fig. 4. Dimensionless flow-weighted-time RTD curve for a Bromide impulse tracer test on Alstonville SSF-CW, 2001.

tracer recovered can be calculated. In the example presented, only 32.8 g was recovered from the 40 g of Br that was added, equating to a recovery rate of 82% which is within the acceptable realms of experimental error. The tracer recovery rate can also be calculated using the zeroth moment, M_0, of the dimensionless RTD function, $C'(\phi)$:

$$M_0(C') = \int_0^{\infty} C'(\phi)d\phi \qquad (9)$$

Tracer Residence Time

An important parameter calculated from the RTD is the tracer detention time (τ), often referred to as the "tracer HRT" or "mean HRT", which defines the average time that a tracer particle spends in the wetland. The tracer HRT is the centroid of the RTD and is calculated using Equation 4. Substantial differences between the tracer HRT and the nHRT indicate the existence of short-circuiting and/or dead zones.

Table II demonstrates the procedure for calculating τ using the Alstonville example tracer study data from Table I. It can be seen that τ is equal to 3.4 days (310 divided by 92).

Variance of the RTD

A second important parameter is the variance, σ^2, of the RTD which describes the spread of the tracer response curve about τ, the tracer HRT (Kadlec, Knight 1996). The variance is calculated by:

$$\sigma^2 = \frac{\int_0^{\infty}(t-\tau)^2 C(t)dt}{\int_0^{\infty} C(t)dt} \qquad (10)$$

The variance represents the square of the spread of the distribution and has units of (time)^2. The calculation of the σ^2 for the Alstonville example is demonstrated in Table II, in which the σ^2 is equal to 3.1 days^2 (280 divided by 92). Note that the last three lines of Table II dominate the sum, contributing 52% of the variance. This is not unusual, and illustrates the unacceptable sensitivity of the variance to small values of concentration far out on the tail of the distribution. A much better procedure is to compute the variance from a model of the response curve, calibrated by a least squares procedure, which minimizes error uniformly across the entire response. Many response curves are of the shape of a gamma distribution. Because that distribution is a function available in the Microsoft Excel™ desktop computer package, such least squares fitting is readily executed. The variance so computed is 1.16 days^2.

The variance of the RTD is created by mixing, dispersion and velocity profiles, as discussed earlier. The variance can be converted into a unitless parameter by dividing by the square of the tracer detention time, to yield σ^2_θ, the dimensionless variance of the RTD:

$$\sigma^2_\theta = \frac{\sigma^2}{\tau^2} \qquad (11)$$

For the Alstonville wetland example, this would equal 0.27 for the moment procedure (3.1 divided by 3.4 squared), or 0.1 using the least squares procedure (1.16 divided 3.4 squared).

Other statistical parameters

Other statistics which can be used to describe the RTD include the mode (time of the peak in tracer concentration), the median (time at which

Table I. Example tracer study data and calculated RTD parameters from Alstonville SSF-CW, 2001. Note: the initial mass of tracer added was 40g.

t (d)	V_{sys} (m^3)	dV_{out} (m^3)	V_{out} (m^3)	Q_{in} (m^3/d)	Q_{out} (m^3/d)	Q_{mean} (m^3/d)	θ –	ϕ –	$C(t)$ (g/m^3)	C –	M_{out} (g)
0.0	1.01	0	0.00	–	–	–	0.00	0.00	0.0	0.00	0.00
0.3	1.01	0.19	0.19	0.48	0.37	0.42	0.14	0.18	0.0	0.00	0.00
0.7	1.01	0.10	0.29	0.43	0.40	0.41	0.28	0.28	0.0	0.00	0.00
0.8	1.01	0.07	0.35	0.42	0.39	0.41	0.34	0.35	0.0	0.00	0.00
1.0	1.01	0.06	0.41	0.42	0.36	0.39	0.39	0.41	0.1	0.00	0.01
1.2	1.01	0.06	0.47	0.42	0.33	0.37	0.43	0.46	1.4	0.04	0.08
1.3	1.01	0.04	0.51	0.42	0.24	0.33	0.44	0.50	4.3	0.13	0.17
1.5	1.01	0.06	0.56	0.42	0.33	0.38	0.56	0.55	7.0	0.22	0.39
1.7	1.01	0.07	0.63	0.42	0.42	0.42	0.70	0.62	10.9	0.34	0.77
1.8	1.01	0.07	0.70	0.42	0.42	0.42	0.76	0.69	24.7	0.76	1.73
2.0	1.01	0.06	0.76	0.42	0.36	0.39	0.77	0.75	33.1	1.02	1.98
2.2	1.01	0.05	0.81	0.42	0.30	0.36	0.77	0.80	42.5	1.31	2.12
2.3	1.01	0.05	0.86	0.42	0.27	0.35	0.80	0.85	38.8	1.20	1.75
2.5	1.01	0.06	0.91	0.42	0.33	0.37	0.92	0.90	38.0	1.17	2.09
2.7	1.01	0.07	0.98	0.41	0.39	0.40	1.06	0.97	36.2	1.12	2.35
2.8	1.01	0.08	1.05	0.41	0.45	0.43	1.21	1.04	32.5	1.00	2.44
3.0	1.01	0.06	1.11	0.41	0.33	0.37	1.10	1.09	28.5	0.88	1.57
3.2	1.01	0.05	1.15	0.41	0.27	0.34	1.06	1.14	27.6	0.85	1.24
3.3	1.01	0.05	1.20	0.41	0.30	0.36	1.18	1.19	27.6	0.85	1.38
3.5	1.01	0.06	1.26	0.42	0.33	0.37	1.30	1.24	23.6	0.73	1.30
3.7	1.01	0.06	1.34	0.28	0.33	0.31	1.11	1.33	21.7	0.67	1.35
4.0	1.01	0.16	1.48	0.50	0.34	0.42	1.67	1.47	19.7	0.61	3.20
4.5	1.01	0.17	1.65	0.42	0.33	0.37	1.67	1.63	13.6	0.42	2.24
5.0	1.01	0.16	1.80	0.55	0.31	0.43	2.14	1.78	8.5	0.26	1.32
5.5	1.01	0:21	2.01	0.76	0.41	0.59	3.20	1.99	4.3	0.13	0.87
6.0	1.01	0.23	2.24	0.48	0.46	0.47	2.82	2.21	3.0	0.09	0.70
6.5	1.01	0.20	2.43	0.55	0.39	0.47	3.03	2.41	1.9	0.06	0.38
7.0	1.01	0.32	2.76	0.39	0.35	0.37	2.58	2.73	0.7	0.02	0.23
8.3	1.01	0.50	3.26	0.32	0.30	0.31	2.55	3.23	0.4	0.01	0.22
10.3	1.01	0.78	3.94	0.38	0.34	0.36	3.69	3.90	0.6	0.02	0.44
12.3	1.01	0.94	4.88	0.42	0.38	0.40	4.84	4.83	0.2	0.01	0.21
15.3	1.01	1.88	6.76	0.35	0.31	0.33	5.01	6.69	0.1	0.00	0.25
					Q_{sys}:	**0.39**			**Total mass recovered:**		**32.8**

t = time since tracer addition; dV_{out} = incremental volume of water exiting wetland between samples

50% of the added tracer mass has passed out of the wetland) and the time that the tracer is first detected. The hydraulic efficiency of the wetland, which is the proportion of the nominal wetland volume that is involved in treatment, can also be determined as the ratio of the tracer HRT and the nominal HRT ($\tau/nHRT$). This provides an indication of the degree of short-circuiting and dead zones present in the wetland. A description of these calculations is provided by Persson *et al.* (1999) and Kadlec (2007 this volume).

A note on modelling the RTD

The parameters presented thus far provide the starting point for describing a wetland's RTD and hydraulic characteristics. Depending on the aim of the investigation, the next step will often be to model the degree of mixing or flow non-ideality. Although beyond the scope of this paper, a number of models of varying complexity are commonly applied to wetland RTDs, including:

- the Plug-flow with axial dispersion (PFD) model (Kadlec, Knight 1996);
- the Tanks-in-series (TIS) model (Kadlec, Knight 1996), which leads to gamma distributions;
- various network models which incorporate combinations of the above either in parallel or series (Kadlec *et al.* 1993; Kadlec 1994; Martinez and Wise, 2003); and
- the Zones of Diminished Mixing (ZDM) model (Werner, Kadlec 2000), a variant of the finite stage model described by Mangelson (1972).

All of these models have their strengths and weaknesses depending on the application. In any case, the modelling process is essentially a curve fitting exercise aimed at producing a model which best describes the tracer response curve for a given

Table II. Computational procedure for calculating the mean HRT (τ) and variance (σ^2) for the Alstonville example tracer study

t (d)	*C(t)* (g m^{-3})	*C(t) dt*	*t C(t) dt*	*(t – τ)^2 C(t) dt*
0.0	0.00	–	–	–
0.3	0.00	0.00	0.00	0.00
0.7	0.00	0.00	0.00	0.00
0.8	0.00	0.00	0.00	0.00
1.0	0.12	0.02	0.02	0.11
1.2	1.37	0.23	0.27	1.12
1.3	4.29	0.72	0.96	2.99
1.5	7.03	1.17	1.77	4.14
1.7	10.94	1.82	3.05	5.34
1.8	24.70	4.12	7.57	9.82
2.0	33.06	5.51	11.05	10.47
2.2	42.47	7.08	15.38	10.39
2.3	38.80	6.47	15.13	7.06
2.5	38.04	6.34	15.89	4.89
2.7	36.22	6.04	16.14	3.06
2.8	32.49	5.42	15.38	1.61
3.0	28.46	4.74	14.26	0.68
3.2	27.59	4.60	14.59	0.21
3.3	27.62	4.60	15.38	0.01
3.5	23.61	3.93	13.80	0.06
3.7	21.65	3.61	13.25	0.30
4.0	19.70	6.57	26.30	2.54
4.5	13.58	6.79	30.61	8.55
5.0	8.52	4.26	21.33	11.21
5.5	4.26	2.13	11.72	9.58
6.0	3.01	1.50	9.03	10.33
6.5	1.93	0.97	6.29	9.42
7.0	0.72	0.36	2.52	4.71
8.3	0.45	0.59	4.96	14.60
10.3	0.56	1.12	11.62	54.37
12.3	0.22	0.44	5.48	35.61
15.3	0.13	0.40	6.12	57.03
		91.55	**309.85**	**280.19**

wetland. The modelling capabilities of the wetland scientist are greatly enhanced by the computer spreadsheet programs readily available today. The derivation of suitable models that adequately describe the mixing characteristics of a wetland will enable more rigorous chemical reaction models to be established for the purpose of wetland design. Kadlec (2007 this volume) provides a good summary of the opportunities in this regard, as well as a range of other wetland tracer study applications.

Conclusions

The hydraulic characteristics and mixing processes within constructed wetlands are important factors governing their treatment efficiency. Carefully planned and executed tracer studies provide a useful means of deriving information about the hydrodynamics of a given wetland. The methods and practical issues to be considered when conducting wetland tracer studies have been outlined. Data from an example tracer study has been used to demonstrate the fundamental computational tools used in presenting and interpreting the results from a tracer study.

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