Multiple-tracer tests for contaminant transport process identification in saturated municipal solid waste^{*}

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Abstract

Two column tests were performed in conditions emulating vertical flow beneath the leachate table in a biologically active landfill to determine dominant transport mechanisms occurring in landfills. An improved understanding of contaminant transport process in wastes is required for developing better predictions about potential length of the long term aftercare of landfills, currently measured in timescales of centuries. Three tracers (lithium, bromide and deuterium) were used. Lithium did not behave conservatively. Given that lithium has been used extensively for tracing in landfill wastes, the tracer itself and the findings of previous tests which assume that it has behaved conservatively may need revisiting. The smaller column test could not be fitted with continuum models, probably because the volume of waste was below a representative elemental volume. Modelling compared advection-dispersion (AD), dual porosity (DP) and hybrid AD-DP models. Of these models, the DP model was found to be the most suitable. Although there is good evidence to suggest that diffusion is an important transport mechanism, the breakthrough curves of the different tracers did not differ from each other as would be predicted based

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on the free-water diffusion coefficients. This suggested that solute diffusion in wastes requires further study.

1 Introduction

There is considerable uncertainty over the mechanisms of flow and transport through biologically active municipal solid waste (MSW). This uncertainty translates into a poor ability to predict the efficiency of contaminant mass removal from a waste body under different flushing conditions. The importance of this relates to the need to understand and predict how the water polluting potential of landfills will reduce over time and hence for how long active leachate control and management measures will be required at a site. Current estimates indicate that management timescale will run into many centuries after a site has closed (Hall *et al.*, 2004). A difficulty in predicting the transport behaviour of degrading, gassing waste is that state variables such as water flow, gas production rate and water content change over time. 'Landfill simulators' therefore typically need to model several coupled processes, combining a large number of assumptions and parameters in a manner which makes it difficult to infer much about the constitutive relationships or to obtain unique parameter values. The purpose of this study is to extricate from this complexity an understanding of the dominant mass-transport processes in waste. Our approach is to conduct an experiment under highly controlled conditions, such that we can decouple physical transport mechanisms (including advection, mechanical dispersion and diffusion) from thermal, biological, and mechanical processes and multi-phase flow effects.

In a landfill experiencing downward infiltration of water, two distinct regimes of flow are normally considered to exist. At the top of the landfill there is two phase-flow, comprised of downward liquid flow and predominantly upwards landfill gas flow. In this zone it is normally assumed that due to capillarity the liquid pressure will be below that of the gas phase, although localised perching is possible. Several authors (Straub and Lynch, 1982; Demetracopoulos *et al.*, 1986; McDougall & Silver, 2005; Kazimoglu *et*

al., 2006) have attempted to address this regime. McCreanor and Reinhart (2000) modelled this zone using the Richards equation and White *et al.* (2004) modelled both liquid and gaseous phases.

Vertical transport in the zone beneath the leachate table has received less attention in the literature. In this zone (which is frequently called the 'saturated zone', although may not be due to the presence of landfill gas), leachate and gas are under positive hydrostatic pressure.

Solutes that are measured at the base of a landfill will have arisen from and travelled through either the saturated zone or both the saturated and unsaturated zones. Contaminant flushing models for a landfill under these conditions will need to simulate both above and below the leachate-table. Concern over the potential for leakage of contaminants through landfill bases means that the leachate table is often maintained at a low level within the waste, making the saturated zone the minority proportion of the landfill volume. Despite the regulatory barriers to raised leachate tables, an advantage of increased water content would be that it would potentially encourage greater microbial activity and a higher flushing efficiency (Beaven *et al.*, 2004). There is therefore a strong motivation for addressing transport in the saturated zone.

There are particular problems for experimentation in the saturated zone. Firstly, it is difficult to obtain representative *in situ* samples. Secondly, the high levels of compressive stress and compaction are difficult to reproduce in the laboratory. Thirdly, the control of liquid flow during gas production is difficult to achieve.

Even with perfect control, single tracer tests can provide insufficient information to unambiguously identify the underlying transport processes (Jury & Roth, 1990). Flow interruption is a standard method for identifying diffusive non-equilibrium during a tracer test (Brusseau *et al.*, 1997; Fortin, 1997), since

the diffusion process continues even though advection has stopped during an interruption in flow. Wehrer & Totsche (2008) applied flow-interruption to MSW incinerator ash. When applied to MSW (Beaven & Hudson, 2002) this technique has provided evidence suggestive of the presence of diffusive exchange with immobile (or less mobile) zones. However, during active degradation changes to flow rates cause changes in the amount of gas within the waste, and therefore also the volume of liquid within the waste. Flow-interruption is therefore not ideally-suited to gassing wastes as a tool for diagnosing transport processes.

One further way to test the importance of diffusion is to inject tracers with different diffusion coefficients into the waste. This method has been used with success in soils and groundwaters (Garnier *et al.*, 1985; Maloszewski & Zuber, 1992; Becker & Shapiro, 2000). Here the method is evaluated with application to waste. Previous studies have used simultaneous application of multiple tracers in MSW (Woodman *et al.*, 2013, Woodman *et al.*, 2014), however the primary focus in these studies was on the effect of operating conditions rather than on process identification.

There have been a few previous column tracer tests on saturated methanogenic MSW wastes that were suggestive of dual-porosity processes (Beaven *et al.*, 2003; Rosqvist & Bendz, 1999; Fellner & Brunner, 2010). However, difficulties in hydraulic control (specifically, flow rate and saturation level) meant that they were not entirely conclusive (Woodman, 2007).

The primary aim of the experiment described here is to test the hypothesis that dual-porosity exchange is the predominant mechanism accounting for solute mixing. Implicit to this hypothesis is the assumption that flow is restricted to a fraction of the porosity (a 'mobile' zone) and that dispersion will be affected by the diffusion coefficient of the solute in question.

2 Method

2.1 Description of experiments

Two column tests ('Test 0A' and 'Test 0B') were designed to emulate contaminant transport in the complex sub-water table environment of biologically active MSW by tracking the flushing of methanogenic high-bromide leachate with water dosed with lithium chloride and deuterium oxide tracers (i.e. indigenous bromide was flushed from the waste whist lithium and deuterium were passed through the waste as a tracer 'pulse'). Test 0A was performed in a 2m diameter column, in contrast to Test 0B which was in a smaller (0.26m) diameter column. Prior to the flushing, a number of separately reported hydraulic tests were performed on the larger column. Subsequently, leachate was recirculated over five weeks to achieve dynamically stable hydraulic conditions and the equilibration of the high bromide leachate throughout the waste mass. Test 0B was packed and manually compressed to the same bulk density as that in Test 0A. Recirculation was also carried out in Test 0B for approximately five weeks (34 days) prior to the test.

Over the course of the tests samples collected from the outputs of the columns recorded flushing (thereby emulating the flushing of a real landfill) as well as the simultaneous recovery of the two introduced tracers. Bromide was selected as a key flushed species. Aside from differing in scale, both tests were performed under very similar conditions. Test 0A, a large-scale test (5.2 m^3) , was performed first. It will be shown that for this test the estimates of lithium (Li) tracer mass recovery were low. Because this result was of concern a second tracer test (Test 0B) was performed in a smaller-scale laboratory column (0.04 m^3) .

2.2 Experiment

Test 0A was performed in the Pitsea compression cell (shown schematically in Figure 1). The compression cell is a 2 m diameter steel cell capable of delivering uniaxial loads representative of those within full-scale landfills, whilst allowing detailed logging of compression, temperature, piezometric pressures through the column, total weight, gas production and leachate electro-conductivity (EC). The cell was loaded in September 2004 with 3563 kg (dried mass) of fresh MSW that was shredded with a hammer mill and passed through an 80 mm screen.

Sub-samples of the waste were characterised for material content and particle size (see Supplementary Information Table S1). Layers of gravel were placed at the top and bottom of the waste to encourage a uniform distribution of flow in and out of the waste (amounting to depths of 0.08 m above and 0.095 m of gravel above and below the waste respectively).

The residual (i.e. drained) water content of the waste in the cell was established from an oven-dried (at 80°C) 10 kg sub-sample obtained at the time of loading. Thereafter the total water content in the waste was estimated based on the cell weight (measured using load cells) and a water balance. This and other key details of both tests are given in Table 1.

The waste was subject to long-term monitoring and a number of hydraulic tests and was then compressed using an upper platen at 87 kPa (thereafter the platen was locked in position to maintain the waste at a fixed volume). Methanogenic leachate with a high bromide content (Table 2) was obtained from Pitsea Landfill and then introduced and recirculated for two months to allow physical and chemical equilibration.

The design of Test 0A was optimised based on parameters previously established from a pilot tracer test in the Pitsea compression cell (Beaven & Hudson, 2002; Woodman, 2007). The leachate re-circulation was achieved using a positive-displacement pump (LMI Milton Roy C785- 139 35T) drawing from a 400 litre Page 6 of 44

supply tank, giving a stable flow of 3.7 L/h. Manual readings from a gas-meter connected to an outlet manifold at the top of the cell indicated stable gas generation rates before the start of the test and monitoring of cell weight during the test indicated no major change to the water content of the waste over the duration of the test (see data for Phase 1 in Woodman *et al.*, 2009). Consequently, a dynamic hydraulic equilibrium is assumed within the cell for the duration of the test (i.e. gas production rate equal to gas release rate).

This flow corresponded to a flux rate of 10,300 mm/y which is high compared to conditions likely to occur in the field. For example, typical effective precipitation in the east of England is in the range 100-200 mm/y and artificial irrigation on re-circulating landfills have achieved flows of up to ~1000 mm/y (Environment Agency, 2009). An upward-flow arrangement was created in order to prevent buoyant gas bubbles that would tend to move upwards being dragged downwards and possibly becoming trapped or interacting with the leachate in an unpredictable manner.

When leachate recirculation in the column was hydraulically stable (i.e. pressure and flow rates not changing with time), and whilst keeping the flow rate constant, the leachate input to the cell was switched from the re-circulation tank to a tank containing the tracers well-mixed in tap-water and the output was diverted to drain (Figure 1). Samples were taken from the output line upstream of the drain. At the end of the injection period the input flow was switched to tanks holding clean water.

Test 0B was performed with an almost identical method but the cell was a small-scale Perspex column, housed in the same building as the compression cell. Test 0B waste came from the same source as the Test 0A waste and was manually compacted to the same bulk density which Test 0A had achieved under 87 kPa compression. Test 0B had 0.05m of gravel both above and below the waste.

A gas flow of 4-11L/day was recorded prior to the start of Test 0A, but a problem with the meter meant that gas production was not measured during the test. The gas production in Test 0B was not measured.

2.3 Tracers

2.3.1 Application of Tracers

To test the hypothesis of dual-porosity transport, two tracers and an indigenous contaminant provided a range of apparent diffusion coefficients $(1.0 \times 10^{-9}, 2.1 \times 10^{-9} \text{ and } 2.3 \times 10^{-9} \text{ m}^2/\text{s}$ at 25°C for lithium, bromide and D₂O respectively, Cussler (1997)). If dual-porosity is important it would be expected that the breakthrough curves (BTCs) would differ significantly due to the different rates of diffusion in a manner that an advection-dispersion model (AD) could not predict.

Tracing in landfills was reviewed by Blakey *et al.* (1998) and by Woodman (2007). The predominant difficulty for tracing in landfills is the generally high 'background' concentration of most elements within the leachate.

Given the reactive nature of leachates and the multi-component nature of the waste medium, the performance of tracers needs to be evaluated cautiously. If an assumption of conservative behaviour is made and turns out to be wrong, there may be an impact on process and parameter deductions. Therefore before models are applied to the tracer breakthrough curve (BTC) data to test our hypothesis, we first examine the tracers and their mass-balances.

Details of the tracer injection are given in Table 2. The tracers themselves are now discussed in turn.

2.3.2 Lithium

Lithium has been used several times as a tracer for transport within MSW (Blakey *et al.*, 1998; Öman and Rosqvist, 1999; Rosqvist & Bendz, 1999; Beaven *et al.*, 2001; Beaven *et al.*, 2003). Its common use in MSW is explained by its relatively low cost and commonly low background concentration (Harris, 1979; Blakey *et al.*, 1998). Batch tests have not shown significant sorption of lithium in leachate onto MSW (Stegemann *et al.*, 2006; Öman and Rosqvist, 1999). However, two recent papers have observed non-conservative behaviour of lithium in MSW under closed loop conditions (Woodman *et al.*, 2013, Woodman *et al.*, 2014)

To achieve a target concentration of 30mg/L, for Test 0A, 74 g of laboratory reagent grade 99% anhydrous lithium chloride (Fisher Chemicals, Fisher Scientific) was added to tap-water in a 397 L input tracer tank. For test 0B, 2 g was added to tap-water in a 10 L input tank. The tanks were agitated to ensure thorough mixing and then covered.

2.3.3 Deuterium oxide (D₂O)

The second tracer selected was the hydrogen isotope, deuterium. There has been a limited use of isotope tracers in municipal solid wastes. Hoen *et al.* (2000) examined ${}^{10}B/{}^{11}B$ ratios. Maloszewski *et al.* (1995) used ${}^{18}O$ and ${}^{2}H$ as natural tracers and Blakey (1982) examined tritium. There are very few reported tests that the authors are aware of where deuterium oxide (D₂O) has been injected to make ${}^{2}H$ an artificial tracer in waste. Woodman *et al.* (2013) documented a closed-loop test and observed upward fractionation of ${}^{2}H$, believed to be due to evaporation and degradation.

For Test 0A, 100 mL of 99% concentration D_2O (CAF number 7789-20-0, Cambridge Isotope Laboratories Inc, product code DLM-4-99-1000) was added to tap water in a 397 L input tank. For Test 0B, 3mL was added to tap-water in a 10 L tank.

Fractionation of the liquid-phase deuterium due to the formation of methane by degradation is a possibility. Although methanogenesis of acetic acid to methane and carbon dioxide does not involve water in the reaction, the acetogenic and acidogenic stages do utilise water in the reaction, potentially fractionating through preferential use of the lighter ¹H fraction (Morasch *et al.*, 2001). Therefore, any fractionation that occurs through this process would tend to increase the deuterium fraction, as would evaporation. Evaporation from the tank was minimised by placement of a cellophane covering. On collection, samples were stored in McCartney bottles to prevent evaporation. The enrichment due to evaporation would be expected to be less than experienced by closed loop tracer tests, where the leachate and tracer is repeatedly recirculated through a storage reservoir where evaporative processes may come more into play. Woodman *et al.* (2014) observed significant enrichment in a closed-loop test, although were not able to distinguish the precise cause(s).

 D_2O concentrations are given on a permil scale (% $_{o}$) relative to the VSMOW (Vienna Standard Mean Ocean Water) standard according to

$$\delta\%_{o} = 1000. \frac{R_s - R_{VSMOW}}{R_{VSMOW}}$$
[1]

Where R_{5} is the ratio of ²H / ¹H and R_{VSMOW} is 155.76 ±0.1 ppm.

The tank water had a deuterium signature of -39%, the lightness probably primarily attributable to its meteoric origin. The isotope ratio for the leachate was -22% and -30% in Tests 0A and 0B respectively.

2.3.4 Bromide

In terms of the flushed species of choice, bromide was monitored because it was found in high concentration and because it is assumed to behave conservatively in some media (Flury and Flühler, 1995). Ward *et al.* (1998) found that out of the available 'solute-type' tracers for aquifers and soils, the Page 10 of 44

halogens are most suitable, of which bromide is often preferred (as it often has lower and more stable background levels). However, Stegemann *et al.* (2006) showed non-linear bromide sorption to waste. The behaviour of bromide cannot therefore be automatically assumed to be conservative in wastes and is best examined for the particular conditions of a test.

Ultimately, deductions as to the conservative nature of tracers are best made based on the BTCs, since there are significant difficulties in relating batch sorption tests to column or field behaviour (Woodman *et al.*, 2011). To do this leachate samples from Test 0A were obtained from the cell's outlet (Figure 1) and were analysed for a broad suite of species by ICPMS including alkali metals, alkaline earth, transition metals and Bromide. The flushing of these species (except Li, as this was an introduced tracer) was compared by normalising each to their starting concentration and plotting on the same axes. This gave a variety of behaviours. A lower-bound to these measured normalised concentrations was shared by Br, Ni, Rb and Mg and the EC also followed this line (Woodman et al., 2009). All other species gave normalised flushing curves above this line which suggests that they were subject to other processes including sorption and production (for example, by dissolution). The deduction is that under the conditions of the test those species on the lower bound, and Br in particular, were behaving conservatively. This behaviour of Br is corroborated by closed-loop tracer tests performed by Woodman *et al.* (2013) in subsequent tests on the same waste.

3 Basic observations

3.1 Breakthrough curve shape

The D_2O and Li BTCs are smooth, monomodal and positively skewed, thereby exhibiting so-called 'tailing'. The Br flushing curves were both reasonably smooth and monotonic (Figure 2). It is perhaps remarkable that such 'classical' BTCs were produced in quasi-steady state gassing MSW. Despite MSW being frequently characterised as 'highly heterogeneous' (Zacharof & Butler, 2004), existing studies in waste column tests have also produced smooth monomodal skewed BTCs similar to those described in many soil studies (Bendz *et al.*, 1998; Bendz & Singh,1999; Rosqvist & Destouni, 2000; Beaven & Hudson, 2002; Woodman, 2007). The lithium breakthrough is first noticed between 1 and 2 days in Test 0A. This is suggestive of preferential flow, since a sharp-front of tracer passing through all of the porespace would be expected to take approximately 31 days to arrive.

This consistent behaviour suggests that an equivalent porous medium assumption may be reasonable, although it remains possible that this behaviour can arise from a 'sub continuum' (Johnston *et al.*, 2009). The absence of multiple peaks or obvious distortion to the BTC suggests that preferential flow in a few dominant channels (in the manner that is observed in Karstic systems for example) is not prevalent in wastes. Examination of fluxes from different parts of the Pitsea compression cell base (Hudson & Beaven, 2002) showed that although flow was not uniform, it was considerably more distributed than what would arise from a small number of pathways. Thus preferential flow is probably via a network of pathways in these columns which might be reasonably considered to be a continuum.

3.2 Mass-balance

The mass recovery cannot be accurately estimated by simply integrating the BTC. This is because for both injected tracers the pre-existing background concentration in the leachate before the tests was significant and also not equal to the concentration in the flushing water. Therefore a more accurate model-independent estimate of mass recovery is adopted that uses the principle of linear superposition. If the unit step response (i.e. the output concentration against time which results from a step input of concentration equal to one unit) of the system is F(t), then for a tracer injection period T_p the output concentration *C* is described by

$$C(t) = C_{L} + (C_{T} - C_{L})F(t) + (C_{W} - C_{T})F(t - T_{P})$$
[2]

Where, the concentration of tracers in the injected solution is C_T , C_W is the concentration in the flushing solution which follows the tracers and C_L is the pre-existing background concentration in the leachate before the tests. Starting from Equation [2], the step response F(t) can be obtained for each BTC, providing the basis for estimation of the mass of tracer recovered (via the trapezoidal rule).

$$F(t) = \begin{cases} 0 & t \le 0 \\ \sum_{n=0}^{\text{Int}(t/T)} \left(\frac{C(t-nT) - C_L}{C_T - C_L} \right) \left(\frac{C_T - C_W}{C_T - C_L} \right)^n & t > 0 \end{cases}$$
[3]

The validity of Equation [3] as a solution to Equation [2] can be verified by substitution.

The recovery in Test 0A was 50.0 % lithium and 72.2 % D_2O . For Test 0B the recovery was 75.3 % and 89.4 % respectively. Thus, in both tests the recovered mass of Li was considerably below 100 %. This corroborates the relative reduction in lithium observed by the closed-loop tracer test reported by

Woodman *et al.* (2014). Figure 2 shows that at the end of the tests all tracers in Test 0B were further into the tail than Test 0A, which may explain why there was a greater measured mass recovery (89.4 %).

The mass discrepancy for lithium could arise from a number of circumstances. A second tracer peak characterising pore space with slower moving fluid could be yet to arrive (such behaviour is implicit in the two-streamtube model of Rosqvist & Destouni, 2000). The tracer 'loss' could be due to measurement error (most particularly an error in the measurement of the injected tracer concentrations), or alternatively the discrepancy could be due to non-conservatism of the tracers.

The waste from Test 0B was tested to assess whether Li was sorbed to the solid matrix. Samples were taken from the column at 10 cm intervals and 60 g subsamples of dried waste were mixed with 500 ml distilled water for three days. The average concentration of Li of the extract was 0.5 mg/kg dry waste. The total amount of water-extractable Li amounted to 0.3% of the Li injected. This suggests that the majority of the "missing" Li was not in an easily extractable form; however, it is possible that it was retained on material that was not sampled in the leaching test. Further work is needed to elucidate the apparent non-conservative behaviour of Li in MSW column tests.

There is a range of cited recoveries in the literature for in-line lithium tracer in wastes. Hudson & Beaven (2002) recovered 64 % in the Pitsea cell, Rosqvist *et al.* (2005) 91-93 % in the laboratory, Rosqvist & Destouni (2000) 52-72 % in a large-scale lysimeter and 34% in the field, and Oman & Rosqvist (1999) 21 % in the field. The exceptionally high recovery found by Rosqvist *et al.* (2005) was in waste with 25 % ash and in relatively short tests lasting between 0.5 and 3 days. Although all of these incomplete recoveries might be attributable to truncation of the tail, there remains the possibility that tracer 'loss' may have also been significant in these tests.

Because simple exponential extrapolation of BTC tails might be an inadequate test of whether the tail might account for the lost mass, we now further investigate mass-loss by fitting transport models to the data. In the presence of a large range of possible mass-loss mechanisms we elect to use a very simple assumption in conjunction with physical models. We assume an instantaneous change in the input concentration, such that the concentration at the input to the waste can be described by $C_i = C_T f$, where the 'mass-adjustment' factor f is in the range $0 < f \le 1$ for a tracer which is 'lost'. If the model produces the best fit for $f \approx 1$ then the inference is that the tracer is conservative and an incomplete recovery would be explained by the truncation of the test (i.e. the remaining mass would be predicted to arrive later). A mass-gain could be simulated by f > 1. This simple approach is consistent with that used in interpretation of previous tracer tests (Maloszewski & Zuber, 1990).

It is possible that 'loss' mechanisms are non-linear and/or time-variable. If this is the case, then the BTC will be affected in a manner which a simple physical model combined with this linear mass-adjustment model cannot predict. Possible time variable mechanisms include kinetic sorption, precipitation, chelation and, in the case of D_2O , fractionation.

4 Modelling of experimental data

4.1 Transport models

Despite previous numerous investigations there remains uncertainty over the underlying nature of flow through MSW. Given the heterogeneous nature of MSW, there is a potentially large spectrum of possible model representations for flow (Woodman, 2007). More complex models are difficult to justify against typical data, since too many parameters result in non-unique parameter sets. Whilst it has been possible to eliminate some models of transport in MSW due to their inability to match the data with physically-consistent parameters (Rosqvist & Destouni, 2000) a healthy scepticism must remain over the true

representativeness of models which cannot be eliminated, and in particular over the meaningfulness of their parameters (Bendz & Singh, 1998). The challenge is to obtain insights by identifying models which are not over-parameterised, yet appropriately capture the physical essence of the transport system. Even physically plausible models such as a dual-permeability flow (Rosqvist & Destouni, 2000) may contain more parameters than can be reliably identified by the data (Woodman & Beaven, 2011).

Accepting the inevitable imperfections implicit in using simple lumped models, we now model three highly simple mass-transport models, thereby examining tracer mass-balance and comparing processes, in particular examining the dual-porosity hypothesis. The models and their parameterisation are first set out, then are fitted to the data by least-squares and then further uncertainty analysis is performed.

We consider a simple Advection-Dispersion model with diffusive Dual-Porosity exchange ('AD-DP') to describe transport through the waste. This model assumes two overlapping continua. One continuum contains a flowing (mobile) porosity which is assumed to be locally well mixed. The other continuum is immobile but solute can exchange with the mobile porosity by diffusion. The gaseous phase is assumed to be fixed and is neglected as if it were part of the solid matrix (a considerable simplification of the dynamic reality). Physical properties are assumed to be homogeneously distributed. The integro-differential equation for AD-DP is given by

$$\frac{\partial c_m}{\partial t} + \sigma A + B = D \frac{\partial^2 c_m}{\partial z^2} - V_m \frac{\partial c_m}{\partial z}$$
^[4]

Where $A = \int_0^t \frac{\partial C_m(u)}{\partial t} C_m B_t(\frac{t-u}{t_{cb}}) du$, $B = \sigma(C_m^0 - C_{im}^0) B_t(\frac{t}{t_{cb}}), C_m$ is the concentration in the mobile porosity, C_m^0 is the initial (uniform) concentration in the mobile zone, C_{1m}^0 is the initial (uniform) concentration in the immobile zone, σ is the ratio of immobile to mobile volumetric water content (i.e. $\sigma = \frac{\theta_{im}}{\theta_m}$) D is the coefficient of dispersion, V_m is the velocity in the mobile zone and z is the distance in the direction of flow. $B_t(t)$ is the 'Block Geometry Function' (BGF) (Barker, 1985). The block diffusion time is defined as $t_{cb} = b^2/D_a$, where *b* is the ratio of volume to area for a block (for a sphere of radius *r*, this is r/3) and D_a is the apparent diffusion coefficient. There are a large number of analytical expressions for BGFs which are the solutions to Fick's second law in different assumed geometries (see Appendix). We further assume that $D = \alpha V_m$, where α is the dispersivity.

Woodman *et al.* (2005) showed that assuming slab-like, spherical or cylindrical block geometries made little difference for fits to a similar tracer test in the Pitsea compression cell. A scarcity of *in situ* observation of the block geometry means there is little prior information to support this assumption. Sub-parallel alignment of plastic may create regions of horizontal flow surrounded by slab-shaped immobile zones. However, it is also probable that the system is made up of a large number of different shapes and sizes of blocks. We work with a spherical geometry to represent agglomerations of waste and assume that this geometry can be adequately characterised with a single lumped diffusion time (corresponding to an average block size) and recognise that the absolute value of the time will be affected by this somewhat arbitrary choice of average block geometry and that such lumping can cause under-prediction of the tail, as shown by Beaven *et al.* (2005). The effect of other simple block geometries are explored in Supplementary Information S2 and are shown to be of minor importance.

Input concentration is described by the upstream boundary condition

$$C_m(0,t) = C_{IN}(t)$$
^[5]

where $C_{IN}(t)$ depends upon the tracer. For Li and D₂O, it was piecewise constant, equal to the tracer concentration for a time T_P , then equal to the concentration of the tracer in the flushing water, C_W . For Br, $C_{IN}(t)$ was equal to C_W for the entire test.

The column is approximated as being infinitely long, providing the following boundary condition,

$$\lim_{z \to \infty} C_m(z,t) = 0$$
^[6]

The initial concentration of each solute in the leachate is assumed to be uniformly distributed, as

$$C_m(z,0) = C_{im}(z,x,0) = C_L$$
[7]

where *x* is depth into the immobile block.

By taking Laplace Transforms of Equations [4-7] we arrive at the following solution for (flux-averaged) mobile concentration *C* at the outlet (z = L):

$$C_m = \frac{C_L}{s} + \frac{\left(fC_{IN} - C_L\right)}{s} f_{\delta} + \frac{\left(C_W - fC_{IN}\right)}{s} \exp\left[-T_P s\right] f_{\delta}$$
^[8]

where s is the Laplace variable and the impulse-response f_{δ} for the AD-DP model is given by

$$f_{\delta} = \exp\left[\frac{t_a}{2t_d}\left(1 - \sqrt{1 + 4t_d g(s)}\right)\right] \text{ where } g(s) = s\left(1 + \frac{\theta_{im}}{\theta_m} B\left(\sqrt{st_{cb}}\right)\right)$$
^[9]

where $t_a = z\theta_m/q$, $t_d = D/V_m^2$, q = Q/A, and B is the block-geometry function (Barker, 1985a). Equation [9] is inverted numerically using the De Hoog *et al.* (1982) algorithm.

The AD-DP model provides the basis for two simpler models. When $\theta_{im} = 0$ the exchange term is zero and Equation [9] becomes a simple Advection-Dispersion model ('AD') as follows

$$f_{\delta} = \exp\left[\frac{t_a}{2t_d}\left(1 - \sqrt{1 + 4t_d s}\right)\right]$$
^[10]

If mechanical dispersion is neglected (i.e. D = 0) Equation [9] collapses to a simple dual-porosity model ('DP')

$$f_{\delta} = \exp\left[-st_{\alpha}\left(1 + \frac{\theta_{im}}{\theta_m}B(\sqrt{st_{cb}})\right)\right]$$
[11]

The connected, mobile and immobile porosities are related by $\theta = \theta_m + \theta_{im}$ Porosity is reported in the literature using various parameterisations. Commonly reported are σ , which is the ratio of the immobile to mobile porosities and β , which is the ratio of mobile to connected porosity.

The DP model is parameterised as per Table 3. For all three of the models (AD, DP and AD-DP) the connected porosity, θ , is a fitting parameter. For the DP and AD-DP models the mobile porosity, θ_m , is also a fitting parameter and θ_{im} is calculated.

Similar studies in soils fixed the connected porosity, θ , equal to the measured total volumetric water content (porosity), θ_T (Schwartz *et al.*, 2000; Zhang *et al.*, 2006). The least-squares (L-S) best-fits for the AD-DP, AD and DP models are now considered.

4.2 Least-squares (L-S) fitting

4.2.1 Fitting

The models and number of fitting parameters are given in Table 3 and the parameter ranges are given in Table 4. The best fit models are shown on Figure 2 against monitoring results. For these models, Levenberg-Marquardt (L-M) L-S fitting was performed using the UCODE programme (Poeter *et al.*, 2005b) and the results are given in Table 5. If a parameter was driven to the upper or lower limits, then it was fixed at that boundary and taken out of the minimisation thereafter without the parameter uncertainty being calculated.

All the models were able to provide good fits to Test 0A. However, all the fits for Test 0B except one were visually poor, implying that the model is inadequate and the parameter values can be neglected (they are therefore not reported). The most significant difference between Test 0B and Test 0A is the spatial scale. The Test 0B cell diameter of 260 mm is only just over three times the maximum particle size (defined by the screen size of 80 mm), compared to 25 times for the Test 0A cell. It is likely, therefore that Test 0B was smaller than the necessary representative elementary volume (REV) given the largest particle size of this waste and therefore cannot be simulated adequately with a continuum mass-transport model. The results from this cell are nonetheless useful from a mass-balance perspective, and have confirmed the non-conservative nature of Lithium in these tests.

The one good fit for Test 0B occurred for D₂O tracer using the AD-DP model. The best-fit parameters were $D=5.8\times10^{-6}$ m²/s, $t_{cb}=3.7$ days, $\theta_m=0.02$ and f=0.87. This mass-adjustment factor is below any of the estimates given by test 0B and possibly is only acting as a fitting parameter. Given that the other tracers could not be fitted by any of the models it is likely that this one reasonable fit is not meaningful. Therefore, we hereafter analyse the parameters of the fit to Test 0A, and neglect the parameters obtained

for Test 0B.

4.2.2 Tracer mass recovery (all models)

The fitted mass-adjustment factor, f, for D₂O in Test 0A ranged between 0.94 and 0.99 for the three models, suggesting that the D₂O was conservative in this test, or very nearly so. Since the D₂O mass estimated via Equation [3] was 72 % this implies the remaining mass would have been expected to arrive in the tail if the test had run for longer. This conservative behaviour is in contrast with enrichment observed by Woodman *et al.* (2014) under closed-loop conditions. It is likely that there was less opportunity for evaporation in this in-line test than in a recirculating test where leachate spent time in a reservoir.

For lithium in Test 0A the estimate for f was in the range 0.68-0.72 for all three models, whereas the measured mass estimated by Equation [3] was 50 %. This measured Li recovery expressed as a fraction of the measured D₂O recovery was 69.4 %, which is consistent with the range of f. Therefore consideration of both the mass recovered and the modelled mass-adjustment indicates that Li was not behaving conservatively in Test 0A. This is consistent with what was observed by Woodman *et al.*,2013; Woodman *et al.*, 2014) in closed-loop tracer experiments. Because of the good fits achieved for lithium, no problems with the mass-adjustment model are identified. However, there remains the possibility that mass loss was not instantaneous, in which case the mass-adjustment approach would introduce model-error.

In summary, the D_2O results were consistent with conservative behaviour, but lithium was more poorly recovered. Independent of the transport model used, the assumed input concentration of lithium consistently needs to be reduced to explain the data, so the low measured recoveries of lithium are not solely attributable to insufficiently long test duration. Therefore, an as-yet unidentified process may be acting to immobilise lithium in the columns.

4.2.3 Advection-Dispersion (AD)

For the AD model, the fitted (Table 5) hydrodynamic dispersion coefficients, D, are significantly larger than typical free-water diffusion coefficients, so the effect of longitudinal diffusion can be neglected under these conditions. From these dispersion coefficients the dispersivity (α) for the Li, D2O and Bromide tracers are estimated as 2.7, 2.6 and 2.5 m respectively (NB: L=1.64m, Table 1) A ratio of the dispersivity to the column length, α/L greater than 0.5 is not physically supportable (Barker, 2003). All estimates of α/L exceed this limit for Test 0A, casting doubt that an advection-dispersion process alone can account for the observed tracer dispersion.

A further problem with the AD model is that it does not explain why there are differences between the different tracer BTCs. Despite this, the AD model may remain useful as a simple simulation tool (possibly for risk-assessment purposes), provided it is appreciated that other processes (most probably dual-porosity exchange) are effectively lumped into the dispersivity parameter. Maloszeweski *et al.* (1995) adopted this approach.

4.2.4 Dual-porosity (DP)

The fits obtained by the DP model are fairly similar to those obtained by the AD model (Figure 2). This is reflected in the goodness of fit statistics given in Table 5. This similarity is unsurprising, because it is well-known that the two models can produce very similar BTCs under certain conditions. Sanchez-Vila & Carrera (2004) showed that the first three moments of the two models can be matched exactly. However, despite the similarity it is also the case that the DP model is consistently a slightly better fit (i.e. the sum of the squares of the errors, SSE, is lower).

The fitted mobile porosity, θ_m , was consistently driven downwards to the lower limit (set at 0.01). Low values of θ_m suggest highly preferential flow. The fact that the lower limit was encountered requires further investigation of the best-fit point; this will be done in section 4.3.

There is no similarity apparent between the ratio of the free water diffusion coefficients and the ratio of the fitted diffusion times. Figure 3 shows the diffusion times in Test 0A for Li and D₂O estimated by scaling according to the ratio of free water coefficients, and based on the fitted t_{cb} of bromide. This suggests a homogenisation of effective diffusion coefficients. It is clear that a much larger value of t_{cb} for Li is estimated by means of the diffusion coefficients than was fitted (indeed one so large that it does not give a reasonable fit to the data). In contrast, estimated t_{cb} for D₂O is similar to the fitted value.

The explanation for this observation could be because the loss of lithium is not simulated accurately, causing the model to fit with apparent (lumped) parameters to compensate. Alternatively, if the correction of mass-loss is reasonable (and the good-fit does not contradict this), then this comparison of the best fit values of t_{cb} would indicate that the effective diffusion coefficients of different species in high strength leachate do not scale proportionally with their free-water values. In this instance it is possible that competition effects (or other diffusion-coefficient modifying effects such as hydration shells forming around the tracers, complexation or sorption to colloids) may have changed the apparent diffusion coefficients of different solutes in leachate would be needed.

It is worth noting that an understanding of dual-porosity transport in saturated conditions is valuable in understanding the more complicated situation in unsaturated wastes, since it is an end-member e.g. with respect to water content.

4.2.5 Advection-Dispersion with Dual-Porosity exchange (AD-DP)

Because of the similarity of the BTCs generated by the single AD and DP processes, fitting of the AD-DP model can have non-uniqueness between the parameters of these two models. Moench (1995) addressed non-uniqueness in fitting this model by first fitting the mechanical dispersion to the early time data, arguing that the first arrival is negligibly affected by DP exchange. Schwartz *et al.* (2000) addressed this problem by adjusting the water content, running separate tracer tests in what they defined to be the microporous region and fitting a dispersivity to that region (which they assumed was also mobile). However, Schwartz *et al.* (2000) still had convergence problems and had to fix parameters. Here, we first fixed θ_m to a typical low value uncovered by the DP models ($\theta_m = 0.01$). If this was insufficient in preventing convergence problems then θ was fixed to the upper limit.

There were two types of best-fit depending on the starting parameters. One best-fit occurred for low t_{cb} and relatively high *D* and a second for a higher t_{cb} and low *D*. For example, the lithium tracer dotty plots (see Supplementary Information Figure S3) gave a best parameter combination with $D=2.43\times10^{-4}\text{m}^{2}/\text{s}$, $t_{cb}=0.08$ days, $\theta_{m}=0.004$ and f=0.68). A second optimum gave $D=1.29\times10^{-9}\text{m}^{2}/\text{s}$, $t_{cb}=57.5$ days, $\theta_{m}=0.007$ and f=0.78. In other words either single AD or DP models gave the best performance, but the possibility of the two processes working simultaneously did not consistently improve the fit. Given this, we can conclude that the additional complexity of the AD-DP model above the DP model is not supported by the data.

4.2.6 Summary of fitting results (comparison of models)

The AD-DP model fitted best when either the AD or DP process dominated, although when the AD process dominated the dispersivity was frequently unrealistically large. For example for the lithium dottyplot optimum $D=2.43\times10^{-4}$ m²/s gives a dispersivity, $\alpha=2.7$ m, which is larger than the column itself Page 24 of 44 (1.64m). Thus, the additional parameter required by the AD-DP model compared to the AD or DP models was not supported by the data. The observation that the AD model could be rejected due to the dispersivity being unrealistically large is consistent with previous tracer studies in waste (Rosqvist & Destouni, 2000; Woodman, 2007). Therefore, the DP model was the best physically-consistent model of all three. Whilst caution should be used in extrapolating the values of θ_m beyond the DP model, it is clearly indicating that a relatively small proportion of the pore space is actively carries the fastest flowing water. This is therefore likely to result in much earlier arrival of solute between two points in a column or in a landfill than would be predicted through the total saturated water content.

4.3 Uncertainty analysis

To more fully understand the L-S fits an appreciation of the error space is needed. This allows a number of questions to be addressed (e.g., whether the confidence intervals on t_{cb} were a reasonable measure of the uncertainty in this parameter).

For models with more than three parameters, visualisation of parameter space becomes increasingly difficult. One method of coping with this is to project the error surface on to single parameter axes. We will examine the so-called 'dotty plot' method for doing this (Zhang, 2006; Beven & Freer, 2001).

To produce a dotty plot, large ensembles of realisations are generated, with each parameter in a set being randomly selected from a probability distribution. Here a uniform or log-uniform distribution is used. The un-weighted SSE between the model and data is calculated for each realisation. The realisation with the minimum SSE is taken as the estimate of the best fit point. The distribution of the dots provides information on the shape of the SSE space. The lower surface of the SSE, described by the dots has previously been used to determine whether a parameter is 'identifiable' or not, where an identifiable parameter would have a clear optimum point. Therefore instead of providing a measure of uncertainty local to the optimum, dotty plots have been used to consider a more 'regionalised' sensitivity (Mathias *et al.*, 2006).

Away from any optima, the distribution of the projected SSE will depend upon the multidimensional surface out of plane and on the range of parameter space being evaluated. False local optima can be perceived in the event that the number of dots being generated is sparse enough to provide randomly generated 'gaps' in the error surface. Taking these considerations together it is clear that interpretations based on the shape of dotty plot projections require caution and an appreciation that the projection can 'lose' information out of the plane of the parameter on the x-axis. The dotty-plot optimum cited here is the minimum SSE out of the total of 25,000 realisations. The parameter ranges are set within the limits given in Table 4.

4.3.1 Uncertainty in parameters of DP model

The dotty plots in Figure 4 show that there was a distinct single global minimum for f, which confirmed the relatively tight confidence intervals estimated by the L-S method. This was the case for both lithium and D₂O (f was not applied to bromide, for which f=1). The SSE is considerably higher away from the minimum f value. For example, for lithium data if the assumption is made that the tracer was conservative (i.e. f = 1) the SEE would worsen from 2.9 mg²/L² at the optimum to 23.9 mg²/L². The loss of mobile lithium therefore seems to be strongly indicated.

Dotty plots for all three tracers for t_{cb} and θ_m are shown in Figure 5. It is evident that there is very little change in SSE for all the tracers over a wide range of θ_m , albeit with a shallow increase in SSE as θ_m is

increased from the lower boundary. The L-S results need to be interpreted with this in mind. Although θ_m was consistently driven to the lower limit (0.01), it is notable that this fit is barely worse than for a ten times smaller water content (0.001). Eventually increases in θ_m reach a point where the SSE increases more steeply. Therefore fitting reveals an upper bound, but provides little information about the optimum θ_m below this. The observed insensitivity means that rejecting the DP model on the basis that the mobile porosity is unrealistically low (driven to the lower boundary) by the L-S optimisation would not be supportable.

The uncertainty in optimum θ_m means that calculated fractional porosities, for example σ and β , are also uncertain. The intractability of θ_m means that it is difficult to make quantitative statements about the nature of the preferential flow (for example, it might be desirable to estimate the percentage of the porosity through which at least a certain proportion of the total flow passes). β is calculated as 1.9×10^{-4} based on the lower bound for θ_m . By comparison, data fitted with stochastic-lognormal models estimated a range for β of 0.015-0.44 (Fellner *et al.*, 2009) and 0.05-0.47 (Rosqvist and Destouni, 2000). Although both these studies examined both field and laboratory data, they were inconsistent in how β changes with scale.

Figure 5 shows that t_{cb} is clearly and unambiguously identified by all three tracers. This is important since to achieve objective of the paper required a meaningful comparison of these estimates. This is fortunate since an inability to obtain a reliable estimate of t_{cb} is common for field tests (Ward *et al.*, 1998; Mathius *et al.*, 2006; Hadermann & Heer, 1996; Haggerty *et al.*, 2000). The difference between the field tests and these well-controlled column tests is that for the latter the flux rate and total porosity are accurately available thus providing better constraint.

5 Conclusions

The primary aim of this paper was to examine the hypothesis that dual-porosity diffusion is a dominant dispersion mechanism for transport through municipal solid waste. Testing this hypothesis required tightly controlled hydraulic conditions suitable for a multiple-tracer test where any difference between breakthrough curves would be attributable to the diffusive characteristics of each tracer. Detailed monitoring demonstrated that the high level of control was indeed attained in this biologically active MSW, despite gas production and other difficulties.

The second prerequisite for testing this hypothesis was that the tracers performed as they were assumed to (i.e. conservatively). Although D_2O and bromide were confirmed to be conservative, lithium was shown not to be. Only 50% of the lithium that was introduced to Test 0A was observed at the outlet. All three models used in this study better fitted the data for lithium if a smaller mass of tracer was assumed than was actually introduced (between 68% and 72%). Therefore, whilst some of the non-recovered tracer would have arrived at the column outlet if the experiment had continued for a longer duration, the models indicate that there remains a substantial discrepancy.

Deductions previously obtained using lithium as a tracer in wastes may need to be reassessed. In order to utilise the lithium data here, a simple mass-adjustment was applied, which assumed that the loss of the tracer occurred instantaneously.

A final prerequisite to testing this hypothesis was that continuum models could be applied to the data. Given that none of the models could adequately simulate the smaller column experiment under identical conditions it was found to be very likely that the smaller column (260 mm diameter) was smaller than the necessary 'representative elemental volume'. Advection-Dispersion (AD) was eliminated as the primary dispersion mechanism due to the unrealistic dispersivity values required to fit the model. The hybrid AD-DP model only fitted well when either the AD or dual-porosity (DP) processes dominated.

The DP model, therefore, appeared to be the most suitable of the three models. Provided the assumption that the mass-adjustment model can be applied to the lithium data, the DP parameters can be compared between the different tracers. The different tracer BTCs did not differ in the manner that would be expected if the characteristic diffusion times were proportional to the free-water diffusion coefficients. This shortcoming does not necessarily imply that dual-porosity effects are unimportant, but suggests that the diffusion of different species in leachate is complex. For both tests only a small fraction of the porosity was inferred to be relatively mobile. This is broadly consistent with previous studies.

Only three very simple models are considered in this analysis. Given the inherent complexity of waste, a more robust understanding of the dominant processes will require the inclusion of a wider range of conceptual models. Robust prediction will probably require a multi-model approach which accounts for both parameter and process uncertainty (for example, Poeter *et al.*, 2005a).

Despite the high level of control and monitoring in these experiments (which were optimised by previous tests in the same apparatus) it is clear that uncertainties still pervade the analysis of BTC data from gassing MSW. There therefore remains considerable scope for experimental improvement, and several recommendations follow from this analysis, as follows.

The performance of lithium as a tracer in landfill waste requires further investigation. In particular further investigation is needed into the possibility that batch tests which follow oven-drying of wastes are not correctly emulating conditions in a column test. This may be because the drying process destroys bio-

films which may be important exchange media. There remains a need to address the effect of scale on flushing from waste. Previous studies which have looked at different scales in MSW (Fellner, 2009; Rosqvist & Destouni, 2000) relied on empirical models to examine scaling. Unfortunately such models are difficult to relate to physical parameters such as diffusion timescales, so there is a need for exploratory modelling and possibly also further experimentation.

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8 TABLES

Parameter	Test 0A	Test 0B	Ratio
Diameter (m)	2.0	0.26	7.7
Area, $A (m^2)$	3.14	0.05	62.8
Flow rate, Q (L/h)	3.7	0.15	24.7
Flux rate (mm/year)	10,300	26,400	0.4
Length of waste, $L(m)$	1.64	0.83	2.0
Volume of waste (m ³)	5.15	0.04	128.8
Volume of Upper Gravel (L)	99	1	99
Volume of Lower Gravel (L)	117	1	117
Total volumetric water content, θ_{T} (-)	0.54	0.48	1.125
Li and D ₂ O injection period, T_P (days)	3	1	3.0
Test duration (days)	32	42.8	0.7
Density at field capacity (t/m ³)	1.0	1.1	0.91
Total compressive stress (kPa)	87	- ^a	-
Mean internal temperature (°C)	10.2	14.4	0.7
Leachate pH (-)	7.3-7.5	8.0	0.91-0.94

Table 1: Key parameters for the two test cells

a. the sample was hand-compressed to achieve the same bulk density of phase 1

	Test 0A			Test 0B		
Item	Li (mg/L)	Br (mg/L)	D2O (‰)	Li (mg/L)	Br (mg/L)	D2O (‰)
Concentration in leachate C_L	0.57	552	-22.5	0.24	107.9	-30.0
Concentration of wash water C_w	0.01	3.3	-39	0.01	3.3	-39
Expected Tracer Concentration C_{TE}	30.3	-	1562	32.7	-	1861
Measured Tracer Concentration C_T	37.1	-	1598	30.37	-	2276
C_{TE}/C_T (%)	82	-	98	108	-	82

Table 2: Tracer details for Test 0A and Test 0B

Table 3: Models and parameters

Model	Fixed parameters	Fitting parameters (N)	Calculated parameters
(BGF in brackets)			
AD	<i>q</i> , <i>z</i> , <i>T</i> _p	$f, D, \theta_m = \theta$ (3)	t _a
DP (sphere, slab, cylinder, hollow cylinder)	<i>q</i> , <i>z</i> , <i>T</i> _p	$f, t_{cb}, \theta_m, \theta$ (4)	$oldsymbol{ heta}_{_{im}}$, $t_{_a}$, $oldsymbol{\sigma}$, $oldsymbol{eta}$
AD-DP (sphere)	q , z , T_p	$f, D, t_{cb}, \theta_m, \theta(5)$	t_{a} , σ , eta

Table 4: Parameter ranges used in dotty plots and L-S fitting. Log-scale and Linear-scales are denoted 'Log' and 'Lin' respectively

Test	Model	D (m ² /s)	f ^a (-)	θ_m^{b} (-)	θ	t _{cb} (days)
ļ	Scale	Log	Lin	Log	Lin	Lin
0A	AD	1×10 ⁻⁹ -1.0	0-1	0.0001-0.54	-	-
	DP	-	0-1	0.0001-0.1	0.1-0.54	0.1-1000
	AD-DP	1×10 ⁻⁹ -1.0	0-1	0.0001-0.1	0.1-0.54	0.1-1000
0B	AD	1×10 ⁻⁹ -1.0	0-1	0.0001-0.1	0.1-0.48	-
	DP	-	0-1	0.0001-0.1	0.1-0.48	0.1-1000
	AD-DP	1×10 ⁻⁹ -1.0	0-1	0.0001-0.1	0.1-0.48	0.1-1000
0B	AD-DP AD DP AD-DP	$ 1 \times 10^{-9} - 1.0 \\ 1 \times 10^{-9} - 1.0 \\ - \\ 1 \times 10^{-9} - 1.0 $	0-1 0-1 0-1 0-1	0.0001-0.1 0.0001-0.1 0.0001-0.1 0.0001-0.1	0.1-0.54 0.1-0.48 0.1-0.48 0.1-0.48	0.1-10 - 0.1-10 0.1-10

a. for D₂O the range for f was 0.0 to 1.5

b. for L-S the lower limit for $\theta_{\!_m}$ was 0.01

Tracer	Model	f	t_{ch}	D	θ_{m}	θ	SSE	r^2
		(-)	(days)	(m^2/s)	(-)	(-)	(mg^2/L^2)	(-)
	AD	0.68	-	1.63×10 ⁻⁶	0.54	-	2.91	0.951
		(0.65-		$(1.49 \times 10^{-6} -$	[UB]			
		0.72)		1.77×10^{-6})				
	DP	0.72	51.3		0.01	0.54	2.72	0.951
Li	(sphere)	(0.68-	(47.2-		[LB]	[UB]	2.72	0.701
		0.76)	55.5)			L- J		
	AP-DP	0.71	51.4	1.00×10^{-9}	0.01	0 54	2 89	0 946
	(sphere)	(0.67-	(47.3-	ILL]	[LB]	IUB1	2.07	0.910
	(5,2,1,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,2,	0.75)	55.9)	[]	[22]	[02]		
	AD	0.94	_	1.56×10^{-6}	0.54	-	8478	0.976
		(0.89-		$(1.45 \times 10^{-6} -$	[UB]			
		0.98)		1.68×10^{-0})				
	DP	0.99	50.8	_	0.01	0.54	6554	0.978
D_2O	(sphere)	(0.95-	(47.8-		[LB]	[UB]		
		1.03)	54.1)					
	AP-DP	0.99	51.4	3.00×10 ⁻⁸	0.01	0.54	6130	0.975
	(sphere)	(0.94-	(48.1-	(1.75×10^{-21})	[LB]	[UB]		
		1.03)	55.0)	-5.15×10^5)				
		1 ^a		1 51	0.54		20148	0.981
	AD	1	-	$(1.35 \times 10^{-6} -$	U.J.4	_	20140	0.701
				1.69×10^{-6})	[0]]			
	DP	1^{a}	54.2	-	0.01	0.54	15353	0.981
Br	(sphere)		(49.3-		[LB]	[UB]		
			59.2)					
	AP-DP	1 ^a	57.0	4.69×10 ⁻⁷	0.01	0.54	11003	0.987
	(sphere)		(49.4-	(-3×10 ⁻⁵ -	[LB]	[UB]		
			65.5)	$3.11 \times 10^{-5})^{b}$				

Table 5: Best fit points for Test 0A established by L-S fitting.95% confidence intervals are given in brackets.UB andLB denote where parameters have stopped at the upper or lower bounds

a. Fixed parametersb. Fitted on linear scale

9 FIGURES



Figure 1: Schematic of Test 0A and 0B apparatus. Dashed lines represent the routing of pipework during recirculation. During the flushing phase, the water tank was regularly refilled from a domestic supply. The gas meter was only used during the recirculation phase of Test 0A.

Test 0A D₂O

Test 0B D₂O



Figure 2: Least-Squares (L-S) best fits for the AD-DP (dotted), AD (continuous) and DP (dashed) models.

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Figure 3: Phase 1 t_{cb} as fitted by the DP model (white bars) using least-squares and scaled using the ratios of free-water diffusion coefficients and assuming that the t_{cb} for bromide is the same as fitted (grey bars). Error bars denote 95% confidence intervals. Free water diffusion coefficients of 2.1,1.0 and $2.3 \times 10^{-9} \text{m}^2/\text{s}$ are assumed for Br, Li and D₂O, respectively (Cussler, 1997)



Figure 4: Dotty plots for lithium and deuterium oxide (D₂O) for the DP model parameter *f*.



Figure 5: Dotty plots for lithium, deuterium oxide (D₂O) and bromide for the DP model parameters t_{cb} and θ_m .

10 APPENDIX

Geometry	$\mathbf{B}(x)$
Slab	$\tanh(x)$
	x
Sphere	$\operatorname{coth}(3x) = 1$
	$\frac{1}{x}$ $\frac{3x^2}{3x^2}$
Infinitely long	$I_1(2x)$
cylinder	$\overline{xI_0(2x)}$
Infinite hollow cylinder (impermeable external surface)	$\frac{1}{x} \left[\frac{K_1(Z_1)I_1(Z_2) - I_1(Z_1)K_1(Z_2)}{I_0(Z_1)K_1(Z_2) + K_0(Z_1)I_1(Z_2)} \right]$ where $Z_1 = \frac{2x}{\rho^2 - 1}$ and $Z_2 = \frac{2\rho x}{\rho^2 - 1}$

Table A.1: Block Geometry Functions (from Barker 1985)