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Overview and Application of the Mitscherlich Equation and its Extensions to Estimate the Soil Nitrogen Pool Fraction Associated with Crop Yield and Nitrous Oxide Emission

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Abstract

Natural levels of soil nutrients are spatio-temporally variable and insufficient for agricultural purposes. Artificial fertilisers are applied to achieve greater crop growth rates and yield. Mitscherlich's equation and Boule's fertilizer units are described and illustrated in relation to crop yield then applied to estimate the nitrogen (N)-pool fraction in the soil that contributes to a component of greenhouse gas (GHG) emission, specifically the nitrous oxide (N_2O) flux. Mitscherlich (1909) proposed a diminishing returns model to extract information about soil N status for production responses. Mitscherlich’s equation was generalised by Baule (1918) and modified by Bray (1945) to account for soil nutrient contributions for multiple fertilisers. These models are examined in this chapter. Their application results in the extraction of further information on soil nutrient variability and N_2O emission across various geo-positions (specific global locations). It is concluded that Mitscherlich’s equation and Boule’s fertilizer units are useful tools to investigate soil-fertiliser interaction and compare soil fertility and GHG emission.

Keywords: Baule units, Dickson formula, Mitscherlich equation, Nitrogen cycle, Nitrous oxide emission, Soil nutrients

1. INTRODUCTION

Our climate's nitrogen (N) cycle supports all biogeochemistry processes and products and is fundamental for sustaining plant and animal life on earth. The cycles and activities of our planet with the sun control the interplay amongst earth-related phenomena, which include photosynthesis, biological N cycling (incorporating nitrification, ammonification, denitrification, N mineralisation), wind, clouds, thunder, rainfall and lightning (Vagstad et al., 1997; Tie et al., 2002). These are all contributory factors in determining the extent of reactive nitrogen (N_r) as part of the soil nutrient pool. Fowler et al. (2013) determine a figure of 413 Tg N yr^{-1} of N_r due to the global N fixation of terrestrial and marine ecosystems. A substantial proportion of this figure, 240 Tg N yr^{-1}, can be attributed to terrestrial anthropogenic activities via soil or vegetation. For details and thorough reviews of the N-cycle and impact and interactions of various factors (positive and negative) see, e.g. Thomas (1992), Galloway et al. (2004), Gruber and Galloway (2008), Ollivier et al. (2011), Fowler et al. (2013), van Groenigen et al. (2015).

A continuing supply of N_r is needed for nature's food web. Liebig's law of the minimum is a principle originally developed in agricultural science by Sprengel (1828) and later popularized by von Liebig (1855). It states that 'growth is dictated not by total resources available but by the scarcest resource (limiting factor)'. This principle has also been applied to biological populations and ecosystem models for factors such as sunlight or mineral nutrients (Gorban et al., 2011). To work out the necessary proportion of nutrients for soil nutrition, Liebscher conducted many experiments with the main nutrients [N, phosphorus (P) and potassium (K)] at the end of 19th century. Based on the results of these experiments he formulated his law of the optimum (Liebscher, 1895). This principle states that 'a production factor that is in minimum supply contributes more to production the closer other production factors are to their optimum' (also see de Wit, 1992).

Along with historical studies of soil-plant interaction and fertiliser use, Mitscherlich (1909) developed his model, often referred to as the law of diminishing returns, to quantify crop response to fertiliser. Spillman (1923) also worked on this idea independently, hence the response model sometimes being referred to in literature as the Mitscherlich-Spillman equation. Baule (1918) generalized the Mitscherlich equation for two or more nutrients; this is known as Baule-Mitscherlich limiting factor equation (Verduin, 1988). To study nutrient interactions, Baule (c. 1920 while working with Mitscherlich in Germany) also developed the idea of half-way points, which are generally called Baule units. Bray (1945) used the Mitscherlich model to study soil nutrient status via soil tests. He extended Mitscherlich's equation to study soil nutrient roles (both from soil and fertiliser) in the production of various crops. He showed how the extended model can be used to predict fertiliser requirement. Following the development of these mathematical models much research was undertaken in relation to the soil and fertiliser nutrient uptake by various crops. For example, Inkson (1964) found no toxic effects of P if applied at more than its optimum level, whilst toxic effects of N and K were observed at higher rates of application. These toxic effects of over-fertilization can result in a non-asymptotic response, which is not consistent with the Mitscherlich-Bray model. A specially constructed quadratic function (Inkson, 1964) proved to be a popular model for the analysis of such cases. Nelder's inverse polynomials were also used as they facilitate improved curve fitting at data end-points (Nelder, 1966).

Baseline soil nutrients are insufficient for agriculture and that necessitates supplementation by the use of fertilisers (e.g. N, P, K or their mix) to optimise crop yield. The N_r needed for crop production is much greater than that available in the soil nutrient pool (as indicated by observed yield from the control plots in crop growth studies). Bray (1945) developed protocols for balanced fertiliser use through tests for soil fertility. Following this research, Bray and his associates proposed a nutrient mobility concept after modifying that developed by Mitscherlich, Baule and Spillman. Bray's concept states that 'As the mobility of a nutrient in the soil decreases, the amount of that nutrient needed in the soil to produce a maximum yield increases from a variable net value, determined principally by the magnitude of the yield and the optimum percentage composition of the crop, to an amount whose value tends to be a constant'. The magnitude of this constant is independent of the amount of crop yield, provided that the kind of plant, planting pattern and rate, and fertility pattern remain constant and that similar soil and seasonal conditions prevail (Gowariker et al., 2009). Combination of N fertiliser (plus P and K as well) and suitable crop varieties, has revolutionised food production. However, the downsides of this practice are the polluting consequences. Losses of nutrients to watercourses via surface runoff and leaching, and emissions to air, e.g. nitrous oxide (N_2O) emission, are major concerns. Like crop growth, N_2O emission is a function of nutrients in soil and the applied N.

The primary purpose of this paper is to revisit fertiliser response models of Mitscherlich, Baule and others, using UK datasets covering a period of over 40 years, and apply them to quantify N_2O-N emission as related to relevant N-forms in the soil and the applied N resource.

2. OVERVIEW AND DATA

2.1 Crop response to nutrient application

2.1.1 Mitscherlich and Baule models

Response curve methodology in relation to soil fertility and growth factor application (e.g. N fertiliser) was developed from the end of 19th century. Von Liebig (1855), for example, used a single node linear curve (maximum A) with a plateau ending at nutrient input x_A:

$$y = y_0 + mx, x \le x_A;\ y = A, x > x_A \tag{1}$$

where y is yield, m is slope (rate of yield increase with respect to nutrient application, x, in a given soil and environment) and y_0 is the y-axis intercept corresponding to $x = 0$, i.e. the ‘control’ yield.

Following on from the work of Liebig and his peers, Mitscherlich (1909, 1928) proposed a mathematical function for crop growth in response to the added growth factor.

(i) Mitscherlich’s law of physiological relationships: Yield can be increased by each single factor even when it is not present in the minimum as long as it is not present in the optimum.

(ii) Mitscherlich’s growth law: Increase in yield of a crop as a result of increasing a single growth factor is proportional to the decrement from the maximum yield obtainable by decreasing the particular growth factor.

His response function related crop growth to nutrients. When plants were supplied with all nutrients except one limiting factor, growth was found to be proportional to the amount of this limiting or efficiency factor, c, when added to the soil. His function was:

$$\frac{\mathrm{d}y}{\mathrm{d}x} = (A - y)c \tag{2}$$

where A is the asymptotic value (maximum) of y. After integration this equation on the log-scale becomes:

$$\ln(A - y) = \ln(A) - cx \tag{3}$$

This can be written in y-axis intercept and asymptote form:

$$y = y_0 + (A - y_0)\left(1 - \mathrm{e}^{-cx}\right);\quad y = y_0 \text{ when } x = 0 \tag{4}$$

However, it is often rewritten in the form proposed by Baule (1918):

$$y = A\left(1 - \mathrm{e}^{-c(x+d)}\right);\ d = \ln\left[A/(A - y_0)\right]/c \tag{5}$$

The parameter d is the soil nutrient applied (for further details see Schneeberger, 2009a, 2010). Once the estimate of d is known, the right-angled triangle of nutrient and yield formed by the 3 points with coordinates $\{x = -d, y = 0\}$; $\{x = 0, y = 0\}$; $\{x = 0, y = y_0\}$ may be used to calculate the linear slope of production response from soil nutrient d.

To study the response to added nutrient alone, Schneeberger (2009a) partitioned the Mitscherlich (Equation 4) into two parts (y_{01} and y_{02}):

$$y = A\left(1 - \mathrm{e}^{-cx}\right) + y_0 \mathrm{e}^{-cx} = y_{01} + y_{02} \tag{6}$$

Here y is the yield, A is the asymptote (ideal maximum yield), in the absence of any toxic effects if nutrient is added at more than the optimum level (Inkson, 1964), and c the efficiency of utilising added nutrient. If adding to a low N-status soil, the yield growth profile may vary. The Mitscherlich-Baule model is summarized in Figure 1.

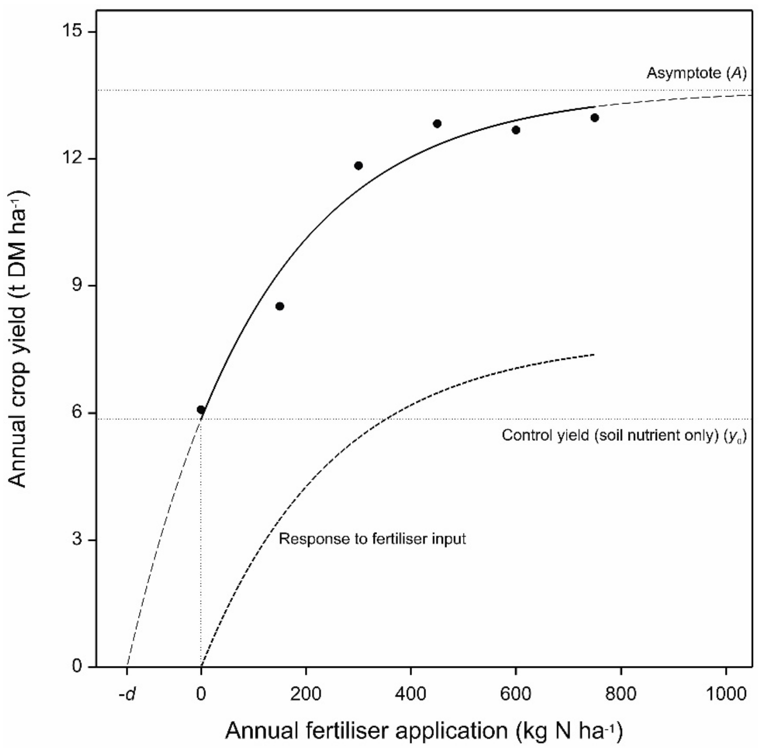

Figure 1 Features of the Mitscherlich-Baule response model. (a) fitted curve (solid line) to Combo site data (dots), (b) control plot yield from soil nutrient only (horizontal dotted line), (c) soil nutrient level d (at the intersection of dashed line and the negative side of x-axis, i.e. at zero crop yield), (d) response to fertiliser input (increasing close dash curve starting from the origin (net of control yield)).

2.1.2 Bray modification

Starting with the Mitscherlich (Equation 3), Bray (1945) studied soil fertility using soil tests and protocols he had developed. He replaced fertiliser x with the amount available in the soil (b_1) as indicated by the soil test, i.e.

$$\ln(A - y) = \ln(A) - c_1 b_1 \tag{7}$$

where c_1 is the efficiency of soil nutrient uptake. Using experimental estimates of A, y and b_1 he was able to obtain estimates of c_1 for various soils and crops. In order to link his equation to applied nutrient, the Mitscherlich-Bray equation was developed:

$$\ln\left(A-y\right)=\ln\left(A\right)-c_1b_1-cx \text{ or } y = A\,(1-\mathrm{e}^{-c_1b_1-cx}) \tag{8}$$

Using these equations, Bray (1945) developed balanced fertiliser protocols for various soils, crop and environment combinations.

Balba and Bray (1956, 1957) further extended this equation to accommodate more than one soil nutrient, viz.

$$y = A\,(1-\mathrm{e}^{-c_1b_1-c_2b_2-cx}) \tag{9}$$

They also proposed the formula $\dfrac{cx}{c_1b_1+cx}$ to calculate contribution of fertiliser to nutrient content of the plant. Among many innovations they expanded this formula to calculation the proportion of nutrient in plant supplied from

(i) The fertiliser $$\frac{cx}{c_1b_1+c_2b_2+cx} \tag{10}$$

(ii) The absorbed form $$\frac{c_1b_1}{c_1b_1+c_2b_2+cx} \tag{11}$$

(iii) The easily acid soluble form $$\frac{c_2b_2}{c_1b_1+c_2b_2+cx} \tag{12}$$

More details can be found in Balba and Bray (1957).

2.1.3 Non-asymptotic response due to toxic effects of over-fertilization

Inkson (1964) found toxic effects of N and K when applied in excess of their optimum levels. In such cases, the Mitscherlich equation will not be applicable. Inkson (1964) proposed a specially constructed quadratic function:

$$y=a_0+a_1\left(x+B\right)+a_2\left(x+B\right)^2 \tag{13}$$

where y is yield, x is the added nutrient and B is nutrient in the soil.

Another applicable option is using inverse polynomials (also known as rational functions) as proposed by Nelder (1963):

$$\frac{1}{y}=\frac{b_0}{x+B}+b_1+b_2\left(x+B\right) \tag{14}$$

Here b_0 is associated with the rising part of a curve and b_2 with the declining part. A biphasic Mitscherlich function can also be used (Schneeberger, 2009b). If the declining part of the response curve is short and nearly linear then ‘Mitscherlich + linear’ may be a simpler option (Powell et al., 2020; Dhanoa et al., 2021).

2.1.4 Incomplete study due to resource limitation and/or environmental vagaries

It may happen that the maximum yield cannot be estimated experimentally due to unforeseen and uncontrollable factors. In such a situation Dickson (1942) described a method of prediction of the maximum yield. In order to do this, experimental yield (y_1, y_2 and y_3) corresponding to three equal interval nutrient applications (x_1, x_2 and x_3) is needed with the condition that $x_2 - x_1 = x_3 - x_2$. Substituting these in the Mitscherlich equation (Equation 3) and solving the resulting three simultaneous equations, we can estimate maximum yield A as:

$$A = \frac{{y_2}^2 - y_1 y_3}{2y_2 - y_1 - y_3} \tag{15}$$

Dickson (1942) also estimated the efficiency of applied nutrient (activity constant c in Equation 3), viz.

$$c = \frac{\ln(A - y_1) - \ln(A - y_2)}{x_2 - x_1} \tag{16}$$

Given estimates of A and c, an estimate of b_1 can now be obtained from the Mitscherlich-Bray equation (Equation 8) as:

$$b_1 = \frac{\ln(A) - \ln(A - y_0)}{c} \tag{17}$$

2.1.5 Possible mitigation of over-fertilization effects

Over-fertilization effects kick in when fertiliser N in excess of the optimum is applied. Crop responses below the optimum N application are largely unaffected. This should allow us to predict the asymptote (see above), assuming there are no toxic effects. Replacing crop response data beyond the optimum (empirically corresponding to the maximum yield) with the predicted asymptote we obtain a response profile that will be consistent with the Mitscherlich response model. This allows the apparent over-fertilisation effects to be quantified.

2.1.6 Baule’s fertiliser units

In order to study nutrient application, Baule developed the idea of units such that the first Baule unit moves a crop response to 50% of the asymptotic value and the second Baule unit moves the response to a point half-way from the 50% to the asymptote, i.e. 75% (= 50%+25%), and so on. The formula for these proportions (ρ_n) being:

$$\rho_n = 1 - \left(\frac{1}{2}\right)^n \tag{18}$$

where n (= 1, 2, 3, …) is the number of Baule units. After the 1st Baule unit, 2nd, 3rd, 4th units will take us to 75% (= 50% + 25%), 87.5% (= 50% + 25% + 12.5%) and 93.75% (= 50% + 25% + 12.5% + 6.25%), respectively, of the asymptote. Nutrient input corresponding to these response points (which will vary with soil fertility, crop and the environment) can be used to compare and contrast different environments at various geo-positions. In the case of two limiting nutrients (e.g. N and P), if soil has 2 Baule units of N and 3 Baule units of P then yield achieved will only be 66% (= 75% × 87.5%) of the maximum yield possible. Note that Baule units (X_n, kg applied nutrient ha^{-1}) are net of absolute soil nutrient; substituting $\rho_n \times A$ for y in Equation (5) gives the nth Baule unit:

$$X_n = c^{-1} n \ln 2 - d \tag{19}$$

where d (control soil nutrient) plus X_n (nutrient applied) make up absolute total nutrient. The estimate of d is on the negative part of the added nutrient axis (Figure 2).

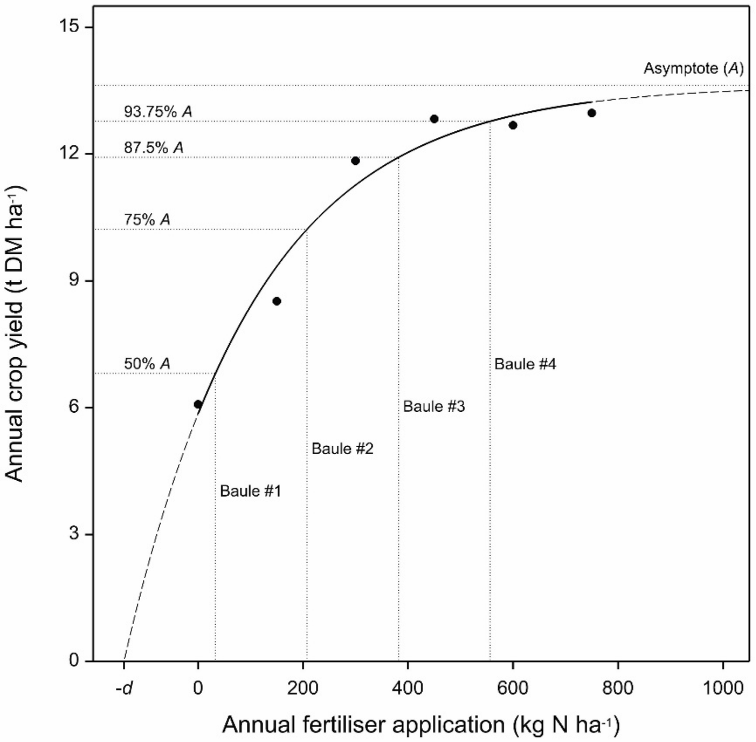

Figure 2 Baule's fertiliser units in relation to the fitted Mitscherlich-Baule response equation such that the 1st Baule unit increases the response to 50% of the asymptote and the second Baule unit moves it to a point half-way between the 50% and the asymptotic value, i.e. 75%, and so on. The figure also shows the intersection of the dashed part of the fitted curve at the negative side of the *x*-axis which gives soil nutrient level.

2.1.7 Baule's sufficiency ratio

Percentage sufficiency is defined by Baule (1918) as the ratio of control yield to maximum attainable yield at a chosen site:

$$\text{Percentage sufficiency} = 100 \times (y_0 / A) \qquad (20)$$

where y_0 is the control yield and A the asymptotic yield. The complement of this is:

$$v = 100 \times (1 - y_0 / A) \qquad (21)$$

which is the percentage deficiency and it is equal to $100 \times \mathrm{e}^{-c_1 b_1}$ as stated in Equation (8).

2.1.8 Baule-Mitscherlich limiting factor equation

While working with Mitscherlich, Baule generalised Mitscherlich's equation to study a system with 2, 3 or more limiting-factors (Inkson, 1964; Verduin, 1953):

$$E = E_{\max}\left(1 - b_1 r_1^{x_1}\right)\left(1 - b_2 r_2^{x_2}\right)\left(1 - b_3 r_3^{x_3}\right)\ \ldots \qquad (22)$$

where E is the rate of a process, $E_{\max}$ is the rate if factors (x_1, x_2, x_3 …) are present in abundance, and the b and the r are constants introduced to facilitate fitting the equation.

Verduin (1988) evaluated this equation for freshwater lakes sampled in the USEPA National Eutrophication Survey (1972–76). He applied it to determine chlorophyll concentration using four limiting factors N, P, carbon and light. The equations listed above have been applied widely, e.g. Harmsen (2000) modified the Mitscherlich equation for rain-fed crop production in semi-arid areas.

2.1.9 Type II linear regression

As the model parameters (fitted or predicted) carry errors, an ordinary least squares regression model is not wholly appropriate, and a Type II model is needed to avoid slope attenuation (Dhanoa et al., 2010). For this purpose, two special cases of the general maximum likelihood solution, i.e. major axis (MA) and reduced major axis (RMA), are sufficient. Quoting Dhanoa et al. (2010), the general maximum likelihood (ML) estimates the slope as:

$$\hat{\beta}_{\text{ML}} = \frac{\hat{\sigma}_y^2 - \lambda_{\text{ML}}\hat{\sigma}_x^2 + \sqrt{(\hat{\sigma}_y^2 - \lambda_{\text{ML}}\hat{\sigma}_x^2)^2 + 4\lambda_{\text{ML}}\hat{\sigma}_{xy}^2}}{2\hat{\sigma}_{xy}} \tag{23}$$

Here $\lambda_{\text{ML}} = \hat{\sigma}_\varepsilon^2 / \hat{\sigma}_\delta^2$ where $\hat{\sigma}_\varepsilon^2$ is the estimator of the error variance of a single *y*-value whilst $\hat{\sigma}_\delta^2$ is the estimator of the error variance of a single *x*-value with the assumption that both $\hat{\sigma}_\varepsilon^2$ and $\hat{\sigma}_\delta^2$ are constant over the range of the data. The variances of *x* and *y* sample values are denoted by $\hat{\sigma}_x^2$ and $\hat{\sigma}_y^2$ respectively and $\hat{\sigma}_{xy}$ is the sample covariance. An alternative form of Equation (23) is the Deming formula (Cornbleet and Gochman, 1979; Deming, 2003):

$$\hat{\beta}_{\text{Deming}: y.x} = U + \sqrt{U^2 + \left(1/\lambda_{\text{Deming}}\right)} \tag{24}$$

where:

$$U = \left[\hat{\sigma}_y^2 - \left(\frac{1}{\lambda_{\text{Deming}}}\right)\hat{\sigma}_x^2\right] \Big/ \left[2r_{yx}\hat{\sigma}_x\hat{\sigma}_y\right] \tag{25}$$

and $\hat{\sigma}_{yx} = r_{yx}\hat{\sigma}_x\hat{\sigma}_y$ with correlation r_{yx}. Here λ_{Deming} is the reciprocal of λ_{ML}, i.e. $\lambda_{\text{Deming}} = \hat{\sigma}_\delta^2 \big/ \hat{\sigma}_\varepsilon^2$.

If we can justifiably assume that $\hat{\sigma}_\varepsilon^2$ and $\hat{\sigma}_\delta^2$ are equal (i.e. $\lambda_{\text{ML}} = 1$) then the MA regression model may be used. For MA, the solution reduces to:

$$\hat{\beta}_{\text{ML}} = \frac{\hat{\sigma}_y^2 - \hat{\sigma}_x^2 + \sqrt{(\hat{\sigma}_y^2 - \lambda_{\text{ML}}\hat{\sigma}_x^2)^2 + 4\lambda_{\text{ML}}\hat{\sigma}_{xy}^2}}{2\hat{\sigma}_{xy}} \tag{26}$$

Similarly the RMA (or geometric mean functional relationship) regression model may be appropriate when $\hat{\sigma}_\varepsilon^2$ and $\hat{\sigma}_\delta^2$ are assumed to be proportional to $\hat{\sigma}_y^2$ and $\hat{\sigma}_x^2$, respectively, giving $\lambda_{\text{ML}} = \hat{\sigma}_y^2 \big/ \hat{\sigma}_x^2$ and Equation (23) reduces to $\pm\hat{\sigma}_y \big/ \hat{\sigma}_x$.

2.2 Experimental data

2.2.1 First experimental data collection

The National Grassland Manuring (GM) series of trials were conducted by ADAS (a major UK agricultural consultancy) and the former Grassland Research Institute, at Hurley, UK. Multi-site experiments were carried out between 1971 and 1984 (Final report, MAFF project code BD 1438). The objectives were (a) to assess the response of grassland to fertiliser N, and (b) to examine contribution of white clover and its interaction with fertiliser N and slurry/excreta. For the purposes of this study, we analyzed the grassland response to N-fertiliser data from the GM20 series of experiments conducted at 21 sites (see Table 1 for locations) over the period 1970-1974 (Morrison et al., 1980).

2.2.2 Second experimental data collection

Data used in this study come from 2 different sites where crop yield and greenhouse gases (GHG) were measured, viz. Hereford, UK (Williams et al., 2017) and Bedford, UK (Cardenas et al., 2017). We used these data to investigate N_2O emission response to added N fertilization.

2.2.3 Third experimental data collection

The third data collection comprises 20 experiments under 4 projects conducted over 7 years at 14 UK sites (Chadwick et al., 2016). We used these data to address the question: do different types of the same nutrient applied affect N_2O emission?

3. APPLICATION AND DISCUSSION

3.1 Using the first experimental data collection

In this section, we explore application of the Mitscherlich-Baule response model. This has different functional forms, e.g.

$$y = A\left(1 - \mathrm{e}^{-c(x+d)}\right) = A\left(1 - \mathrm{e}^{-cx}\mathrm{e}^{-cd}\right) = A + BR^{x} \tag{27}$$

where $B = -\mathrm{e}^{-cd}, R = \mathrm{e}^{-c}, c = -\ln R$.

Statistical package Genstat (VSN International, 2015) uses the form $y = A + BR^x$ as the initial estimate of parameter R must lie in the interval [0.0→1.0] for an asymptotic response. From the fit of the full Mitscherlich-Baule model one can derive the following important information that will characterise a specific site or geo-position regarding:

(i) Efficiency of utilising the added nutrient (N in this example) and other parameters
(ii) Yield from the nutrient pool in the soil alone (Equation 3)
(iii) Maximum derivable yield *A* at the particular geo-position (including the control yield)
(iv) Baule's nutrient units at the selected sites (for 50% *A*, 75% *A* …) (Equation 18)
(v) Baule’s sufficiency ratio (Equation 20) regarding control yield and asymptote yield
(vi) Most of these curves have well defined asymptotes, so our data sets are suitable for testing the Dickson formula (Equation 15) for asymptote prediction

(vii) Dickson (1942).also proposed the formula to predict the Mitscherlich efficiency (*c*) of applied nutrient utilisation, and the efficiency of the same nutrient from the soil (Bray's b_1, kg ha^{-1}).

All these site characteristics are specific to the soil potential at that site, both from the relevant nutrient available from the soil, and also that which can be activated in response to the same nutrient when added to the soil. These characterising features can be used to compare, contrast and classify the chosen sites. The differences can be displayed (Figure 3) for all 21 sites; and show the *y*-axis yield response, when no fertiliser is added ($x = 0.0$). The Figure 3 data profiles were quantified using Equation (27).

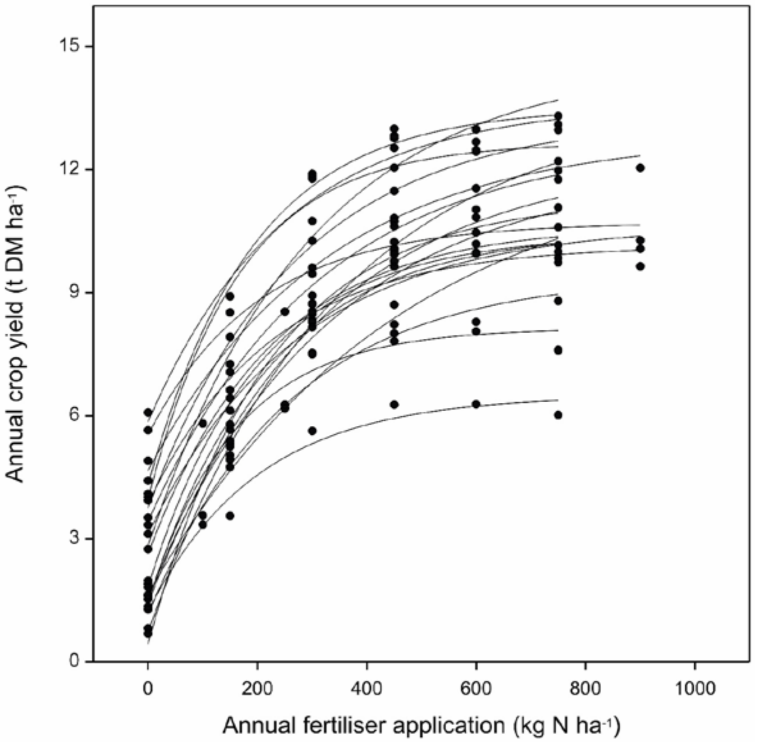

Figure 3 The GM 20 series data as collected from the 21 selected sites. When no nutrients were added the control yield (*y*-axis intercept) varies considerably. These control yield differences contribute to the major differences among the fitted asymptotes.

The parameter estimates *R*, *B*, *A* for each of the 21 sites are listed in Table 1. The individual curves may differ in terms of the values of both the linear and non-linear parameters. For this purpose, parallel curve analysis, i.e. nonlinear regression ANOVA (Heitjan, 1989), was carried out by separating variance accounted for by the model parameters, and subjecting these components to a variance ratio test (*F* test). Linear parameters (*y*-intercept and asymptote) were shown to differ ($p < 0.05$) among the 21 sites but the shape parameter, *R*, (efficiency of use of added nutrient) was similar ($p > 0.05$) across all sites. Further output and other meaningful quantities are listed in Table 2, viz. adjusted R^2, control (unfertilised) yield, added nutrient asymptote (i.e. net asymptote), Baule's sufficiency ratio, relevant nutrient from the soil (i.e. absolute numerical value of the *x*-axis intercept), efficiency of added nutrient utilisation and magnitude of the Baule unit at each site. The dendrogram showing a hierarchical clustering analysis for site similarity (Earle and Hurley, 2015) is shown in Figure 4.

Table 1 Parameter values* obtained by fitting the Mitscherlich-Baule response model (Equation 27) to annual perennial ryegrass yield (t DM ha^{-1}) versus annual fertiliser application (kg N ha^{-1}) at each of 21 sites from the GM20 series of trials.

Site	*R*	*B*	*A*	S.E. *R*	S.E. *B*	S.E. *A*
Cambo	0.9960	-7.77	13.62	0.00135	0.987	0.883
Harewood	0.9948	-9.19	13.52	0.00074	0.492	0.362
Drayton (1)	0.9968	-10.87	12.30	0.00037	0.487	0.488
Morley	0.9940	-8.69	12.66	0.00142	0.776	0.517
Gleadthorpe	0.9955	-10.86	11.29	0.00137	1.226	0.998
Cambridge	0.9950	-5.26	6.50	0.00136	0.540	0.411
Bridgets	0.9951	-8.58	10.42	0.00109	0.712	0.547
Oxford	0.9966	-11.80	14.63	0.00093	1.246	1.219
Rowsham	0.9963	-9.54	13.29	0.00088	0.848	0.791
Hurley (1)	0.9969	-10.42	11.99	0.00082	1.075	1.089
Wye	0.9955	-8.02	10.65	0.00082	0.550	0.454
Pluckley	0.9971	-12.91	13.64	0.00025	0.453	0.468
Cannington	0.9955	-9.03	10.50	0.00083	0.620	0.507
High Mowthorpe	0.9938	-6.67	8.14	0.00091	0.442	0.232
Hurley (2)	0.9962	-8.26	9.43	0.00056	0.450	0.435
Jealotts Hill	0.9968	-9.27	12.70	0.00037	0.410	0.422
Drayton (2)	0.9978	-10.76	12.43	0.00062	1.435	1.541
North Wyke	0.9951	-5.17	10.71	0.00186	0.800	0.614
Pant-y-dwr	0.9956	-6.30	10.16	0.00161	0.953	0.770
Ponterwyd	0.9964	-7.54	10.67	0.00116	1.006	0.891
Selborne	0.9969	-8.18	12.84	0.00106	1.177	1.119

*S.E. denotes standard error.

Table 2 Derived parameter and other values associated with nutrient uptake and yield obtained by fitting the Mitscherlich-Baule response model (Equation 27) to annual perennial ryegrass yield (t DM ha^{-1}) versus annual fertiliser application (kg N ha^{-1}) at each of 21 sites from the GM20 series of trials.

Site	Adj. R^2	y_0 (t DM ha^{-1})	Net *A* (t DM ha^{-1})	Baule's sufficiency (%)[§]	Soil N (*d*) (kg N ha^{-1})	*c* (kg^{-1})	Baule unit (kg N ha^{-1})
Cambo	0.942	5.85	7.77	43.0	141.2	0.00398	174.3
Harewood	0.987	4.32	9.20	32.0	73.8	0.00522	132.7
Drayton (1)	0.994	1.43	10.87	11.6	38.4	0.00321	215.6
Morley	0.963	3.97	8.69	31.4	62.6	0.00601	115.4
Gleadthorpe	0.948	0.44	10.85	3.9	8.7	0.00456	152.1
Cambridge	0.954	1.24	5.26	19.0	42.4	0.00499	139.0
Bridgets	0.970	1.84	8.58	17.6	39.4	0.00493	140.6
Oxford	0.967	2.83	11.80	19.4	63.5	0.00339	204.7
Rowsham	0.973	3.75	9.54	28.2	89.5	0.00371	186.9
Hurley (1)	0.973	1.58	10.41	13.1	45.2	0.00311	222.6
Wye	0.981	2.63	8.02	24.7	63.4	0.00447	155.0
Pluckley	0.997	0.73	12.91	5.4	18.9	0.00290	238.6
Cannington	0.980	1.47	9.03	14.0	33.3	0.00453	153.0
High Mowthorpe	0.958	1.47	6.67	18.1	32.2	0.00619	112.0
Hurley (2)	0.992	1.17	8.26	12.4	34.4	0.00383	180.8
Jealotts Hill	0.996	3.43	9.27	27.0	97.4	0.00323	214.8
Drayton (2)	0.985	1.66	10.76	13.4	66.1	0.00217	318.9
North Wyke	0.919	5.54	5.17	51.8	147.2	0.00495	140.0
Pant-y-dwr	0.924	3.86	6.30	38.0	108.1	0.00443	156.6
Ponterwyd	0.946	3.13	7.54	29.3	95.6	0.00363	191.0
Selborne	0.945	4.66	8.18	36.3	145.8	0.00309	224.2

[§] Baule sufficiency ratio for each site is given by y_0 divided by gross *A* (shown in Table 1).

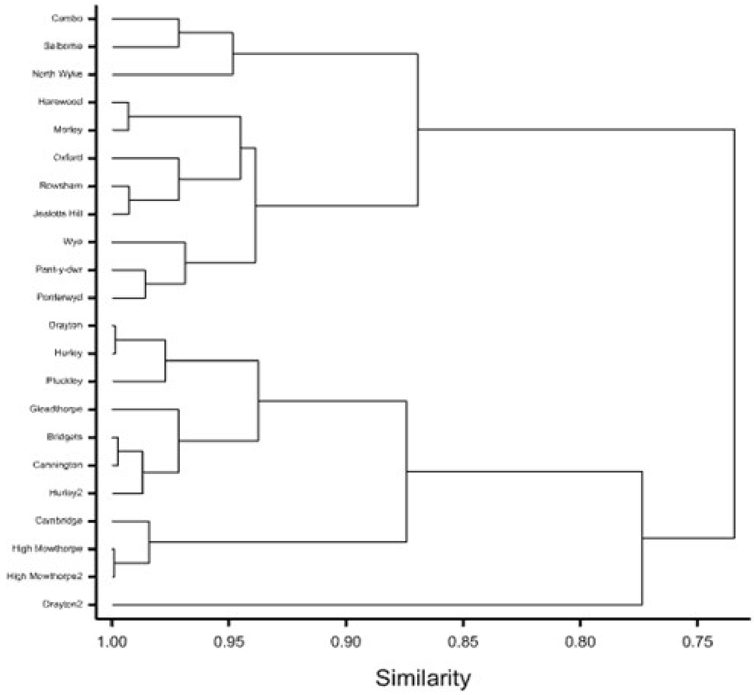

Figure 4 Dendrogram showing a hierarchical clustering analysis for site similarity (after Morrison et al., 1980). Similarity is a dimensionless quantity ranging between unity and zero.

In order to apply the Dickson formula for asymptote prediction (Equation 15), three equal interval nutrient inputs (x_1, x_2, x_3) and their corresponding yields (y_1, y_2, y_3) were required. Here we demonstrate applications of N input at 150, 300 and 450 kg ha^{-1} and at 300, 450 and 600 kg ha^{-1}. To cover the earlier part of the response curve, applications $y_1 = 150$, $y_2 = 300$, $y_3 = 450$ were used and the estimated asymptote values at each site calculated as pA_1. Likewise, to cover the later part of the curve, applications $y_1 = 300$, $y_2 = 450$, $y_3 = 600$ were chosen and the estimated asymptotes at each site calculated as pA_2. These results together with the fitted asymptote A are shown in the Table 3. To check the reproducibility of these estimates (pA_1, pA_2), Lin's concordance correlation coefficient (CCC) was used relative to the estimate from the response model (Lin, 1989; Dhanoa et al., 1999). Results for the 14 sites where both pA_1 and pA_2 were estimated give CCC = 0.9618 (slope with respect to the reference value, $C_b = 0.9950$) and CCC = 0.9344 ($C_b = 0.9679$), respectively; results which suggest using applications covering th, earlier (steeper) part of the response curve are preferable to those covering the later (flatter) part when using the Dickson formula. Dickson asymptote prediction is illustrated in Figure 5 where the fitted lines were obtained using four types of regression analysis (y on x, x on y, MA and RMA). Best prediction was obtained using Type II linear regression (MA and RMA). Figure 5 clearly shows that inclusion of 3 of the 4 additional sites (i.e. North Wyke, Pant-y-dwr, Selborne) majorly distorts prediction of pA_1.

Table 3 Predicted asymptotes* from the Dickson formula (Equation 15), pA_1 using N applications 150, 300 and 450 kg ha^{-1}, pA_2 using N applications 300, 450 and 600 kg ha^{-1} and the fitted asymptote A, estimated from the model $y = A + BR^x$.

Sites	pA_1	pA_2	A
Cambo	13.25	12.70	13.62
Harewood	13.64	12.99	13.52
Drayton (1)	13.55	11.49	12.30
Morley	12.75	12.48	12.66
Gleadthorpe	11.86	11.16	11.29
Cambridge	6.56	6.28	6.50
Bridgets	11.26	9.99	10.42
Oxford	14.71	13.00	14.63
Rowsham	14.63	12.55	13.29
Hurley (1)	11.88	10.69	11.99
Wye	11.03	10.24	10.65
Pluckley	12.88	14.41	13.64
Cannington	10.21	10.07	10.50
High Mowthorpe	7.87	6.82	8.14
Hurley (2)	-	-	9.43
Jealotts Hill	-	-	12.70
Drayton (2)	-	-	12.43
North Wyke	21.76	-	10.71
Pant-y-dwr	14.55	-	10.16
Ponterwyd	11.75	-	10.67
Selborne	16.62	-	12.84

*Missing values (-) not available, i.e. selected fertiliser levels were not applied at those sites.

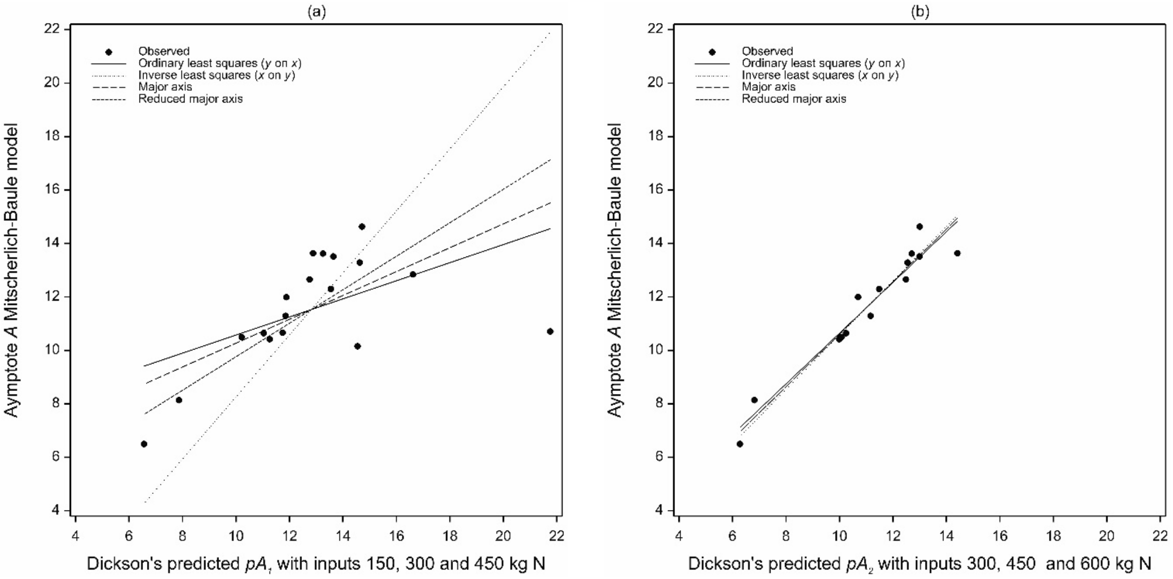

Figure 5 Dickson asymptote prediction with annual inputs (a) 150, 300 and 450 (using estimates from 18 sites) and (b) 300, 450 and 600 kg N ha^{-1} (estimates from 14 sites).

3.2 Using the second experimental data collection

As with control crop yield, control N_2O emission is also related to the innate nutrient in the soil. Likewise as applied to crop yield, the Mitscherlich-Baule model can be used to obtain information on a set of soils in order to study their capacity to emit N_2O. N_2O data were not collected along with the crop yield data for the 21 sites of the first data collection. For the purpose of illustration, we use the second data collection from different UK sites (Hereford and Bedford; Williams et. al., 2017 and Cardenas et al., 2017 respectively), where winter wheat yield and GHG were measured. We have found that N_2O emission is not always consistent with the Mitscherlich-Baule model, as is the case with crop yield data in situations of over-fertilization, but if for example soil moisture content is low the N_2O flux will most likely plateau at a low level (Cardenas et al., 2017). Herein we just focus on the asymptotic shape of N_2O profiles. Any attributes of a GHG producing source can be helpful in designing mitigating protocols, hence the inspiration to conduct this study with the use of the long established Mitscherlich-Baule model.

The fits obtained with the Mitscherlich-Baule response model are shown in Figure 6 and the associated parameter estimates given in Table 4. Though not the case with this example, soil nutrient estimates in relation to N_2O are generally lower when compared to the corresponding estimates from crop yield modelling. However, the crop yield incorporates effects related to root functionality and plant growth, and these are related factors that are not part of the measured N_2O flux, which is the product of chemical reactions and other factors in the soil ecosystem.

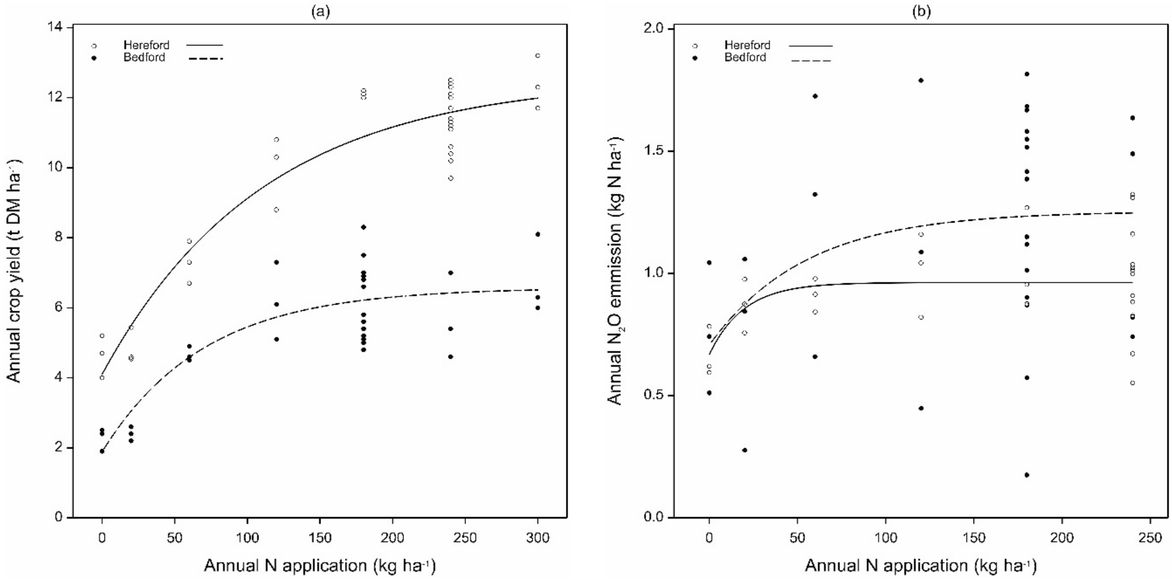

Figure 6 Mitscherlich-Baule response model fitted to (a) winter wheat yield and applied N and (b) N_2O emission and applied N (Hereford and Bedford data).

Table 4 Estimates of parameters obtained fitting the model $y = A + BR^x$ to the Hereford and Bedford, crop yield and N_2O emission data.

	Hereford		Bedford	
Parameter	Estimate	Standard Error	Estimate	Standard Error
(a) Fitting crop yield versus applied N				
R	0.9910	0.00221	0.9845	0.00682
B (t DM ha^{-1})	-8.45	0.625	- 4.58	0.596
A (t DM ha^{-1})	12.55	0.650	6.44	0.471
Soil N (*d*; kg N ha^{-1})	43.85	-	21.79	-
Baule unit (kg N ha^{-1})	76.85	-	44.45	-
(b) Fitting N_2O emission versus applied N				
R	0.9552	0.0413	0.9818	0.0270
B (kg N ha^{-1})	- 0.302	0.107	- 0.547	0.254
A (kg N ha^{-1})	0.973	0.0357	1.254	0.162
Soil N (*d*; kg N ha^{-1})	25.49	-	45.22	-
Baule unit (kg N ha^{-1})	15.11	-	37.78	-

3.3 Using the third experimental data collection

In addition to spatial and temporal variability, nutrients input to soil can cause further variability. So it is necessary to look if different sources and types of added nutrients affect soil nutrient status, leading to some impact on N_2O emission flux to the same extent, or different, across geo-positions. For this purpose, data are required for the same soil with the added nutrients_coming from different sources (for example using N fertilization from various sources). The data we use here comes from 20 experiments under 4 projects conducted over a period of 7 years at 14 sites (Chadwick et al., 2016). Added N nutrients were of 22 types across 11 arable and grassland crops. The response variable was N_2O flux with soil attributes pH, crop yield, soil organic carbon percentage, bulk density and clay percentage. This collection of data from individual sites is not entirely suitable for fitting the Mitscherlich-Baule model. However, site-to-site variability can be illustrated by the overall fit of the model to annual N_2O flux data (Figure 7). The average control emission of N_2O flux from this fit works out to be 0.359 kg N ha^{-1} per year.

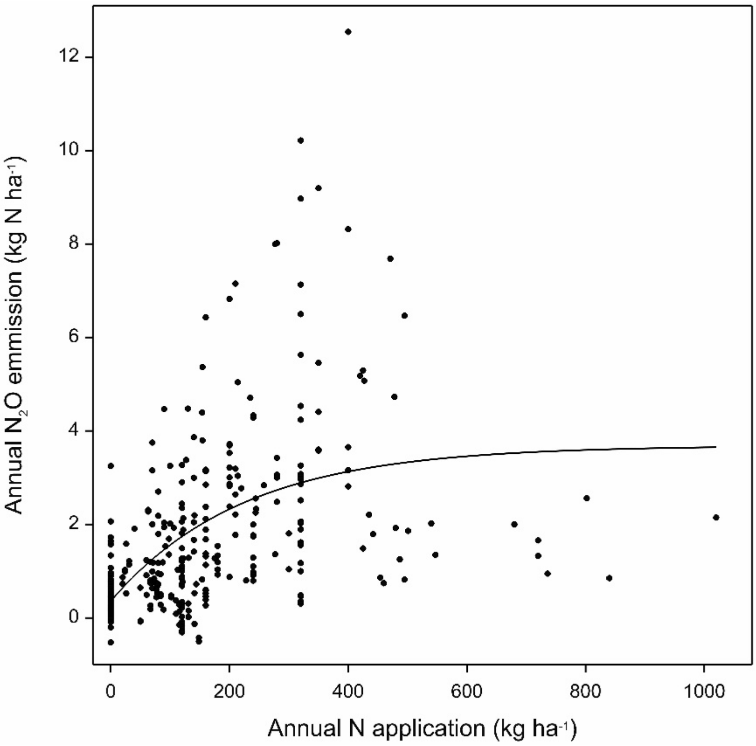

Figure 7 The Mitscherlich-Baule model fitted to N_2O emission and various N types (UK county data).

Boxplots of N_2O emission by site and by N type are shown in Figure 8. The vertical differences in Figure 8a are due to site totals that were caused by all relevant factors. N_2O flux was lowest in Oxfordshire and next lowest in County Down, Devon and Midlothian. Data skewness and a large range are apparent at several sites. Similar patterns can be seen by inspecting the boxplot by N type (Figure 8b).

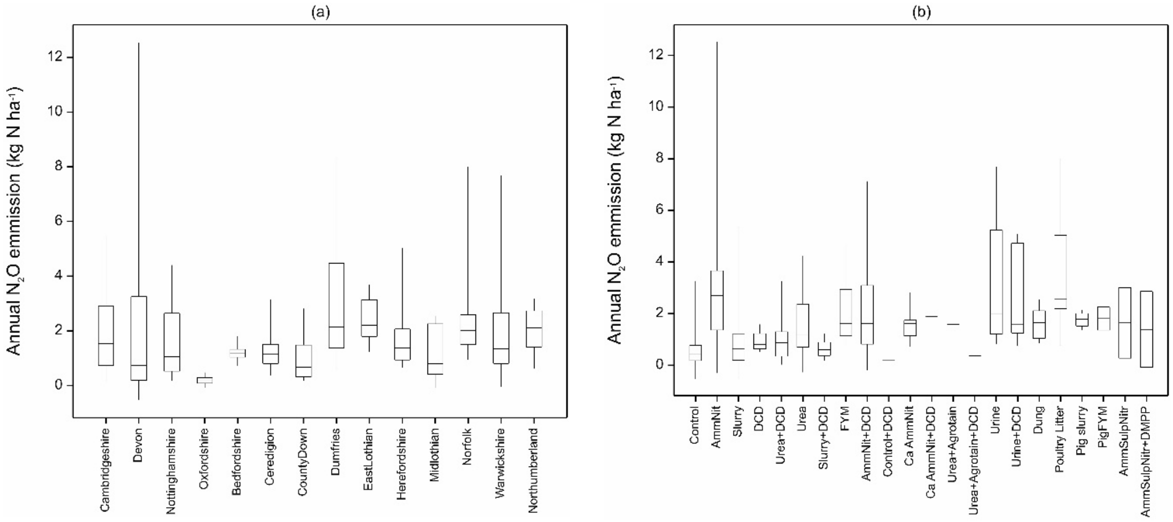

Figure 8 Boxplots of annual N_2O flux (kg N ha^{-1}) (a) by site and (b) by N type (using UK county data). Boxes and horizontal lines indicate interquartile range and median, whiskers indicate range of data.

Although crop yield data were tested for fitting with the Mitscherlich-Baule model, they only followed the model loosely and produced a variable spread of yield, as it is not wholly appropriate to compare crops of different grass, clover and cereal types incorporating a wide range of yields. Figure 9 shows the site variation in yield and soil pH. Crop yield in Midlothian is the lowest but others are similar or skewed. Soil pH tends to be variable across geo-position both naturally and by management practice. The value is highest for Cambridgeshire and lowest for Devon, Ceredigion and Dumfries. In such a diverse collection of data with many factors and covariates, some missing combinations are not a surprise, though that rules out standard multivariate analyses such as principal components analysis and cluster analysis. To look at more than two factors or covariates together we suggest using a regression tree modelling approach (Breiman et al., 1984).

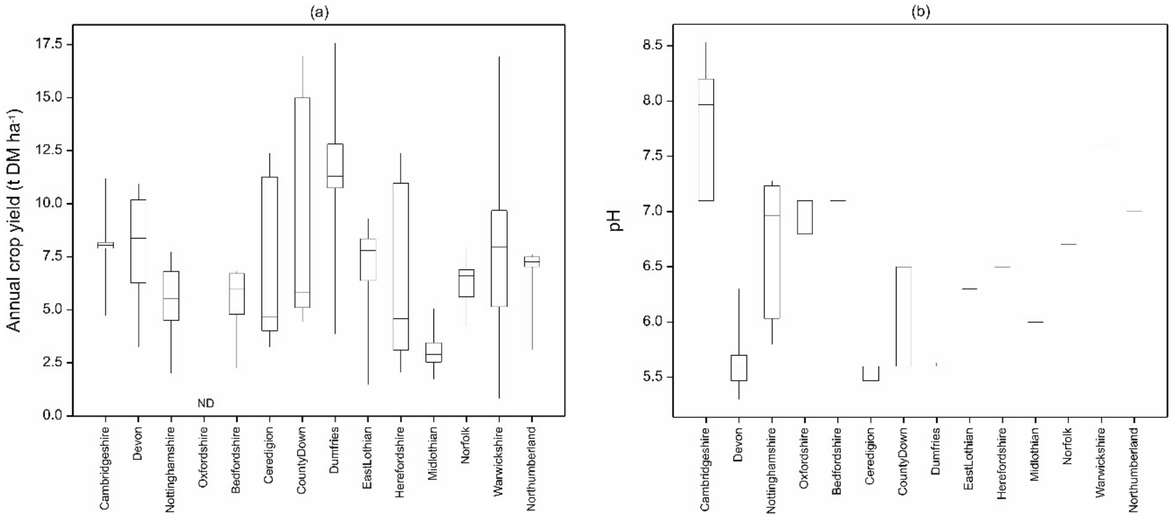

Figure 9 Boxplots of site variation in (a) annual crop yield (t DM/ha) and (b) annual pH (using UK county data). Boxes and horizontal lines indicate interquartile range and median, whiskers indicate range of data. ND = not determined

4. CONCLUSIONS

Application of the Mitscherlich-Baule model results in valuable site treatment specific information that enables geo-positions and their relevant ecosystems to be compared and contrasted. The nutrient estimate in the soil is the result of local environment and local soil type and composition that determine the control plot yield and potential for further yield in response to added growth factors. Baule units may be used to quantify this input for the required percentage of estimated local asymptotic yield. Information on N_2O emission potential of a given soil can help design mitigation strategies.

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