Soil Use and Management (1999) **15**, 240–246

Measurement of solute fluxes in macroporous soils: techniques, problems and precision

A.C. Armstrong[1]*, P.B. Leeds-Harrison[2], G.L. Harris[1] & J.A. Catt[3]

Abstract. Preferential flow has been increasingly recognised as a major component of water movement in many soils, particularly clays. This paper reviews problems in the measurement of solute fluxes in these soils, and discusses the solutions that have been adopted in UK studies of cracking clay soils. The estimation of solute fluxes is subject to many sources of error, which are best reduced by replicated measurements, such as those available in multi-plot experiments.

Keywords: Pesticides, nitrate, leaching, macropores, preferential flow, measurement

INTRODUCTION

A major impetus for research over the last 30 years has been the observation that many water sources contain dissolved ions in excess of those considered safe for human consumption or the health of wildlife such as fish stocks. As a result, standards have been set, (e.g. Council of European Communities, 1980), and programmes have been put in place to ensure these are met (e.g. MAFF, 1991).

A major component of the contamination of rivers and lakes is the diffuse movement of solutes from wide areas, generally termed 'non-point-source' pollution. Agricultural usage of fertilizers has been widely identified as a major contributor to such pollution, although it is a gross over-simplification to relate increasing nitrate levels in surface waters to increased use of nitrogen fertilizers (Addiscott *et al.,* 1991). Pollution of surface water by pesticides is more immediately attributable to agriculture, although non-agricultural uses of pesticides may contribute to the problem. Nevertheless, it is clear that movement of solutes from agricultural land to surface waters is a problem, and that measures are needed to control this pollution source.

The mechanisms of solute movement to surface waters are still uncertain. In permeable soils, water moving downward through the soil can carry some of the solutes in the soil profile, which are then usually carried to groundwater. However, in impermeable soils, water generally moves laterally, either across the surface or through the surface soil layers to surface channels, which receive the water. Again, the water may pick up solutes, and transfer them to the receiving watercourses.

These processes, originally described in the last century, correspond to the two major processes of surface runoff and soil water drainage. Lawes *et al.* (1882) identified two modes of water movement in drainage: slow percolation through the soil profile, and the more rapid movement in response to intense rainfall inputs. The second was largely ignored for much of the following period, as soil science developed theories of water movement in soil as a uniform porous medium. Thus water movement in soil was explained simply by an equation for movement of liquid in saturated-unsaturated systems (the Richards' equation) and movement of associated solutes by the convection-dispersion equation (see for example Wagenet, 1990: Hutson & Wagenet, 1991)

THE IMPORTANCE OF PREFERENTIAL FLOW

Since the 1970s field evidence has accumulated for rapid water movement through soils that were previously considered to be impermeable (Bouma & Raats, 1984). This was identified as concentrated in discrete paths associated with either biological (e.g. root or earthworm channels) or physical features (e.g. desiccation cracks) of the soil. Consequently, it was initially identified as macropore flow. It can occur when the soil is either (a) saturated, in which case it is identified as the regions of high transport rate within a saturated medium or (b) unsaturated, in which case it is then identified as bypass flow, as it bypasses unsaturated regions. Rapid movement of some water through soils has been identified in many situations and is now generally termed preferential flow. However, preferential flow can occur in various circumstances other than in macropores, including: fingering, which appears to be a result of instabilities in the flow regime (e.g. de Rooij, 1996); and concentrated flow as the consequence of soil heterogeneity (e.g. Webb & Anderson, 1996). Although preferential flow is a widespread phenomenon, occurring in a variety of circumstances, and in various soil types, this review will concentrate on preferential flow in strongly structured soils, where it is largely associated with macropores.

WATER MOVEMENT

The physical framework for the study of all water movement is based on Darcy's law and the Richards' equation, which derive from the observation that all water movement is in

[1]ADAS Land Research Centre, Gleadthorpe, Meden Vale, Mansfield, Nottinghamshire, NG20 9PF, UK.
[2]School of Agriculture, Food and Environment, Cranfield University, Silsoe, Bedfordshire, MK45 4DT, UK.
[3]Soil Science Department, IACR-Rothamsted, Harpenden, Herts, AL5 2JQ, UK.
*Author for correspondence.

response to an energy gradient. In unsaturated soils this includes the contribution of the variation in water potential within the soil. Although it is possible to describe all the movement of water in soils from these physical principles, the patterns are extremely complex in macroporous soils (Youngs & Leeds-Harrison, 1990), and a number of simplifying assumptions are usually made. Without macropores, it is possible to assume that the water potential is essentially one-dimensional, varying with water content and therefore with depth. However, with macropores, the situation is complex and three dimensional, with many air-filled pores intersecting peds with varying degrees of local saturation. In this system, there are two major routes of water movement: through the macropores, and within the peds.

Water movement in air filled cracks is normally rapid, and normally described by Poiseuille's law, which shows the rate of flow in linear cracks to be proportional to the third power of the crack spacing (Armstrong *et al.,* 1995). The rate of flow in cracks can become large compared to the potential rainfall fluxes (even in intense rainfalls) if much of the crack network is full of water. It is thus rare for cracks to be a constraining system, so normally the limitation of water movement in cracks is the supply of water to them.

SOLUTE MOVEMENT

Solute moves within the soil as the result of two distinct processes: movement of the water in which it is dissolved, and the diffusion of solute from high to low concentrations. Together these two processes can be combined in the convection-dispersion equation (Wagenet, 1990). As water moves through soil, it tends to equilibrate with the soil water it passes. The chemical characteristics of water moving through the profile thus tend to become like that of the pore water in the soil. Water which is low in solutes tends to remove solutes from the soil, and move them in the direction of water transport. Similarly, water rich in solutes may deposit them in zones of low solute concentration.

If the water moving through the soil were in perfect equilibrium with that in the soil surrounding it, then the water leaving the profile would be a perfect reflection of the solute concentration in the soil at the base of the profile. However, this is frequently not the case, and soil scientists have long recognised that two major processes distort the simple process. The concentration of solute in water draining from soil is either decreased or increased compared to that of the bulk soil. This led to the development of the ideas of (a) 'immobile' water which is held tightly in small pores and which does not readily equilibrate with moving water, leading to the slow release of solute, and (b) 'mobile' water or preferential flow leading to the rapid movement of solutes to depth. The difference in rates of mobility for different water components can be expressed in two ways: the slow movement of solutes in relatively immobile water, and rapid movement in preferentially mobile water.

These phenomena thus lead to two patterns of leaching from the base of the profile, which are expressions of the limitations of the diffusion system and the contact time for equilibrium. The first occurs where water is rich in solutes close to the surface, and as it moves rapidly to depth, those solutes are transported without much opportunity for readsorption by the soil. In this condition, the concentrations of solute leaving the base of the profile are greater than those in the lower soil layers, and they appear as 'spikes' in the graphs of concentrations with time. This sort of behaviour is to be expected for materials whose rate of interaction with the soil is slow, so that once dissolved they do not appreciably re-adsorb.

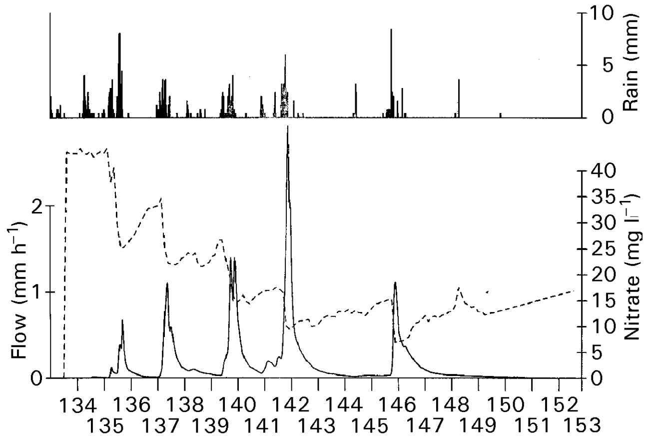

Fig. 1. Flow (solid line) and nitrate concentrations (pecked line) at the Brimstone Farm experiment, for days 134 (12/Dec/89) to 153 (31/Dec/89).

The second mode of behaviour is encountered, when rapidly moving water low in solutes moves through a soil with relatively high solute concentrations. If the water moves sufficiently rapidly it does not equilibrate with that in the soil, and the flush of water leaving the base of the profile dilutes earlier flow. This phenomenon is to be expected in soils where the rate of movement from the ped interior to the ped surface is limited.

Preferential movement may thus result in both spikes and troughs in the solute concentration curves, depending on whether (a) the movement out of the peds to the water is limited or (b) solutes move from water into the peds. In preferential flow systems, the important factor is thus the rate of transfer between the flow in the macropores and the soil water within the peds.

Field evidence for both modes of behaviour has been recorded at several locations, notably at the Brimstone Farm site (Harris & Catt, 1999) but also at other locations (Armstrong & Harris, 1996). Trafford & Rycroft (1973) noted rapid drain flow in soils of apparently low conductivity. Direct evidence of the role of macropores in generating these flows was obtained by Hallard & Armstrong (1992) who used dye tracers to demonstrate the role of rapid transport in the generation of mole channel hydrographs. Other evidence for dilution effects with diffusion limited flow is often seen in the patterns of nitrate concentrations. Observations for a short period in December 1989 at Brimstone Farm (Fig. 1) show repeated dilutions with successive flow peaks.

MEASUREMENT OF FLUXES

Solute fluxes at a point may be defined by the equation:

$$\text{Solute Flux} = \sum_{\text{sources}} \sum_{\text{time}} \text{Flow} \cdot \text{Concentrations} \qquad (1)$$

This deceptively simple equation states that to measure the solute flux in the landscape, it is necessary to measure all the flows that are carrying it, and also all the concentrations. Its simplicity, however, hides several problems: identifying all the sources of water movement; measuring and estimating all the flows of water: and measuring the concentrations.

Identifying all the flows of water

Before any field investigation is started, it is necessary to know what the main components of the hydrological cycle are, otherwise they cannot be measured. It is thus necessary to know the nature of the fluxes at a site before it can be instrumented to record their magnitude. This problem is particularly acute when we move away from the classical hydrological paradigm of a single gauging station recording a single catchment (Chorley, 1969), especially when we ask questions about fluxes within soil.

In most soils, fluxes can be divided into at least four distinct types:

(1) Surface flow. This is water that does not enter the soil system, but flows across the soil surface. This can be in response to an excess of rainfall over infiltration capacity ('infiltration excess flow') or in response to local saturation of the soil by returning groundwater ('Saturation excess flow'). The pattern of this runoff is spatially variable, particularly in the context of a catchment, where wedges of saturation build up at slope bases (Beven, 1977). At Brimstone Farm, this component is generally small on drained plots, and restricted to short periods during high intensity rainfalls. However, its importance is affected by management of the soil structure, particularly the cultivation regime (Harris *et al.,* 1993). On undrained clay soils, which frequently saturate to the surface, this mode of flow can be as large as the drainage component of drained areas (Armstrong & Garwood, 1991). It can be collected by shallow surface ditches or gutter systems at the base of the slope (as for example at both Brimstone Farm and at IGER North Wyke), but its spatial pattern is difficult to evaluate.

(2) Plough layer flow, or shallow interflow. This is water that moves horizontally within the soil at shallow depths, often in zones of saturation overlying the topsoil/subsoil discontinuity, where a 'perched' water table occurs. The water moves down the gradient, and can then be intercepted, as at Brimstone Farm, by shallow trenches extending to the depth of the discontinuity that creates the flow.

(3) Drainage. This water moves through the saturated zone of the soil to either peripheral or artificial within-field drains. It is the dominant flow in clay soils that have been drained, as at Brimstone Farm. The flows here are, however, a mixture of soil matrix flow and water moving rapidly through macropores that intersect the drainage. This flow can be collected and measured quite easily by intercepting the drain lines and installing weirs or similar measuring systems (see Harris *et al.,* 1984 for a description of the system as installed at Brimstone Farm).

(4) Deep seepage. This is water that leaves the soil at the base of the profile, in an essentially vertical direction. It is generally assumed that it will continue to move in this direction to the deep groundwater. In clay soils, which are generally considered to be impermeable, this contribution is usually very small, although it is of major importance for many other soil types. It may be recorded by inference from either piezometric or tensiometric measurements, but generally, it is deduced as the residual term after the calculation of a water mass balance at a site, and is thus error prone, even when it is a major component. Although such calculations indicate that this mode of flow does occur in clay catchments such as Brimstone Farm, it is generally small.

Measuring and estimating all the flows of water: unsaturated fluxes

Although flow measurement techniques are well established, there are still at least three unresolved problems. The fluxes of water through the soil in the unsaturated zone above the water table can in general only be estimated indirectly from other data, either from changes in water content, or in response to tension changes. The moving water is not itself measured. Additionally, the techniques that can be used to measure water content and tension (tensiometers, neutron probes, or time domain reflectometry) all cause problems by disturbing the soil, and so may introduce fallacious patterns by providing new preferential paths for water movement.

Methods of field sampling can also influence accuracy in the determination of concentrations and loadings of solutes in water flowing through soil. Four main methods are currently available for measuring leaching of solutes: lysimeters, porous suction cups, repeated soil sampling and field drainage systems like those of the Brimstone Farm experimental plots. The last is the most expensive, followed by lysimeters, porous cups, and soil sampling. The most frequently adopted technique is porous suction cups (Ballif & Muller, 1990; Addiscott, 1990), but they give samples (if at all) only between field capacity and about 0.75 bars tension, and so do not sample all the pores in the soil. Consequently, interpretation of the results is uncertain (Webster *et al.,* 1993; Lord & Shepherd, 1993). As suction cups and tensiometers are still operated manually, it is also difficult to obtain a sufficiently detailed time series for analysis and integration. Where, however, large numbers of samples are required, and in particular for more freely draining soils, porous cups have been widely used satisfactorily.

However, comparisons of the three cheaper methods when used for nitrate leaching (Webster *et al.,* 1993) suggest that none of them is a satisfactory substitute for the field drainage system. The main problem is that all three give values for a single point or a very small volume of soil, and thus do not take into account the textural and structural heterogeneity across a field or larger area. Suction cups and soil samples taken with an auger give direct measurements of the solute concentration in soil water, but require an estimate of the drainage volume in order to calculate fluxes over periods of time, and this has to be derived from meteorological observations and evapotranspiration equations. Lysimeters allow drainage volumes to be measured, but often under-estimate them because the matric potential at the base of the lysimeter is less than that of the subsoil in the field. To simulate field conditions some suction should be applied to the base of a lysimeter, but this is difficult to calculate. In addition, the concentrations of solute measured in soil samples are often much less than those measured at the same depth in suction cups or lysimeters. This is probably because the nitrate extracted from soil samples comes from the whole range of pores sizes, whereas that sampled from porous cups or from lysimeters comes only from larger pores, Indeed in strongly structured clay soils, such as that of Brimstone Farm, it is possible to insert porous cups either into fissures and obtain large amounts of soil solution, or into the centres of peds and obtain no water even at high suctions.

Of the four methods of measuring leaching losses, drained field plots, which are hydrologically sealed beneath by a naturally impermeable substrate and at the side by impermeable membranes, come closest to simulating real conditions in a farmer's field, not least because they can be large enough to cultivate in exactly the same way as a farmer does.

Preferential flow. Probably the biggest unresolved field problem is the measurement of water and solute movement where preferential routes of water movement exist, given the similarity in scale of the soil structural units and the instruments available for measuring water movement or sampling soil water. A tensiometer or suction cup may pass though a crack, or be embedded totally in a ped. If placed in a crack, suction may intercept water moving through the crack structure, but if the rate of movement is very rapid, the cup may be unable to remove water because there is no free water in the system when suction is applied, even though water has passed it. However, if placed in the centre of a ped, it may equally extract no water, because in that location there is no mobile water that can be extracted. There is, in general, no overall method of measuring or sampling soil water in such a way as to know where it comes from in relation to the ped structure. Major advances in the study of solute movement in the field depend upon the successful resolution of this field problem.

A closely allied problem is the identification of conditions in microsites within a soil, particularly in relation to the position within a ped. The surface of a ped may be aerobic, and hence the locus of processes such as nitrification; while at the same time the centre of the same ped might be locally anaerobic and subject to processes such as denitrification. The unequivocal measurement of processes at microsites within a soil is not possible with current field techniques.

Boundary fluxes: rainfall and evapotranspiration. An important source of error and uncertainty in estimating solute fluxes is the error in measuring the water flux at the surface, rainfall and evapotranspiration. Hudson & Gilman (1993) suggest that rainfall inputs to the upper Severn catchment are measured with an uncertainty of $\pm 4.3\%$. At Brimstone Farm and elsewhere, multiple replicate rain gauges over a small area of 5–10 ha can give values which vary over a week by as much as 10%, often in a non-systematic and apparently random way. In all hydrological studies there remains an uncertainty about the most basic variable, the rainfall input, which places a limitation on the accuracy with which it is possible to calculate the hydrological balance.

There is an even bigger problem with the other meteorological component of the water balance: the estimation of evaporation and transpiration (Vereecken & Dust, 1996). The normal procedure is to calculate the Reference Evapotranspiration (ET_0) using the Penman-Monteith equation or some similar method, as few sites have the data necessary to calculate ET_0 directly. In order to do this, it is again normal practice to use data for some (if not all) variables derived from synoptic meteorological data. These values then have to be altered to give the actual transpiration rate from the crop growing on the site, and this requires use of a crop-sensitive model, such as MORECS (Thompson *et al.*, 1981), or IRRIGUIDE (Bailey & Spackman, 1996). The values derived from such models can at best be only estimates, and so there remains some uncertainty over the upward flux at the surface.

The problems associated with these uncertainties are particularly critical for pesticide leaching models. Here, as at many other sites, the major herbicide leaching event is normally the first major storm after the autumn application of herbicide to the soil. The time difference between the application and the runoff event determines the extent to which the pesticide has degraded and has become adsorbed to the soil. The shorter the difference in time between the two events, the greater the concentration of pesticide. Predicting the first drainflow event requires prediction of the return to field capacity. At Brimstone Farm, the model uses the meteorological data from the synoptic station at Brize Norton, less than 10 km away, with local observations of rainfall. It is usually possible to fit the hydrological results of a model for any one year at this site just by assuming that the ET_0 estimates input into the model are incorrect by a small percentage, often by less than 5%. Such *post hoc* adjustments however should be avoided unless supported by physical argument.

Measuring solute concentrations

The last major problem is measuring the solute concentrations in water flows through the soil. There are two main aspects to this.

The analytical aspect. For most solutes, there is no alternative but to remove samples for analysis in the laboratory. With reactive solutes, such as nitrate and pesticides, changes in concentration can easily occur between field and laboratory. It is therefore necessary to limit microbial activity in the sample by storing at a low temperature (usually $<4°C$) and to limit light-induced changes by storage, for example, in darkened bottles. Nevertheless some changes can occur, and the period of storage should be minimized as far as possible.

With pesticides it is difficult to measure the very low concentrations of complex molecules typically found in drain water (Harris *et al.*, 1991; Harris *et al.*, 1994). Expensive equipment, such as high performance liquid chromatography linked to a mass spectrometer, is usually necessary to reach a limit of detection close to the European Union maximum permitted concentration of a single pesticide in drinking water ($0.1\ \mu g\, l^{-1}$). Consequently the number of samples that can be analysed is often limited by cost, and this is a major constraint on studying changes in concentration with application rate, flow rate, tillage condition and time.

Choice of a suitable sampling strategy. Even with modern electronic water sampling equipment, the strategy for sampling is constrained by the number of samples that can be obtained, stored and analysed. Samples collected at regular time intervals may be suitable for slowly changing systems, but if they are widely spaced they can easily miss major events in rapidly changing situations. Flow proportional sampling overcomes this problem (Vivien & Quinton, 1993), but only if the fluctuations in concentration are fairly infrequent, otherwise it can quickly generate too many samples for easy analysis. Recently, ADAS has used a complex scheme for sampling drainage and stream flow for pesticide analysis. During the rising limb of an event, samples are taken frequently until the peak flow has passed, then less frequently over the falling limb and finally at regular but larger time intervals during the trickle flow between large events. Information is then transferred by telemetry to the laboratory, so that the filled sample bottles can be recovered without delay and replaced with empty bottles to await future events. From previous experience it is also possible to know which events are likely to carry significant amounts of pesticide, and concentrate analytical efforts on these. At other times, samples can be bulked before analysis to give an estimate of background concentrations between important events.

PRECISION OF RESULTS

Equation (1) identifies the source of errors in the estimation of solute fluxes, in particular that estimating the total flux involves summing all the errors. Multi-plot replicated experiments, such as those at Brimstone Farm or North Wyke, allow an estimation of the degree of uncertainty associated with the measurements. Normally studies are concerned with the general behaviour of all sites, of which the experimental plot is just one small example, and the concern is not with individual behaviour of each plot, but with the generalized behaviour of all such sites. It is therefore important to establish the degree to which the behaviour of any one point is representative of generality (Bunge, 1966), which is not normally possible without replication.

These ideas can be explored using the example of the nitrate flux data for a single year at Brimstone Farm, from a single representative location, Plot 7 (Fig. 2). The magnitude of the error in the calculation of the total solute load in a whole year due to the uncertainty of individual measurments, was investigated by taking the basic information about flows and concentrations for the representative year, adding random error to the measurements, and then recalculating the loads. Errors in the measurement of both water discharge (Q) and solute concentrations (C) were generated by adding independent normally distributed random error terms, z_t and z_t^*, to each of the components of Equation (1). These random errors were scaled in relation to the standard deviation of the relevant variable (σ_Q or σ_C) by a scaling factor λ, and the resulting perturbed data were truncated to be non-negative.

$$\text{Flux} = \sum_t (Q_t + \lambda\sigma_Q z_t)(C_t + \lambda\sigma_C z_t^*) \qquad (2)$$

The standard deviation of the estimate of the flux was then calculated from 50 separate realisations of the randomly perturbed data, and is presented in Table 1 as a function of the magnitude of the scaling factor, λ.

These errors increased, as expected, in a non-linear way as the magnitude of the scaling factor increases, a reflection of the fact that errors in both terms are multiplied together. However, even with the error scaled by as much as 20% of the standard deviations, the error in the flux was still less than 1 kg nitrate-N ha^{-1} $year^{-1}$.

The Brimstone Farm dataset also provides information about the variation between replicate plots. Figure 3 illustrates this by showing the flows through four replicate plots for a period of a few days in December 1985. This shows that there was considerable variation, even in a carefully controlled experiment. Similar variation has also been noted for water tables recorded in the plots at North Wyke (Armstrong,

Table 1. Standard deviation of the flux estimate in relation to the error scaling factor.

λ	σ Flux (kg nitrate-N ha^{-1} $year^{-1}$)
0.020	0.105
0.040	0.157
0.060	0.253
0.080	0.389
0.100	0.408
0.120	0.490
0.140	0.516
0.160	0.626
0.180	0.729
0.200	0.829

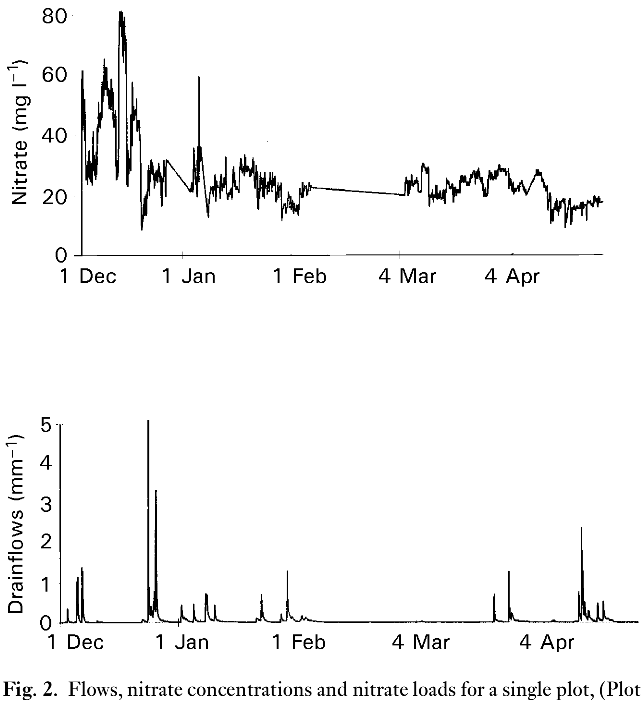

Fig. 2. Flows, nitrate concentrations and nitrate loads for a single plot, (Plot 7, 1985–6) used for the analysis of load calculations.

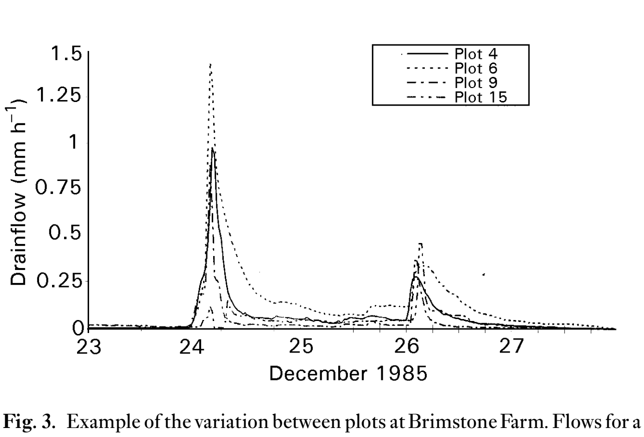

Fig. 3. Example of the variation between plots at Brimstone Farm. Flows for a single drain flow event, December 1985 for four replicated plots.

Table 2. Brimstone Farm. Nitrate Fluxes from replicate plots 1985–6.

Plot	Tillage	Load (kg nitrate-N $ha^{-1} yr^{-1}$)
1	Plough	57.9
7	Plough	44.2
10	Plough	57.3
16	Plough	43.6
4	Direct Drill	54.0
6	Direct Drill	43.3
9	Direct Drill	32.3
15	Direct Drill	58.8

1987). During the first phase of the Brimstone Farm experiment, there was five-fold replication of the measurements for each drainage treatment (Cannell *et al.*, 1984; Harris *et al.*, 1984). The values of the fluxes for each of the replicated plots for one year (Table 2) were used to calculate a standard error of the mean; this had a value of 9.30 kg N ha^{-1}. A complete analysis of multiple years with variable levels of replication gave a similar standard error of the treatment means of 10.8 kg N ha^{-1} (D. Wilson, pers. comm.). These standard errors of the treatment means are an order of magnitude greater than those associated with the lack of precision in the individual measurements that make up the load calculation. It is thus clear that accuracy in the field measurement of solute fluxes can be achieved to a greater extent by increasing the replication of the measurements than by greater precision in the individual measurements.

Without doubt, confidence in the measurement of solute fluxes would be increased if balances of inputs and losses could be constructed. This has been attempted for nitrogen at certain well-documented experimental sites, such as the Rowden Moor grassland plots at North Wyke (Garwood, 1988) and the Broadbalk winter wheat experiment at Rothamsted (Jenkinson & Parry, 1989). However, even here there are many uncertainties. With respect to nitrogen these are associated, for example, with inputs to the soil from dry deposition from the atmosphere and from non-symbiotic nitrogen fixation by free-living soil microorganisms, and gaseous losses by denitrification. Attempts to measure the last of these on some of the Brimstone farm plots have given very variable results (0–30 kg N ha^{-1} yr^{-1}), up to approximately the same order of magnitude as the leaching losses, so they have not improved precision in the construction of the nitrogen balance. Reasons for this variability include changes in the rate of denitrification with temperature and soil moisture content, and the spatial heterogeneity of soil moisture and organic matter.

Balances for pesticides are also difficult to construct. For pesticides applied as sprays, there are initial losses as drift, which are usually unknown but can exceed 10% of the application, even in quite calm conditions (Harris *et al.*, 1992). For the same reason, an experimental site can acquire pesticides from surrounding areas in both wet and dry deposition (Turnbull, 1995). Other losses to the atmosphere may occur by evaporation after application, but are difficult to quantify because they are influenced by wind, temperature, humidity, and possibly other meteorological variables. Further losses can then occur by adsorption on soil organic matter or clay and by microbial degradation in the soil. Both of these can be measured in soil samples taken in the laboratory but are very variable because of soil heterogeneity, for example in organic matter content through the irregular incorporation of straw.

CONCLUSIONS

This paper has identified some of the unresolved problems that we encounter in solute flux studies, illustrated by the example of Brimstone Farm. Three major issues are identified:

(1) Studies of solute fluxes (and also models of those fluxes) need accurate hydrological balances. However there is considerable uncertainty in the meteorological boundary conditions, notably rainfall inputs, and the actual (as opposed to the theoretical) evapotranspiration flux. If field studies and models do not use correct water fluxes, then there is little chance of correctly estimating solute fluxes.

(2) There is an urgent need for better field techniques capable of examining and recording water movement at the ped and macropore scale, and also for estimating conditions at microsites within the soil profile. Particularly, it is necessary to identify the differences between aerobic and anaerobic conditions within a single ped. However, it will still be necessary to use this microscale information at the larger scale, and the use of mechanistic models offers many opportunities in this respect.

(3) It is essential that in the search for precision of estimates and scientific understanding, the issue of replication is adequately considered in the experimental design. Multi-plot replicated experiments, such as those at Brimstone Farm and North Wyke, are one of the few ways of achieving any measure of the precision of estimates of solute fluxes.

ACKNOWLEDGEMENTS

The financial support of the Ministry of Agriculture Fisheries and Food is gratefully acknowledged. IACR receives grant-aid support from the UK Biotechnology and Biological Sciences Research Council.

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