Determining the Reaeration Coefficient and Hydrodynamic Properties of Rivers Using Inert Gas Tracers

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ABSTRACT
Various contaminants which can be aerobically degraded find their way directly or indirectly into surface water bodies. The reaeration coefficient (K_2) characterises the rate at which oxygen can transfer from the atmosphere across the air-water interface following oxygen depletion in a water body. Other mechanisms (like advection, dispersion and transient storage) determine how quickly the contaminants can spread in the water, affecting their spatial and temporal concentrations. Tracer methods involving injection of a gas into the water body have traditionally been used for direct (in-situ) measurement of K_2 in a given reach. This paper shows how additional modelling of tracer test results can be used to quantify also hydrodynamic mechanisms (e.g. dispersion and storage exchange coefficients, etc.). Data from three tracer tests conducted in the River Lagan (Northern Ireland) using an inert gas (krypton, Kr) are re-analysed using two solute transport models (ADM, TSM) and an inverse-modelling framework (OTIS-P). Results for K_2 are consistent with previously published values for this reach (K_2 (20) ~10-40 d^{-1}). The storage area constituted 30-60% of the main cross-section area and the storage exchange rate was between 2.5×10^{-3}-$3.2\times10^{-3}s^{-1}$. The additional hydrodynamic parameters obtained give insight into transport and dispersion mechanisms within the reach.

Keywords: Modelling; River reaeration; Solute transport; Tracers; Transient storage

1.0 INTRODUCTION

The capacity of surface waters to assimilate oxygen-depleting contaminants (e.g. BOD pollution) depends critically on the oxygen (O_2) mass transfer (or reaeration) coefficient (K_2,) which characterises the rate of O_2 absorption across the air-water interface. Direct measurement in the field via dissolved gas tracer studies has proven the most reliable method to quantify K_2 (Reid et al., 2007). Hydrodynamic processes such as advection, dispersion, dilution (mixing) from groundwater base flow and exchange with storage zones affect also the spatial and temporal concentrations of non-volatile pollutants and tracers alike (Chin, 2006).

The direct tracer method for determining K_2 involves injecting (dissolving) in a stream body a non-volatile, conservative tracer (to assess physical advection, dispersion, and mixing effects) and a volatile, gas tracer (to assess additionally mass transfer across the air-water interface). The concentration-time curves (or *breakthrough curves*, BTCs) of the tracers at two predetermined downstream locations are then monitored. Conventionally, results from field tracer BTCs are interpreted first by normalising the concentration of the gas tracer to that of the conservative tracer (Kilpatrick *et al*., 1989). A first-order loss coefficient for the gas is then determined from logarithmic relations between concentration and travel times at the upstream and downstream sampling sites using either the normalised peak concentrations (*peak method*) or the total mass for the gas tracer calculated from the area under the BTC (*area method*) and the volumetric flow (Reid *et al*., 2007). The main drawback of these approaches is that although K_2 is quantified, the physical transport and dispersion parameters that affect concentrations and which may be of interest for water quality modelling are not. Tracer modelling approaches (e.g. ADM - Advection Dispersion Model, TSM – Transient Storage Model) are now being used generally, and particularly to quantify hydrodynamic parameters of solute transport in river systems (e.g. D'angelo *et al*., 1993; Hart *et al*., 1999). Chapra and Wilcock (2000) used conservative and gaseous tracers (bromide (Br^-)) and sulphur hexafluoride (SF_6) respectively) and a solute transport modelling framework to characterise both transport and gas transfer in Piako River (NZ). They report results showing close agreement in K_2 values calculated from the ADM, TSM, and a modified peak method. However, for the transport characteristics they have queried the capability of the ADM to correctly capture the skewness of the BTCs for the given system with a storage zone effectively constituting about 20% of its total cross section area. Their study needs extending to different flows and other rivers of different sizes and morphology if greater insight into transport and dispersion effects and impacts on gas exchange is to be gained.

In the current paper, the K_2 and hydrodynamic parameters are determined for the River Lagan (Northern Ireland). Original data from a series of RWT and Kr tracer experiments have been reported already for which conventional peak and area methods were applied (Reid *et al*. 2007). Three of these tracer tests are re-analysed here using solute transport and inverse modelling approaches.

2.0 METHODS

2.1 Study site and field tests

Field tests were conducted during 2004 and 2005 in the River Lagan, Northern Ireland (Fig.1). Tracer (RWT, Kr) injection, monitoring, and analysis methods for eight separate tests are detailed by Reid *et al*. (2007) who have reported previously on K_2 parameter estimations using the peak and area methods. Mean daily volumetric flow (m^3s^{-1}) for the period is provided by Rivers Agency (NI) for the Newforge gauging station. The tracer release site is a disused road bridge at Shaw's Bridge; sampling points were at Newforge Bridge (600m downstream) and Red Bridge (1200m downstream). Estimates for the distance for vertical and lateral mixing under given river conditions suggest that full mixing was achieved before Newforge Bridge (Fig. 1) such that one dimensional (1-D) formulations could be used in analysis of the BTCs. Full lateral mixing at Newforge Bridge has been checked during two tracer tests conducted using RWT only. Concentrations near the left and right banks of the river were found to be within 95% of that at the centre, signifying full mixing laterally (Chin, 2006).

2.2 Modelling and simulation procedures

Two 1-D transport models were used to simulate the measured tracer BTCs: the TSM because it is known to give a better understanding of transport phenomena; however, the ADM is used also here due to its widespread application in water quality modelling. A presumption in both models is that flow and dispersion parameters do not vary spatially within the reach. The TSM (Bencala & Walters, 1983) is given by:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + D_x\frac{\partial^2 C}{\partial x^2} + \frac{1}{A}\left(C_L q_{Lin} - Cq_{Lout}\right) + \alpha\left(C_s - C\right) - KC \qquad (1.a)$$

$$\frac{\partial C_s}{\partial t} = \alpha\frac{A}{A_s}\left(C_s - C\right) - K_s C_s \qquad (1.b)$$

where: A and A_s are the main channel and storage zone cross-section areas (m^2), respectively; C and C_L and C_s are the main channel lateral inflow and storage zone solute concentrations ($mg.m^{-3}$), respectively; x is the longitudinal space coordinate in the flow direction (m); D_x is longitudinal dispersion coefficient (m^2s^{-1}); Q is the averaged cross-sectional flow (m^3s^{-1}); α is the storage zone coefficient of mass exchange (s^{-1}) with the main channel flow; q_{Lin} and q_{Lout} are the inflow and outflow rates over the reach ($m^3s^{-1}m^{-1}$), respectively; K and K_s are the first-order loss coefficients (s^{-1}) for a volatile tracer in the main channel and storage zones, respectively. For a conservative solute (cf. RWT) $K = K_s = 0$. The ADM is of similar form to the TSM but with $\alpha = 0$, i.e.

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - KC \qquad (2)$$

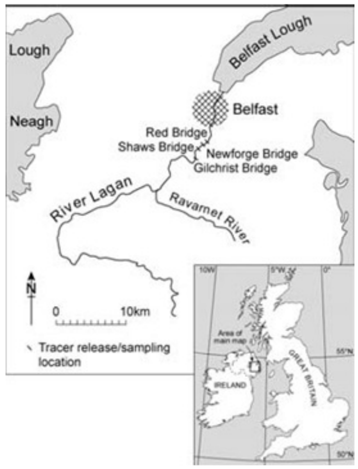

Figure 1 Map of the River Lagan (from Reid *et al*. 2007).

The well-established OTIS (*One-Dimensional Transport with Inflow and Storage*) code (Runkel, 1998) was used to solve numerically both the TSM and ADM to obtain values of the model parameters by an inversion routine minimising the square of the difference between field measurements and the model simulated values of concentration (the objective function) using non-linear least squares regression. Analysis assumes that any lateral inflow and outflow to and from the river between the two sampling stations is negligible. The BTC at the first sampling point is used as the upstream boundary condition. The conservative tracer (RWT) BTC is used initially to calibrate the hydrodynamic processes of advection, dispersion, and transient storage separately for the TSM (A, D, α, A_s) and ADM (A, D). Values of the optimised hydrodynamic parameters obtained from calibration then are fixed for Kr and only K is allowed to vary. The output from this modelling process is a suite of parameter values for the reach between the two sampling points that gives the best model fit to the measured BTCs. The reliability of TSM parameters derived from the RWT data is checked using the Damköhler Index (DaI) which characterises the rates of exchange between the stream and storage zones versus advection:

$$DaI = L\left[\frac{A}{A_s} + 1\right]\alpha / \left(\frac{Q}{A}\right) \qquad (3)$$

Where L(m) is the length of the experimental reach (Wagner & Harvey, 1997). Transient storage parameter uncertainties are considered high outside the limits 1.0< DaI <10.

2.3 Determining K_{Kr} and K_2

Values of K for Kr (i.e. K_{Kr}) for each test were obtained from inverse fitting. For comparative purposes, two other methods were used to compute values of K_{Kr} (and thence K_2): the *area method* (Kilpatrick *et al*., 1989; Reid *et al*., 2007) and the *modified peak method* (Tsivoglou *et al*., 1968; Chapra & Wilcock, 2000). The area method is based on calculating the total mass of tracer at each sampling station from the product of discharge and area under the Kr BTC:

$$K_{Kr} = \ln\left[M_u / M_d\right] / \left(t_d - t_u\right) \qquad (4)$$

where M_u and M_d represent the mass of Kr at the upstream and downstream sampling stations respectively and t_u and t_d are the corresponding travel times (Kilpatrick *et al*. 1989). In the modified peak method data points at and near the peaks of both the upstream and downstream BTCs are used to obtain a log-linear plot using Eq. 5:

$$\ln\left[C_{RWT} / C_{Kr}\right] = K_{Kr} t + c \qquad (5)$$

Where C_{RWT} and C_{Kr} are the concentrations of RWT and Kr at time t (at and near the peaks of the BTCs), K_{Kr} (the gradient of the graph) is the mass transfer coefficient for Kr at the particular temperature during the test, and c is a constant. K_{Kr} obtained from all three methods is then converted to K_2 using the following relationship, established by Tsivoglou *et al.* (1965):

$$K_{Kr} / K_2 = 0.83 \pm 0.04 \quad (6)$$

Calculated K_2 values at temperature T^oC are subsequently adjusted to a standard 20^oC using:

$$K_2(20) = K_2(T) \times 1.0241^{(20-T)} \quad (7)$$

3.0 RESULTS AND DISCUSSION

3.1 RWT behaviour

Photo-degradation and sorption potentially can lead to loss of RWT but only in relatively long tracer experiments lasting for days (Keefe *et al.*, 2004). All tests here were completed in under 1.5hrs, and the given flow conditions are assumed to be steady during these test periods. In order to confirm RWT conservation, the total masses observed at the upstream and downstream sampling stations were compared. Results for the three tests presented show that the mass of RWT recovered at Red Bridge was 98.5% (Test A), 97.4% (Test B), and 95.5% (Test C) as a percentage of the initial mass at Newforge Bridge. Other studies report percentage recoveries for RWT as low as 89% having little impact on the accuracy of estimated parameters (Jin *et al.*, 2009).

3.2 Graphical comparison of models

The measured and simulated BTCs for RWT are shown in Figure 2. Even though all simulations are optimised to the same observed data, the two models clearly provide different fits to the BTCs, with the TSM generally fitting the observations better than the ADM. Values for the least squares objective function for the TSM are 0.68 (Test A), 2.27 (Test B), and 0.97 (Test C) whilst corresponding values for the ADM are an order of magnitude more at 9.34, 13.18 and 17.62, indicating the superiority of the TSM fit.

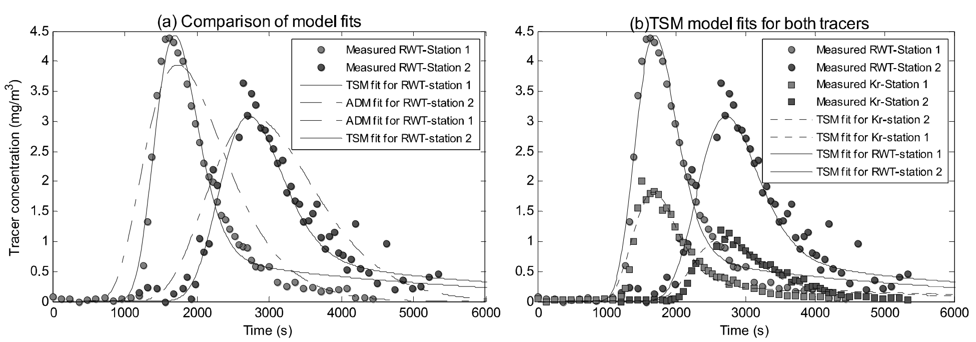

Figure 2 Example measured and simulated RWT and Kr breakthrough curves (BTCs) for Test B (Date: 10/12/04. Flow: 4.13m^3/s). (a) Comparative TSM and ADM fits for RWT tracer only; (b) TSM fits for both RWT and Kr. Similar plots were obtained for Tests A and C.

Observed BTCs also have sharper rise times and longer tails generally than can be simulated by the ADM (Fig. 2 (a)). These features generally are attributed to exchange mechanisms and the slow release of tracer from transient storage zones (Bencala & Walters, 1983). The better fit between the TSM and the field data together with the values of DaI (Table 1) indicate that the TSM formulation generally gives more representative values of transport parameters in this reach of the River Lagan. The BTC for Kr then are simulated by fixing values of the hydrodynamic parameters derived from the RWT fit and fitting to the first-order loss coefficient, K_{Kr} (Fig. 2 (b)).

Table 1: Optimised parameters for the TSM and ADM fits

	Parameter estimates for Tests A, B and C					
	Transient Storage Model			Advection Dispersion Model		
	A	B	C	A	B	C
Flow[a](m^3s^{-1})	7.460	4.131	4.015	7.460	4.131	4.015
D_x(m^2s^{-1})	0.028	0.014	0.014	7.39	23.25	14.80
A(m^2)	14.20	6.79	7.78	18.11	9.10	12.35
A_s(m^2)	4.00	3.62	4.20	n.a	n.a.	n.a.
$\alpha(s^{-1}) \times 10^{-3}$	2.45	3.11	2.59	n.a.	n.a.	n.a.
DaI	9.18	6.28	6.13	n.a.	n.a.	n.a.
A_s/A	0.28	0.53	0.54	n.a.	n.a.	n.a.
Travel time (min)	16	15	18	n.a.	n.a.	n.a.
$K_{Kr}(d^{-1})$	15	25	7	14	23	6
$K_2(20)$ (d^{-1})	26	39	13	24	36	9

[a]Source: DARD Agency. n.a. = not applicable

3.3 Hydrodynamic parameters

The best-fit model parameters for both the TSM and ADM are given in Table 1. Obviously analysis of more field data sets obviously is required, but tentative comments may be made here**.** The dispersion coefficient (D_x) derived from the ADM fit for each test is several orders of magnitude higher than that for the TSM. ADM estimates generally lie within the range 4-25 m^2s^{-1} cited by other researchers for similar rivers by Rutherford (1994). However, that comparative range itself is based on studies using the ADM approach. The D_x values estimated in the current work by the ADM do not correlate particularly well with flow, as seen also in other published studies. This might be due to the fact that for fully turbulent flow, D_x is related only to the spatial and temporal velocity distributions of the flow rather than its magnitude or velocity (Rutherford, 1994). However, the TSM results show that the highest value for D_x corresponds in fact to the highest Q, in line with e.g. D'Angelo *et al*. (1993). Tests B and C give the same value for D_x, as expected for similar flow conditions. In both the TSM and ADM, D_x generally characterises the spreading of the leading edge of the BTC; however,, in the TSM this parameter describes solute spreading due to shear dispersion and transverse turbulent diffusion only, whereas in the ADM, D_x compounds the processes of shear dispersion and transverse turbulent diffusion, with further dispersion due to transient storage (D'angelo *et al*., 1993; Rutherford, 1994).

Estimates of cross-sectional area (A) from the ADM and TSM simulations are of a similar order of magnitude for all flows, and are comparable with an average value of c.11.4m^2 obtained from physical measurements (21/06/2002) at both Newforge and Red Bridges for a flow of 5.73m^3s^{-1}. The cross-sectional area of the main channel derived from the TSM fit increases with Q; values of A_s/A for all experiments are within the range 0.1-1 reported for other similar rivers and flows (Laenen & Bencala 2001). The lowest A_s/A ratio here corresponds to the highest Q, similar to tracer test results seen by D'Angelo *et al*. (1993) who postulated that during high flows, transient storage zones merge into the main, free-flowing zones, whereas at low flows they function autonomously.

Damköhler Indices for all experiments were within $0.1<DaI<10$ indicating that the estimated transient storage parameters are representative of the reach. Under test flow conditions, values of α apparently do not trend with Q, as found also in other studies (Hart *et al*., 1999). Wagner and Harvey (1997) have suggested that α is less easily identifiable for DaI >>1. Wide variability in α also has been reported in the literature for rivers where storage is provided predominantly via surface stagnant waters rather than hyporheic zones (Hart *et al*., 1999). In the River Lagan case, it is possible that the signature of storage exchange here is influenced and dominated by the backwater effects of the upstream weirs in this study reach.

3.4 The reaeration coefficient (K_2)

Mean velocities, calculated from Q and estimates of A, and $K_2(20)$ values from ADM and TSM simulations, the area method (Eq.4) and modified peak method (Eq.5) are compared in Table 2. Kr losses from storage zones here are considered negligible as the bulk of the tracer mass transport is in the channel flow. Values of K_2 estimated generally are in close agreement; slight differences between ADM and TSM estimates may reflect that the former aggregates storage characteristics into the main channel flow, whereas the latter separates out the main-channel characteristics (where most gas loss takes place) from storage zones (where there is negligible loss). Results initially suggest that K_2 increases with mean velocity (i.e. higher gas desorption at higher turbulence). But it is noted here that tests B & C conducted under similar flow conditions apparently produce different K_2 values.

Table 2: $K_2(20)$ estimated from model simulations, area, and modified peak methods

			Reaeration coefficient $K_2(20)$ (day^{-1})					
			Model Simulations*		Other methods		Earlier Study**	
Test No.	Mean Velocity ($m.s^{-1}$)	Temp (^oC)	ADM	TSM	Area[(a)]	Modified Peak[(b)]	Area	Peak
A	0.53	7.6	24	26	26	27	34	65
B	0.61	8.0	36	39	33	25	33	32
C	0.52	7.8	9	13	11	13	3	11

* From Table 1. ** Reid *et al*. 2007. [(a)] Areas under the curve of simulated Kr BTC are calculated using Trapezium rule (with integral time-step of 4s). Area method estimates are based on the entire simulated curve, whereas Reid *et al*. (2007) used the measured data points.[(b)] Refer to Fig.3.

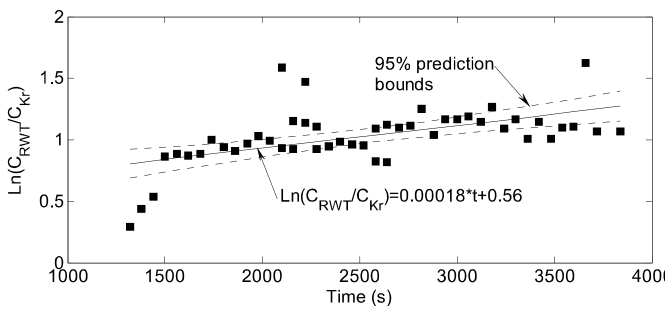

Figure 3: Example *modified peak method* plot of natural logarithm of RWT and Kr concentration ratios versus time for Test B (Date: 10/12/04. Flow: $4.13m^3/s$). K_{Kr} is determined from the gradient of the linear least squares fit of $\ln(C_{RWT}/C_{Kr})$ versus t (Eq.5) and then conversion to $K_2(20)$ (Eqs.6 & 7).

4.0 CONCLUSION

1-D transport and dispersion TSM and ADM approaches have been applied to observed tracer (RWT, Kr) test data from the River Lagan (Northern Ireland) using the 1-D OTIS program coupled with a non-linear parameter estimation code. Model fits show that the classical ADM generally proves unable to capture fully features such as the skewness of the tracer breakthrough, and is not reliable for explaining transport and dispersion in the experimental reach. Results for the reaeration coefficient, $K_2(20)$ of 10-40 d^{-1}, are consistent with previously published values for this reach using conventional peak and area method approaches to data analysis (Reid *et al*., 2007). The TSM, however, gives improved insight into the processes contributing to the overall transport processes in the reach. Under the test flow conditions, the total cross-sectional area of the river was calculated to range between 9-19m^2 of which stagnant zones constituted 30-60% and the exchange rate (α) with these zones was between 2.5×10^{-3}-$3.2\times10^{-3}s^{-1}$. Interestingly, for the K_2 estimation for the two apparently valid tests conducted under similar flow conditions (tests B & C) and producing similar hydrodynamic parameter values, the different K_2 values determined suggests some other control than hydrodynamic processes per se that may have to be accounted for.

This study shows that stream tracer tests traditionally designed for determining K_2 in-situ can be analysed by inverse modelling (e.g. TSM) to provide additional hydrodynamic information of environmental significance relating to the transport and dispersion characteristics of a reach. With the introduction of the (stable) inert gas Kr as an environmentally-friendly tracer, it is now more attractive to do gas tracer tests to obtain K_2 and also quantify physical transport parameters important for water quality modelling and surface water management.

5.0 ACKNOWLEDGEMENT

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