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Evaluation of a novel technique for measuring reaeration in rivers

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Abstract

Depletion of dissolved oxygen (DO) is one of the most common forms of river pollution. In extreme cases, it can result in fish kills, foul odours and can prohibit the use of water for drinking and other purposes. Regulatory authorities therefore place great importance on their ability to predict depletion of DO in waters which receive wastewater discharges and agricultural runoff.

To date, predictive water quality models have relied almost totally on empirical methods to estimate the overall controlling factor for mass transfer of oxygen from the atmosphere into water bodies, the reaeration coefficient (K_2). However, this coefficient varies from one river to another and changes with changing hydraulic conditions within a reach. Poor estimates have often led to inaccurate predictions of water quality.

This paper describes the development of a novel method for the direct measurement of the reaeration coefficient in any river. This direct approach utilises two tracers – one volatile, one conservative – but, unlike previous tracer studies reported by other authors, it does not rely on the use of radioactive materials to achieve sensitive and precise measurement. Instead both tracers used are generally deemed 'environmentally friendly': the inert gas, Krypton, and the recognised fluorescent water tracer, Rhodamine WT, are used to quantify the reaeration coefficient. The adopted method is based on highly sensitive measurements of these substances using Gas Chromatography Mass Spectrometry (GC-MS) and fluorimetry techniques respectively.

The outcome of field tests in a major river in Northern Ireland is reported. Issues affecting the precision of the method are addressed and the practicalities of applying it are discussed.

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1 Introduction

1.1 Oxygen-demanding pollutants and reaeration in rivers

The introduction of any oxygen-demanding material (such as wastewater or agricultural runoff) into an open water system tends to deplete the dissolved oxygen (DO) in the water. As early as 1925, Streeter and Phelps [1] modelled the relationship between Biochemical Oxygen Demand (BOD) and DO in surface waters, and this is still used extensively for estimation of DO mass balance for a given stretch of water. They considered that when biodegradable waste was discharged to a receiving water it consumed oxygen, which was renewed only by surface reaeration. Differentiation of the classic Streeter-Phelps model yields a function that relates the oxygen demand and re-oxygenation as a result of reaeration:

$$\frac{d(\Delta DO)}{dt} = K_1 L - K_2 (\Delta DO) \tag{1}$$

where $d(\Delta DO)/dt$ is the change in oxygen deficit (ΔDO, mg O_2/l) per unit time, K_1 is the BOD oxygen utilisation constant (day^{-1}), L is the BOD load (mg O_2/l) of the river at a given time, t, and K_2 is the reaeration coefficient (day^{-1}). The equation may be rearranged to give a value for ΔDO in terms of K_1 and K_2. K_1 can be measured in the laboratory (using standard BOD_5 and/or BOD_{20} tests). This is not, however, the case for the reaeration coefficient, K_2, the key parameter in the evaluation of the mass transfer of oxygen across the air-water interface.

Because of its importance in determining the rate of recovery of oxygen-deficient waters, K_2 has been the subject of various investigations in the past. Some techniques for measurement of the coefficient rely on indirect methods, in which the coefficient is inferred from the measurement of other parameters and subsequent calculations. This technique is not considered reliable, and so researchers such as Tsivoglou *et al.* [2] used a direct approach, originally using radioactive tracers. However, with growing pressure to avoid environmental tests which in themselves cause environmental damage, a need was seen for a similar method which uses acceptable tracers. The limiting factor was the availability of suitable "environmentally friendly" tracers, which are capable of performing the required tasks and are detectable with the reliability and precision required to calculate the reaeration coefficient.

1.2 Technique for measuring K_2 using a gaseous tracer

The technique described here involves the simultaneous release of two such tracers within a river. One tracer is conservative in the river system, so any changes in concentration of this substance are assumed to be due solely to dilution and dispersion. The second tracer is volatile and is therefore capable of transfer across the air/water interface. This second tracer allows estimation of

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the loss of gas from the water to the atmosphere along a given reach, a process which is effectively the reverse of reaeration (the mass transfer of gas (oxygen) from the atmosphere to the water body). Any changes in concentration of the volatile tracer are assumed to be due to dilution, dispersion or gas transfer to the atmosphere. The tracers are transported within the flowing water and their concentrations are subsequently measured at two or more downstream locations. The measured concentrations may then be used to evaluate the reaeration coefficient.

Evaluation is based on the following principles. For a well-mixed river, both the flow characteristics and the water quality are assumed to uniform throughout any cross section. The concentration of a non-reactive gas can be described using the one-dimensional advection dispersion equation. It can be shown that, for an instantaneous input of a gas in such a river, the concentration of gas C (kg/l) at a point x (metres) downstream and time t (days) after release is given by:

$$C(x,t)=\frac{M}{A\sqrt{4\pi Dt}}.exp\left[-\frac{(x-ut)^2}{4Dt}\right].exp[-K_{gas}t] \qquad (2)$$

where M (kg) is the total mass of gas added, A (m^2) is the cross-sectional area of the channel, K_{gas} (day^{-1}) is the gas transfer coefficient which determines the loss of volatile gas across the air/water interface, D (m^2/day) is the longitudinal dispersion coefficient and u (m/s) is the stream velocity averaged across the cross-section of the river. Equation 2 is also valid for a conservative tracer but, in this case, the transfer coefficient (K_{gas}) has a value of zero.

If a gaseous tracer and a conservative tracer are released simultaneously and their peak concentrations, C_{gas} and $C_{conservative}$, are measured at two points A and B downstream of the release location, then it is possible to calculate a value for K_{gas}. This is achieved by rearranging Equation 2, and using the measured concentration of the conservative tracer to eliminate unknown factors such as the dispersion coefficient. The resultant equation is:

$$K_{gas}=\frac{1}{t_A-t_B}Ln\frac{\left(\frac{C_{gas}}{C_{conservative}}\right)_B}{\left(\frac{C_{gas}}{C_{conservative}}\right)_A} \qquad (3)$$

It is worth emphasising that, as the technique is based on the principles of one-dimensional flow, there is an inherent assumption that tracer concentrations at locations A and B are uniform across the cross-section of the flow. In practice, this requires that full mixing of tracers has taken place prior to their arrival at the first measurement point, location A.

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2 Method adopted for measuring the reaeration coefficient

In order to prove the method described, using tracers considered acceptable for use in rivers, various laboratory and field trials were performed. These are documented in a paper by Murphy *et al.* [3]. All of the field tests conducted to date were performed on the River Lagan in Northern Ireland.

2.1 Gaseous tracer

The tracers used included Krypton (Kr) - one of the noble gases - an inert, non-reactive, non-sorbing gas, which has a low molecular diffusion coefficient and which occurs naturally at trace ambient levels in the atmosphere. Krypton is non-toxic and lacks both odour and colour. It has no known sources or sinks in the natural environment, so detection of substantial levels of Krypton may be attributed solely to man-made release. These properties, and its suitability for high-precision measurement using Gas Chromatography-Mass Spectrometry (GC-MS), render it a suitable tracer for environmental studies. McNeill *et al.* [4] describe its properties and its use in groundwater investigations.

Another advantage of using Krypton is that the relationship between the gas transfer coefficients for Krypton and oxygen is already known. Once K_{gas} (in this case, K_{Kr}) is quantified, it is possible to calculate K_2, the reaeration coefficient, using the following relationship, established by Tsivoglou et al. [5]:

$$\frac{K_{Kr}}{K_2} = 0.83 \pm 0.04 \tag{4}$$

For the purpose of comparisons, it is normal to report the reaeration coefficient at a standard temperature of 20°C. This may be achieved using the following equation, reported by Roldão [6]:

$$K_2\,(20^o C) = K_2(\theta) * 1.0241^{(20-\theta)} \tag{5}$$

where θ is the sampling temperature (°C).

2.2 Conservative tracer

The other tracer used was the fluorescent dye, Rhodamine WT, which has been utilised extensively as a water tracer in studies of dilution and dispersion. In this case, the measurement technique was fluorimetry. Using a 'GGUN-FL' portable field fluorimeter (produced by the Geomagnetism Group, at the University of Neuchâtel in Switzerland), even the smallest concentrations of Rhodamine WT could be detected. The Rhodamine, which acted as the conservative tracer in these tests, therefore had the advantage of being detectable *in situ* for prolonged periods after the initial visual impact had subsided. For this reason, it was used

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also to indicate when water samples should be collected for laboratory analysis (Krypton is not detectable on site).

3 Testing of methodology in preliminary field trials

Early field trials (carried out from October 2000 to January 2001 and reported by Murphy *et al.* [3]) demonstrated the practicality of the method and permitted an evaluation of the reaeration coefficient, K_2, under several different weather and fluvial conditions. The tests provided confidence in the method, but also highlighted several aspects that required further attention.

3.1 Tracer release method

Values of K_2 calculated on the basis of the early field tests highlighted several issues which are crucial to the success of the measurement. The first of these was the method of tracer release. Laboratory tests had shown that the most effective way of ensuring identical and 'instantaneous' release of the two tracers was by preparing a solution of both tracers in a vessel which was rapidly emptied into the flow. This technique was not, however, practical for use on site, as the quantity of solution required to achieve adequate detection of the gas tracer was prohibitive. Instead, the gas was released directly into the water through a perforated PVC diffuser, weighted to maintain its intended position on the river bed. The diffuser was 10m long and was placed laterally across the river, which had a total width close to 10m at all of the release locations used. Krypton was bubbled through the diffuser for a period of 30 seconds. Simultaneously, a prepared solution of Rhodamine WT was released from a 2.5 litre bottle held close to the water surface at the centre of the channel. The earliest tests used 60g of Rhodamine throughout, but in later tests this value was refined (and reduced) according to the particular conditions on site at the time of the test. This particular release method was chosen mainly due to practical considerations. Issues of non-simultaneous measurement of peak concentrations for Krypton and Rhodamine WT have raised some queries as to whether the approach suffices. Although comparative tests are planned, they have yet to take place.

3.2 Storage, preparation and analysis of samples

A second aspect that required detailed attention during tests was the storage, preparation and analysis of samples for Krypton using the GC-MS. Protocols had been established for each stage in the procedure. These included:

- collection of samples in 40 ml standard glass Volatile Organic Compounds (VOC) bottles, which were filled to the brim and sealed immediately using Teflon-lined septa and phenolic screw top caps to prevent gas exchange between the sample and the atmosphere, as recommended by Jones [7];
- storage of samples at a constant temperature of 4°C, for a maximum duration of 250 hours prior to analysis, as recommended by Jones *et al.* [8];

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- preparation of samples by extracting 5 ml of water through the septum seal with a syringe, simultaneously replacing the water by injecting a (5 ml) pure-Helium headspace into the sample and leaving the samples overnight, stored inverted, to equilibrate;
- extraction of a sub-sample of up to 100 µl of the headspace gas, which was analysed by manual injection into a ThermoQuest "Voyager" Gas Chromatograph with mass-spectrometric detection.

When it came to field tests, practical issues that could not easily be predicted (such as the limiting rate at which samples may be analysed and occasional instrument failures) had an adverse impact on the data obtained. As a result, standard operating procedures have now been refined, with duplicate sampling introduced as the norm to avoid loss of data or return of questionable values.

3.3 Confirmation of Rhodamine WT concentrations by laboratory analysis

In the early tests, the fluorimeter was used to monitor Rhodamine WT concentrations and assess the timing of grab samples for Krypton analysis. These tests also confirmed the need for laboratory measurements of Rhodamine WT in addition to *in situ* measurements. Values measured during field tests were found to overestimate those determined from grab samples analysed in the laboratory. Values determined *in situ* were between 5 and 45% higher than those from the corresponding samples analysed in the laboratory. The discrepancy was attributed to the turbidity of the flowing river water, a factor eliminated by allowing settlement of suspended solids in grab samples prior to laboratory analysis. The effect of turbidity on measurements is a recognised problem in fluorimetry. In this particular case, it is easily overcome by relying on laboratory measurements only when performing calculations. However, the importance of these extra measurements in the laboratory is stressed: the use of data recorded *in situ* may lead to a significant overestimate of Rhodamine WT concentrations and a corresponding unreliable assessment of the reaeration coefficient.

4 Subsequent field tests

4.1 Results of tests

Having assessed the results from preliminary field trials, a second series of tests was conducted. These tests were also performed in the River Lagan, but this time at a location more than 10 km downstream of the initial test sites. The tests were carried out between June and September 2001. Tracers were released from a disused road bridge and sampled from footbridges approximately 600m and 1100m downstream. Tests were conducted during a period of stable weather conditions, with relatively low flows in the river throughout. Full details of these tests are provided in a report by Lynch [9].

The data obtained during this test series were analysed more critically than those from the early tests which, due to exceptionally difficult weather conditions, were considered to provide only rather crude measurements of the

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reaeration coefficient. Data were screened for anomalies, prior to processing within a spreadsheet. A typical result is shown in Figure 1.

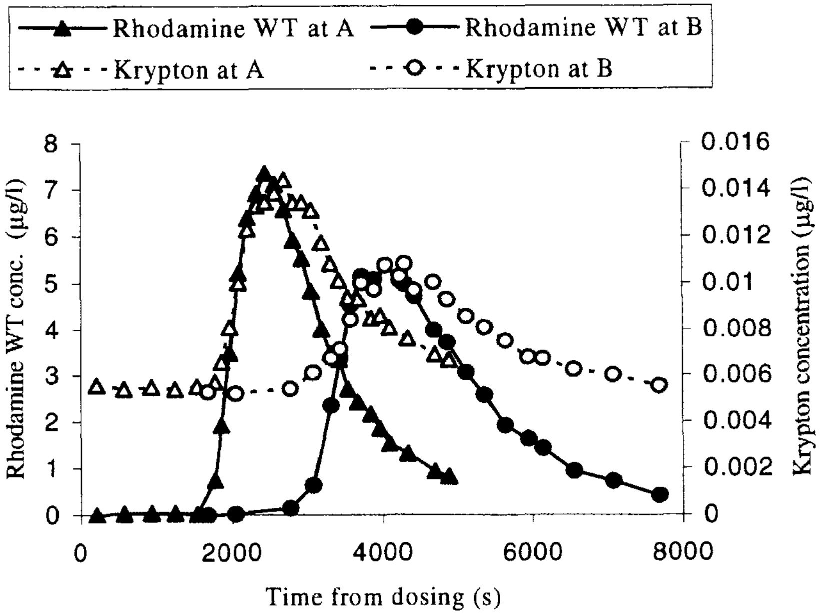

Figure 1: Tracer concentrations recorded in River Lagan, 4 September 2001 (based on material compiled by Lynch [9])

The data shown in Figure 1 illustrate the rise and fall in concentrations of both tracers at the two sampling locations. The overlap between successive peaks arises due to the proximity of the two sampling stations used. In longer stretches of river (such as those used in preliminary tests reported by Murphy *et al.* [3]), the pairs of peaks recorded at stations A and B are separated, due to the elapse of time between detection of tracers at successive stations.

4.2 Discussion of results and methods used

After plotting and visual examination, the results were analysed in two different ways. The first of these, the 'peak concentration' method, involved a straightforward calculation of K_{Kr} on the basis of Equation 3, using the peak concentration of tracer recorded at each measurement location. The second method, the 'area' method, involved summation of the values under the tracer versus time graph at each location, and hence the calculation was based on the total quantity of each tracer passing the two measurement locations.

The first method, while theoretically correct, is subject to errors associated with sampling. For example, the delay between collection of successive samples

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can result in the true peak concentration being missed. Other factors also tended to complicate the calculation. For example, on some occasions, the peaks for the two tracers did not occur simultaneously, suggesting either an imperfect tracer release or dissimilar transport and dispersion, either of which could lead to erroneous results.

By comparison, the second method was thought to be more reliable, in that it yielded a value for K_{Kr}, but also allowed checks on tracer loss to be carried out, using a simple summation of masses. However, this method does require that the full tracer curve (from the baseline to the peak concentration and back to the baseline) is recorded.

The data recorded during the summer of 2001 yielded K_2 values ranging from 6 to 126 day^{-1}, which are comparable with those reported by other researchers such as Willcock [10] and Wanninkhof *et al.* [11] who used alternative methods in rivers with similar characteristics.

4.3 Practicalities of applying method in different rivers

The field tests carried out to date have all been conducted in one river, although tests have been performed successfully at various sites. In an attempt to provide a practical method that can be applied with relative ease, the use of bridges for release and sampling was maximised. In most cases, the distance between successive sampling points did not exceed 2 km. On a river such as the River Lagan, which has many bridges, this was possible in most of the locations used; the monitoring of tracers was straightforward as the fluorescent dye was detectable on an almost continuous basis, at one location or another. However, it is recognised that this would not always be the case. The main issue when working in a river with limited access is ensuring that the tracers are detected at adjacent points

In some cases, tracer release and measurement from bridges was not practical and a small boat was required. In this case, safe and accessible points for launch of the boat were required. For safety reasons, use of the boat, and therefore the performance of these tests, was restricted at times of high river flow.

One of the main issues to ensure a successful test is the introduction of an appropriate quantity of tracer. The earliest tests were performed on a 'trial and error' basis, but subsequent work has been carried out to ascertain appropriate quantities. The appropriate quantity was deemed to the minimum amount of tracer to be detected without ambiguity above background levels at the furthest sampling point. In this way, any impact of the tracers on the river (including visual impact) was minimised. Optimisation tests conducted in a range of flows at one particular site have produced significant information in this respect, although further consideration is required before the data could be used in other rivers.

The successful introduction of the tracer was found to depend on the characteristics of the river at the release location. With the direct release of the gas to the river, the depth of water at the release location was considered important, with better results obtained when releasing into deeper water. The

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choice of sampling locations is also important, particularly on a river system with tributaries (which change the overall flow in the river) and side channels (which might divert water from the main stream). In the Lagan system, stretches of disused canal linked to the river proved problematic in some areas, as there was potential for both water and tracers to be retained within these stretches, distorting the results. In the tests reported here, these areas were avoided.

In its present form, the technique is labour intensive, requiring a minimum of four persons on site for any one test. Future investigations are planned to address this issue, examining the potential for reduced personnel while still maintaining the quality of the work and meeting the relevant safety requirements.

5 Conclusions

The results of tests conducted in the summer of 2001 demonstrate that it is feasible to use the combined inert gas/conservative tracer approach to provide a direct evaluation of the reaeration coefficient. The method is reliant, however, on certain specific measures, including the assurance of total mixing prior to measurements, complete measurement of the tracer versus time graph at each measurement station and careful adherence to the established sampling and analysis protocols.

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