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# Measuring and modelling nitrogen leaching: parallel problems

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## Abstract

In studies of nitrate leaching both experimenters and modellers experience problems arising from soil variability. Because of the small-scale heterogeneity that gives rise to mobile and immobile categories of water, both measurements and modelling are easiest in homogeneous sandy soils and most difficult in strongly structured clay soils. There are also parallels at plot and field scale in the problems caused to experimenters by log-normal distributions of nitrate concentrations and those caused to modellers by non-linearity in models. All researchers need to be aware that a reliable estimate of the mean from a set of measurements or a model may necessitate considerations of variances as well as means.


## Introduction

Measurements and models of nitrate leaching are both influenced by the physical and statistical properties of the soil. There are parallels between the problems these properties cause to experimenters and those they cause to modellers. Researchers in both categories have to take account of the heterogeneous nature of the soil, and the uncertainties that arise from measured values that are not normally distributed have something in common with those that occur because models are not linear with respect to their parameters. This paper examines these parallel problems with particular reference to their impact at various scales.

## Problems associated with small-scale soil heterogeneity

### *Measurements of nitrate leaching*

The problems of measuring nitrate leaching are essentially those of capturing the water that is about to move beyond the rooting zone of the soil. The determination of the nitrate concentration in this water is a matter of routine chemical analysis.

Measurements of nitrate leaching can be made most readily in the most homogeneous soils, which usually means sandy soils. These soils permit the use of porous ceramic cups, which are usually the easiest and the cheapest technique for measuring nitrate concentrations in soil water. Webster et al. (1993) give an up-to-date account of the use of porous cups, together with a note of precautions that need to be taken and results from two different sites. Their advice on installing porous cups is particularly important; incorrect installation can lead to misleading results as discussed in earlier reviews (Addiscott, 1990; Addiscott et al., 1991).

As the percentages of clay and silt in the soil increase, the soil becomes more structured and less homogeneous, with clearly-defined mobile and immobile categories of water in the soil matrix and, particularly in the most clayey soils, cracks and other channels by-passing the whole soil matrix. At the same time porous ceramic cups become less and less useful for collecting the water likely to pass from the soil. This was illustrated by a study made by Barbee and Brown (1986) who installed porous cups in three types of soil adjacent to collecting pans inserted beneath the soil at the same depth. Chloride was applied to the soil surface and allowed to leach under natural rainfall. Weekly samplings showed no significant differences between the chloride concentrations measured by the two systems in a sandy soil, and the peak concentration occurred after about 100 days in both. In a moderately-structured silt soil, however, there were

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clear differences in the patterns found, with the porous cups recording the peak concentration after 8 days and the horizontal collecting vessels after 42 days. In a clay soil, the porous cups produced a large enough water sample for analysis on only one occasion and seemed to be by-passed by the water flow on all other occasions.

Soil heterogeneity is a problem for users of porous cups because of the scale of the measurement. In sandy soils, the volume of the soil from which the cup extracts water is large compared with the scale of the variability in soil properties. In heavier soils, the volume from which the cup extracts water is probably smaller than in sandy soils while the scale of the variability is larger. This can lead to the problems found by Barbee and Brown (1986). Thus porous cups are most effective in sandy soils, but it does not prevent their use in heavier soils, provided they are used with a clear idea of what they measure. Goulding and Webster (1992) placed porous cups in plots of the Broadbalk Experiment at Rothamsted that had field drains. They concluded that in this silty clay loam soil the porous cups sampled the immobile water while the field drains collected the mobile water. As a result, the nitrate concentrations sampled by the porous cups were larger than those in the drainage before fertilizer applications, because most of the nitrate was produced by microbes in the soil, but smaller after fertilizer N had been applied and was at risk of being carried down in the mobile water.

The results of Goulding and Webster (1992) described above make it clear that porous cups are not suitable for estimating losses of nitrate from heavier soils without supplementary measurements. Lysimeters provide a better, but more labour-intensive, approach. There are two basic categories, Ebermeyer lysimeters and monolith lysimeters. The construction and use of these devices are reviewed elsewhere (Addiscott, 1990; Addiscott et al., 1991), and Belford (1979) gives a useful account of the setting-up of monolith lysimeters. We concentrate here on the problems that may be encountered in their use.

Ebermeyer lysimeters are constructed by inserting a collecting vessel into a horizontal aperture in the soil, usually from a trench. A monolith lysimeter is made by driving a suitable casing, often a fibreglass pipe, into the soil and cutting the soil away around it, so that the column of soil it contains can be severed at the base. The monolith can then be installed either where it was taken, so that it can be subjected to the same agronomic practice as the soil around it, or in a bank of lysimeters elsewhere. In either event a suitable collecting vessel must be attached to the base.

Both types of lysimeter can be constructed with relatively little disturbance to the soil within them, and the scale of the lysimeter is sufficiently large to accommodate the heterogeneity that leads to the presence of mobile and immobile water. The Ebermeyer lysimeter has a degree of uncertainty that arises because the water that is collected may have moved laterally as well as vertically and may not have come from directly above the collector. The casing of the monolith lysimeter avoids this uncertainty, but there can be problems of preferential water flow if the soil shrinks away from the casing (Belford, 1979).

There is, however, one problem that affects both types of lysimeter, and that is the air-water interface at the base of the soil above the collector. Because many of the pores that conduct water through the soil are continuous, there is a 'hanging column' of water that extends to a reasonable depth in the soil. Cutting this hanging column has the effect that the surface tension that arises from the air-water interface holds back the water from draining until the soil becomes saturated, even in a freely-draining soil (Richards et al., 1939). Webster et al. (1993) found clear evidence of this effect in an experiment on a sandy soil in which the movement of a pulse of chloride was followed using porous cups and lysimeters. The peak chloride concentration was delayed in the lysimeters and the experimenters attributed the delay to the air-water interface. Only by applying suction can the effect of this interface be overcome; Coleman (1946) showed that suction controlled both the rate of drainage and the amount of water in the base of the soil. The suction applied to the base of a lysimeter should be as close as possible to that corresponding to the hanging column of water. Morton et al. (1988) achieved this by adjusting the suction with reference to tensiometers inserted in nearby soil to the depth of the lysimeter's base. This question of appropriate suction is not just an academic one. Haines et al. (1982) found that subjecting the collector in an Ebermeyer lysimeter to a 1 m hanging column of water doubled the average water flow and changed its nitrate concentration by a factor of three.

The heaviest clay soils often have subsoils that are so nearly impermeable to water that they need artificial drainage. This is a situation that can be turned to the experimenter's advantage, because most of the nitrate that is leached from the soil is carried through the drainage pipes and can be measured. The Brimstone Experiment near Wantage in the UK is an example of such an experiment (Cannell et al., 1984). This experiment has plots that are large enough to permit fairly normal agricultural practice, separated from each other by vertical barriers of heavy-gauge polythene sheet. Three categories of water can be collected and analysed for nitrate; surface run-off, interflow (flow at the base of the plough layer) and water carried by the drainage system. Goss et al. (1993) recently reported nitrate losses in several years from plots subjected to various treatments.

The plots in this experiment give few physical problems because the conditions at the interface between air and water are the same as in fields elsewhere subjected to the same standard drainage practice.

*Models of nitrate leaching*

Just as measuring nitrate leaching is simplest in the most homogeneous soils, so is modelling nitrate leaching. It is in sandy and other homogeneous soils that the classic mechanistic modelling approach to leaching, the Richards equation used with the convection-dispersion equation (Wagenet, 1983), can be applied most relevantly. Soils of this kind also permit the use of several simple models for leaching, such as the early 'piston-flow' model of Rouselle (1913) and the leaching model and equation developed by Burns (1974, 1975). Both categories of model have been investigated and used reasonably widely.

All the models cited above presume the soil to be homogeneous, with water and solute moving equally freely in all parts of the soil. Like porous cups, therefore, they become less relevant as the soil becomes more structured and less homogeneous and the water becomes divided into mobile and immobile categories, with by-pass flow becoming a possibility. For soils such as these models that take account of mobile and immobile water become necessary. Probably the earliest 'mobile-immobile' model for leaching in the soil was that of Van Genuchten and Wierenga (1976). This was an adaptation of the classical mechanistic approach that included a category of 'stagnant' water, the movement of solute into which was governed by a transfer coefficient. This model was applied mainly to columns of soil in the laboratory, but Barraclough (1989) used an adaptation of it at the field scale. A simpler 'mobile-immobile' model developed by Addiscott (1977) was intended for use at field plot or field scale. Despite its simplicity this model gave a good simulation of the intricate nature of the 'break-through curves' obtained when chloride was applied to the Drain Gauges (lysimeters) at Rothamsted (Addiscott et al., 1978).

The simple mobile/immobile model, and the Burns leaching model and equation, are classified as 'capacity' models because their main parameters derive from the volumetric moisture contents, $\theta$, of the soil at various suctions. The classical approach has as its main water parameter the hydraulic conductivity and is therefore classified as a 'rate' model. One model, the SLIM model of Addiscott and Whitmore (1991) has both a capacity parameter and a simplified rate parameter. A recent development of this approach is the SLM model of Hall (1993) which takes account of water moving at various rates.

A rather different approach has evolved for heavy, cracking clay soils in the form of the CRACK model of Jarvis and Leeds-Harrison (1987). This model takes account of the cracking and swelling of clay soils and the resulting changes in water flow pathways. This was originally a water-flow model but it has recently been adapted to simulate nitrate leaching (P B Leeds-Harrison, pers. commun.). Jarvis et al. (1991) recently developed the MACRO model, which is also intended for heavy soils.

## Problems arising from variability at plot and field scale

*Measurements of nitrate leaching*

Statistically-related problems in both soil measurements and soil modelling arise from the variability of the soil. In measurements of nitrate leaching we are concerned mainly with the variability of nitrate concentrations. These can arise in part from the physical properties of the soil, but some of the variability in nitrate concentrations arises from non-uniform excretion by organisms of various types at widely ranging scales. The nitrate concentrations measured with porous cups in arable soils by Webster et al. (1993) were not particularly variable, with coefficients of variation in the range 14–20 percent. There are probably two reasons for this relatively small variability. One is tillage, which tends to smooth out variability by mixing the soil. Another is the fact that the organisms excreting ammonium or nitrate are mainly microbes and the scale of even a porous cup measurement is so much larger than that of the variability of the excretion that the latter is not detected by the measurement. The factor most likely to increase variability in nitrate is the irregular distribution of crop residues at harvest.

Grassland that is cut for hay or silage but not grazed would probably have nitrate concentrations showing as little variability as arable land, or possibly less because the grass would tend to even out the variability by taking up most nitrate where most was available. Most grassland, however, is grazed by farm animals, usually cattle or sheep. These animals excrete at a scale that is very readily picked up by porous cups or soil sampling. A cow, for example, may deliver 2 L of urine on an area of about 0.5 $m^2$, giving a localized application of about 500 kg $ha^{-1}$ of N, far more than the grass can use. The concentrations of nitrate found by Cuttle et al. (1992) using porous cups in grassland grazed by sheep ranged over four orders of magnitude and were distributed log-normally. Similar degrees of variability were found by White et al. (1987) in soil samples for nitrate in grassland.

When measurements deliver a skewed population of concentrations that includes same very large values, some care is needed in choosing a suitable statistical estimator to represent the distribution. The type of estimator needed will depend on the precise nature of the information required. If concern is centred on the concentration per se, because of the EC nitrate limit, for example, the estimator needed is one that will not be influenced excessively by a few large values among mainly smaller ones, so the mean of the log distribution is likely to be the most reliable estimator; this is equivalent to taking the geometric mean. If, however, our main concern is with the overall loss of solute from the area of land, we need to take full account of those few large values because they contribute so much to the loss. This means that we need the arithmetic mean of the concentrations, but if calculated directly this can be an inefficient estimator for skewed distributions, because the skew gives a large error to the estimate. To obtain an efficient and unbiased estimate it may be better to back-transform from the log distribution. There are two methods for doing so.

The simpler method is that of Aitchison and Brown (1957) which estimates the mean $\mu$ and variance $\sigma^2$ of a population represented by a log-normal distribution from the sample mean $m$ and variance $s^2$:

$$\mu = \exp\left(m + \frac{1}{2}s^2\right) \quad (1)$$

$$\sigma^2 = \mu^2[\exp(s^2) - 1] \quad (2)$$

The other method developed independently by Finney (1941) and Sichel (1952) estimates $\mu$ and $\sigma^2$ through a power series:

$$\mu = \exp(m)\Psi\left(\frac{1}{2}s^2\right) \quad (3)$$

$$\sigma^2 = \exp(2m)\left\{\Psi(2s^2) - \Psi\left[\frac{(n-2)}{(n-1)}s^2\right]\right\} \quad (4)$$

where the power series $\Psi$ is given by:

$$\Psi(t) = 1 + \frac{t(n-1)}{n} + \frac{t^2(n-1)^3}{n^2(n+1)2!} + \frac{t^3(n-1)^5}{n^3(n+1)(n+3)3!} + \frac{t^4(n-1)^7}{n^4(n+1)(n+3)(n+5)4!} + \cdots \quad (5)$$

where n is the sample size.

The key point to note in both sets of equations is that the estimate of the population mean has to take account of the sample variance as well as the sample mean. Similarly the estimate of the population variance has to take account of the sample mean as well as the sample variance.

These equations were evaluated by Parkin et al. (1988) who wished to find out (a) whether it was necessary to use these equations rather than the simple untransformed mean and variance of the sample, and (b) whether there was any benefit from using the more complex Finney-Sichel equations. Their conclusions can be summarized as follows:

1 Use the standard untransformed estimator to estimate the mean of a slightly-skewed population (skew about 1.625 or less).

2 Use the Finney-Sichel estimator to estimate the means of moderately- to markedly-skewed distributions (skew about 4.0 or about 16.0 respectively). For large samples and moderate skews the Aitchison-Brown estimator may be used.

3 Use the Finney-Sichel estimator for the variance with all combinations of skew and sample size, except when small samples (4–20) are taken from a slightly skewed population, when the standard untransformed estimator should be used. The Aitchison-Brown estimator may be used for sample sizes greater than 40 from slightly-skewed populations.

4 Use the Finney-Sichel estimator for the coefficient of variation for all combinations of skew and sample size. The Aitchison-Brown estimator may be used when more than 40 samples were taken or when more than 20 were taken and the skew was slight.

Parkin et al. (1988) studied populations that were generated mathematically and whose distributions were clearly defined, but the results cited above that

Cuttle et al. (1992) and White et al. (1987) obtained in the field generally support their conclusions.

*Models of nitrate leaching*

The previous section was concerned mainly with the problems caused by the variability in nitrate concentrations. Here we are concerned with the variability in the parameters of models. The underlying problem can be seen in some equations presented by Rao et al. (1977) that relate the mean of a function f(*x*,*y*) to the means and variances of *x* and *y*, $\mu_x$, $\mu_y$, $\sigma_x^2$ and $\sigma_y^2$ where *x* and *y* are distributed normally:

$$\mu_{f(x,y)} = f(\mu_x, \mu_y) + C \qquad (6)$$

That is to say, the mean of the function is not necessarily the function of the means. They are the same only when *C* is zero, and *C* is given by:

$$C = \left(\frac{\partial^2 f(x,y)}{\partial x^2}\right)\frac{\sigma_x^2}{2} + \left(\frac{\partial^2 f(x,y)}{\partial y^2}\right)\frac{\sigma_y^2}{2} + \rho\left(\frac{\partial^2 f(x,y)}{\partial x \partial y}\right)\frac{\sigma_x \sigma_y}{2} \qquad (7)$$

where $\rho$ is the product moment correlation of *x* and *y*. Thus *C* is zero and $\mu_{f(x,y)}$ is equal to f($\mu_x$, $\mu_y$) only if the second partial differentials are all zero or if the variances are all zero (or both).

If we take f(*x*,*y*) as a very simple representative of models we can see another parallel between problems in measurements and problems in modelling. Just as the estimate of the population mean obtained by back-transforming a log-normal distribution depended on the variance of the log-normal distribution as well as its mean, so the mean obtained from the function or model depends on the variance of the parameter as well as its mean if the function or model is non-linear with respect to the parameter. The non-linearity shows itself in the fact that the second partial differentials are not zero.

This parallel is not, however, a complete one. In the back-transformation of the log-normal distribution, not only did the population mean depend on the variance of the distribution, but the population variance depended on the mean of the distribution. The equation given by Rao et al. (1977) for the variance of f(*x*,*y*) shows it to depend only on the variances of *x* and *y* and not on their means:

$$\sigma_{f(x,y)}^2 = \left[\frac{\partial f(x,y)}{\partial x}\right]^2 \sigma_x^2 + \left[\frac{\partial f(x,y)}{\partial y}\right]^2 \sigma_y^2 \qquad (8)$$

The problems caused by the term *C* in Equation 6 vary greatly between different types of model. The volumetric moisture content of the soil usually varies relatively little, so capacity parameters such as those used in the models of Burns (1974) and Addiscott (1977) usually have coefficients of variation of the order of 10 percent. These models are also more or less linear with respect to their parameters, so the term *C* does not cause any problems. By contrast the classical approach to modelling leaching, the combination of the Richards equation and the convection-dispersion equation, has problems of both kinds. The main parameters of these equations, the hydraulic conductivity and the dispersivity, are highly variable and the models are not linear with respect to these parameters.

The difference in behaviour between capacity parameters and rate parameters such as the hydraulic conductivity is illustrated by a study made by Addiscott and Bland (1988) on the SLIM model (Addiscott and Whitmore, 1991), which has both a capacity parameter and a simplified rate parameter. The model was run with or without allowance for the variances of these parameters. Ignoring the variance of the capacity parameter had little or no effect on the ability of the model to simulate the proportions of a pulse of applied nitrate found at various depths down to 1 m (Table 1), but ignoring the variance of the rate parameter clearly made the simulation less satisfactory. The latter effect was not very large because of the 'stabilizing' influence of the capacity parameter.

*Table 1.* Effects of including or omitting the variances of the rate parameter, $\alpha$, and the capacity parameter, $W_r$, in the simulations of the downward movement of surface-applied nitrate with the SLIM leaching model. (From Addiscott and Bland, 1988)

| Treatment of variance | LOF Mean Square[a] |
|---|---|
| All variances included | 11 |
| All variances omitted | 47 |
| Variance of $\alpha$ omitted | 26 |
| Variance of $W_r$ (topsoil) omitted | 12 |
| Variance of $W_r$ (subsoil) omitted | 11 |

[a] Lack of fit mean square as defined by Whitmore (1991). The smaller the value, the better the simulation.

## Discussion

Both experimenters and modellers seek true representations of processes occurring in the soil. Both should therefore be expected to find the same types of problems if they are effective in their depictions of what is happening in the soil. This seems to happen. The heterogeneity at small scales that results in mobile/immobile water phenomena gives broadly similar physical problems in both measurements and models of nitrate leaching, such that both are easiest in homogeneous sandy soils and most difficult in strongly-structured clay soils. The variability problems met by experimenters and modellers also have parallels in the problems caused to the former by log-normal distributions of concentrations and to the latter by nonlinearity in models. The possibility that a reliable estimate of the mean from either a set of measurements or a model may necessitate the consideration of variances as well as means is one that both experimenters and modellers ignore at their peril.

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