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RESEARCH ARTICLE

Investigating the accuracy and comparability of various lime prediction methods for Irish grassland mineral soils

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Abstract

Soil pH is a foundational element of agronomy, profoundly influencing biological, chemical and physical soil processes. Adjusting soil pH is a paramount factor for enhancing soil health and productivity with far-reaching environmental benefits. Over time soil naturally tends towards acidity, a process expedited by intensive agriculture practices. To determine the extent of necessary pH corrections, precise soil pH testing is imperative. Various methods including buffer systems, titrations, lime incubations and algorithms considering soil texture are used to assess a soil's lime requirement and each method carries distinct advantages and disadvantages. The Shoemaker–McLean–Pratt (SMP) buffer method is extensively used in Ireland and internationally; however, safety concerns owing to the use of hazardous chemicals required within the method have been highlighted. This study investigates various soil lime requirement tests and compares their performance against a lime incubation study. A proposed alternative to the SMP buffer test for Irish grassland soils is also investigated. Analysis of results obtained indicates that the SMP buffer method demonstrated the highest r^2 value of .497 when correlated with lime incubation results, while the calcium hydroxide titration method closely aligns with the SMP buffer method with an r^2 value of .816, followed by the modified Mehlich buffer method with an r^2 value of .763.

KEYWORDS

grassland mineral soils, lime incubations, lime requirement, organic matter, SMP buffer, soil pH

1 | **INTRODUCTION**

Soil pH has been described as a master variable as it affects a diverse array of physical, chemical and biological processes that impact soil fertility, plant development and ultimately crop yield (Neina, [2019](#page-13-0)). Soil pH significantly dictates the accessibility of plant nutrients, microbial activity and even the stability of soil aggregates (Song et al., [2019](#page-13-1)). At lower pH levels, key plant macronutrients are less available than at a neutral pH of around 7. Moreover, certain micronutrients tend to leach and pose toxicity risks at lower pH values (aluminium toxicity hampers crop growth in acidic soils $\left[\langle 5.5 \rangle \right]$. Generally, pH values between 6 and 7.5 allow optimal plant growth (McCauley et al., [2009](#page-12-0)). Correcting the pH of soil generally involves the application of a liming material.

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The lime requirement (LR) of soil is significantly influenced by various soil factors, with buffering capacity and cation exchange capacity (CEC) playing pivotal roles. Buffering capacity is a soil's resistance to pH changes in its solution and is affected by the accumulation of clay and organic matter (OM) (Cherian & Arnepalli, [2015\)](#page-12-1). Soils abundant in clay and OM possess a higher buffering capacity, necessitating a larger lime application to induce significant pH changes. This is a result of their ability to absorb and neutralize added lime effectively with their higher charge retention capacity (Nduwumuremyi, [2013\)](#page-12-2).

Moreover, the CEC of a soil, representing its ability to retain and exchange positively charged ions (cations), plays a crucial role. Soils with higher CEC can retain a greater quantity of calcium ions from lime, requiring a higher lime application to achieve the desired pH alterations (Lemire et al., [2006](#page-12-3)). In essence, buffering capacity, influenced by clay and organic matter, impacts lime requirement by determining the amount of lime needed for a pH change. Concurrently, CEC affects lime requirement by regulating the quantity of lime necessary to counteract the soil's innate acidity-holding capacity (Ross & Ketterings, [2011\)](#page-13-2). In a study completed by Kumar et al. [\(2012\)](#page-12-4), 20 soil samples with similar pH levels (4.51 ± 0.05) but varying OM contents and clay contents were investigated. Despite the uniform pH, LR varied threefold (5.6 to 18 t/ha). Soils with higher OM content showed greater buffering capacity and LR. The study revealed a significant correlation between soil OM content and LR $(r^2 = .862)$, emphasizing OM's substantial influence on LR variations (Kumar et al., [2012\)](#page-12-4). In another study, Keeney and Corey ([1963](#page-12-5)) looked at the LR of 26 Wisconsin soils along with various soil factors. Among the soil factors considered, OM showed a significant correlation with lime requirement $(r^2 = .620)$.

Various methods for determining LR have been developed including soil–buffer methods, titrations, incubations and equations based on soil characteristics (Nguyen, [2022](#page-13-3)). Most commonly, estimates for LR are derived through the utilization of buffer methods, owing to their ease of use, swift analysis and cost-effectiveness (McFarland et al., [2020\)](#page-12-6). Alternatively, soil incubation with either $Ca(OH)_{2}$ or $CaCO_{3}$ at field capacity for an extended period has been recognized as a dependable technique, however, its labour-intensive and timeconsuming nature makes it unsuitable for routine soil testing. Liu, Warneke, and Jacobsen ([2004](#page-12-7)), Liu, Kissel, et al. [\(2004\)](#page-12-8) describe an alternative approach involving direct titration using diluted alkalis, such as $Ca(OH)_{2}$; however, these streamlined approaches may yield incomplete reactions and underestimate soil pH-buffering capacity.

Online LR calculator tools, like the Rothlime model developed by Rothamsted Research in the United Kingdom (Holland et al., [2019](#page-12-9)), help determine LRs based on soil properties such as texture, pH values and cropping history. RothLime considers factors like soil type, crop type, neutralizing value (NV) of the product and regional acid deposition. However, it is important to note that regional variations may require specific equations tailored to unique soil characteristics and environmental factors (Goulding, [2016\)](#page-12-10).

Soil–buffer equilibrations are probably the most used technique for determining LR and involve the equilibration of a soil sample with a buffer solution, followed by the measurement of pH in the resulting soil–buffer mixture (Vogel et al., [2020](#page-13-4)). Different regions utilize various buffer compositions, designed to react with soil-acidifying components and exhibit a linear decrease in buffer pH as soil acidity or LR increases. The Shoemaker–McLean–Pratt (SMP) buffer method has been widely used since it was first described to determine lime requirement in soils (Shoemaker et al., [1961\)](#page-13-5). It is the standard method of pH soil determination in several jurisdictions including Ireland. However, the use of the SMP buffer test presents a disadvantage because of the hazardous nature of its reagents, such as para-nitrophenol and potassium chromate. Para-nitrophenol is highly toxic and environmentally hazardous, while potassium chromate is toxic, carcinogenic and mutagenic, posing risks to laboratory workers' health and the environment. Consequently, the European Chemicals Agency has categorized potassium chromate as a 'substance of very high concern' in the REACH directive, leading to its phase-out. Hence, there is a pressing need for a sustainable and reliable alternative method to determine lime requirement (Metzger et al., [2020\)](#page-12-11).

Sikora ([2006](#page-13-6)) developed a buffer method designed to replicate soil–buffer pH values like the original SMP single-buffer method but without the hazardous chemicals. The toxic substances, p-nitrophenol and potassium chromate, were substituted with 2-(N-morpholino) ethane sulfonic acid monohydrate (MES) and imidazole. In testing on 255 Kentucky soils, Sikora found that the new buffer produced soil–buffer pH values comparable to those of the SMP buffer, with r^2 values of .974 and .967 when compared with SMP buffer values on Kentucky and North American proficiency testing (NAPT) soils, respectively.

Hoskins and Erich [\(2008\)](#page-12-12) made modifications to the original Mehlich ([1976\)](#page-12-13) buffer method. The original Mehlich buffer ingredients included barium chloride and because of the hazardous nature of $BaCl₂$, they substituted Ba with Ca in the Mehlich buffer. The modified

buffer exhibited similar buffering capabilities as the original buffer. Moreover, the modified buffer showed extended linearity over a pH range of 6.6 to 3.0 (Van der Berg, [2017](#page-13-7)).

The Santa Maria (TSM) buffer was developed to estimate potential acidity in Brazilian acid soils, closely resembling the behaviour of the commonly used SMP buffer. TSM consists of four weak bases and calcium chloride to regulate ionic strength. Evaluation on 21 Brazilian soils showed that TSM's pH values matched those obtained from the SMP buffer, making it a reliable predictor of potential acidity in tropical and subtropical soils (Santanna et al., [2010\)](#page-13-8).

Incubations with a liming material in laboratory settings are commonly used as a reference method for determining LR (Hirpo et al., [2020](#page-12-14)). Here, soils are mixed with $Ca(OH)_{2}$ or $CaCO_{3}$ powder, brought to field capacity through moistening and subsequently incubated at room temperature for extended periods, with occasional stirring. After incubation, the soil pH is measured, and LRs are extrapolated from the lime–response curve. Although regarded as the most accurate means of determining LR, the protracted incubation time along with the different calibration points associated with this approach renders it impractical for routine testing.

A diverse range of grassland mineral soil samples (50) were collected for this analysis across the south of Ireland, selected to encompass variations in pH levels, clay content and OM levels, with the understanding that differing clay and organic matter content would likely yield variations in CEC and thus LR. The objective of the study is to investigate several lime requirement tests, including buffer methods (SMP, MM, Sikora test and the TSM buffer method), the Rothlime method and a $Ca(OH)_{2}$ titration. These tests will then be correlated to a 4-week lime incubation, using standard Irish agricultural grade lime (Government of Ireland, [1953\)](#page-12-15) to predict lime requirements. Finally, results from all these tests will be compared and correlated with the SMP buffer test to identify an alternative to the SMP test for Irish grassland mineral soils.

2 | **MATERIALS AND METHODS**

2.1 | **Materials**

Chemicals were sourced from Merck Sciences, Ireland. Ground limestone with an Irish standard specification (Government of Ireland, [1953\)](#page-12-15) was sourced from Ardfert Quarries, Co. Kerry, Ireland. pH measurements were conducted using a Jenway 3510 pH meter equipped with a glass electrode. Prior to measurements, the pH meter was calibrated at the beginning of the working day with three

2.2 | **Selection and analysis of soil samples**

sure linearity $(r^2 > .98)$.

Fifty independent soil samples were collected throughout Ireland, with the majority of soils being located in the south and southwest of the country. For each soil sample, ca. 2kg of soil was taken to a depth of 15cm from three separate digs per independent soil sample. Soils were identified with the aid of local agronomic advisors with a clay range from 7% to 38% and a water pH of less than 6.8. All the soils sampled were under permanent pasture. Once collected all samples were identified by field, farmer and coordinates.

2.3 | **Processing of soil samples**

Once received in the laboratory, all samples were inputted into an Excel file (with location coordinates), labelled (*soil 1*, *soil 2*, etc.) and dated. Soils were dried in a convection oven at 40°C until they were a constant weight before being mixed and crushed with a pestle and mortar. All soils were then sieved (<2mm) and stored in preparation for laboratory analysis.

2.4 | **Particle size determination**

The particle size distribution (PSD) method (adapted from Carter and Gregorich [\(2006](#page-12-16))) was used to analyse the soil textural composition. A 40 g soil portion was mixed with 10mL of 33% hydrogen peroxide. The mixture was heated to 90°C and stirred on a hotplate for 30min, after which a solution containing 100mL of 5% sodium hexametaphosphate and 200mL of deionized water was added while heating and stirring for an additional hour. The resulting mixture was poured onto a pre-weighed 0.063mm sieve to separate the sand fraction. This was dried at 105°C and weighed to determine the % sand.

The remaining silt and clay fraction was placed in a 1-litre graduated cylinder, filled with deionized water and agitated by manually inverting the cylinder 20 times. After 7h of settling, 25mL of soil solution was extracted in duplicate from each cylinder. These samples were transferred to pre-weighed metal dishes, heated at 105°C until completely dry and weighed to calculate the % clay content. The percentage of silt in the samples was determined by subtracting the sand and clay content from 100. The USDA soil classification triangle was then employed to categorize the soil into 1 of the 12 textural classes.

2.5 | **Soil organic matter (SOM) determination**

SOM was quantified following the method by Sikora and Moore [\(2014](#page-13-9)). Individual dry soil samples (ca. 1.5g in duplicate) were added to pre-weighed crucibles. After further drying at 105°C, the crucibles were weighed again to obtain the dry weight. They were then heated in a 550°C furnace for 8h. The % soil organic matter content was calculated by the following formula:

 $\%$ SOM = $\frac{Dry \text{ weight} - \text{Ash weight}}{Dry \text{ weight}}$

2.6 | **Cation exchange capacity (CEC)**

The CEC is defined as the total negative surface charges on a soil sample, and it can be determined indirectly by quantifying all of the acidic and basic cations on a soil sample. The CEC analysis was determined for all soil samples following a modified procedure outlined by Ross and Ketterings [\(2018\)](#page-13-10). The procedure involves determining the exchangeable cations in soil using an ammonium acetate (NH4OAc) extraction. Initially, 25.0g of soil is mixed with 125mL of 1M NH4OAc and allowed to stand for 16h. The soil is then filtered through a Buchner funnel with retentive filter paper. The soil residue is washed with $NH₄OAC$ solution four times. The soil is then washed with 95% ethanol to remove excess $NH₄OAC$ solution. The basic cations (Ca, Mg, K and Na) were then quantified from the filtrate using an Agilent 7800 inductively coupled plasma mass spectrometry (ICPMS) while the acidic cations were calculated using the exchangeable acidity values obtained with the SMP buffer. CEC, expressed as meq/100g soil, is quantified by adding the sum of the basic and acidic cations.

2.7 \vert **CaCl**₂ **pH** measurement

The CaCl₂ pH was determined using the method outlined by Eckert and Sims ([2009](#page-12-17)). A 5g of soil sample was dissolved in 10 mL of 0.01 M CaCl₂ solution. After stirring for 15 s, the mixture was left to stand for 30min before the pH was measured.

2.8 | **Buffer pH tests**

The SMP and MM buffer test was carried out using the method outlined by Eckert and Sims ([2009\)](#page-12-17), while the Sikora buffer test procedure was as described by Sikora [\(2006\)](#page-13-6), and the TSM test was described by Santanna et al. [\(2010](#page-13-8)). For each test, a standard reaction and stirring

time of 15min was applied, followed by allowing the soil– buffer solution to stand for a further 15min, after which the pH was measured.

2.9 | **Calcium hydroxide titration method**

The calcium hydroxide titrations were carried out as described by Liu, Warneke, and Jacobsen [\(2004\)](#page-12-7), Liu, Kissel, et al. (2004) (2004) using $0.022M$ Ca $(OH)_2$ solution added in known aliquots via a burette to an agitated soil water solution (1:2). After each addition, the sample was stirred for 15min before the pH was measured. The soils were titrated until reaching a final pH of 6.8.

2.10 | **Lime incubations**

The procedure for incubations was conducted following the method outlined by Liu, Warneke, and Jacobsen [\(2004\)](#page-12-7), Liu, Kissel, et al. ([2004](#page-12-8)). Incubations were carried out with Irish-grade agricultural lime (calcium carbonate) that was crushed to ensure all 100% passed a sieve of 3.35 mm, with a minimum of 35% passing a sieve of 0.15 mm. It had a neutralizing value of at least 90% and a moisture content of less than 3% (Government of Ireland, [1953](#page-12-15)). Incubations were carried out in 120 mL containers containing 40 g of soil and lime at five application rates, each in triplicate (0, 4, 8, 12 and 16 tonnes hectare¹). A 6 mm hole was drilled at the bottom of each container for drainage. Additionally, three similar holes were created in the lids of the containers to facilitate aeration. Soil moisture was maintained at field capacity using deionized water and soils were stirred three times per week. The samples were incubated at room temperature (20 \pm 4°C) for a duration of 4 weeks.

2.11 | **Statistics**

All statistics and correlations were carried out using Microsoft Excel and the statistical software tool XLSTAT. Correlations (r^2 and Pearson values) were determined via linear regression analysis and by carrying out the Pearson correlation test, respectively.

3 | **RESULTS AND DISCUSSION**

3.1 | **Properties of soils**

The LR of soils is intricately linked to their texture and composition, shaping the amount of agricultural lime needed for optimal pH adjustments to support plant growth (Goulding, [2016\)](#page-12-10). Table [1](#page-6-0) describes the various characteristics of the 50 grassland mineral soils including the sand, silt and clay content (for texture), total organic matter and the cation exchange capacity (CEC).

In total, there are five separate textures represented from the 50 soils, including sandy loam (5), silty clay loam (5), sandy clay loam (6), loam (18) and clay loam (16). Soil texture, in particular the clay content, can play a profound role in the lime requirement of soil to such an extent that they are integrated into lime prediction equations (Han et al., [2023](#page-12-18)). The Rothlime method also uses the soil texture as a variable for calculating the LR of soil. In general, soils with higher clay content, exemplified by Soil 43 (36%) and Soil 44 (38%), typically exhibit higher CEC values of 27.40 and 28.00, respectively, giving them the capacity to retain a higher concentration of cations (both acidic and basic). Consequently, these clay-rich soils might necessitate more substantial lime application to effectively raise pH owing to clay's propensity to bind with introduced lime (Parfitt et al., [2008\)](#page-13-11). There is a wide variation of clay from these soils, ranging from 7% to 38%. In contrast, soils characterized as sandy loam, such as Soil 8 (50.1% sand content) and Soil 6 (62.1% sand content), have relatively lower CEC values of 9.26 and 3.58meq/100 g, respectively. The lower CEC values in sandy/loam soils suggest a reduced capacity to retain cations and thereby maintain the desired pH. This characteristic may result in a lower LR to achieve the intended pH adjustments.

The soil organic matter (OM) content also plays a significant role in soil acidity dynamics, in particular the CEC of soil (Ramos et al., [2018](#page-13-12)). In addition, OM decomposition releases organic acids, contributing to soil acidification and consequently demanding additional lime application to neutralize acidity (Neina, [2019](#page-13-0)). The OM content varies from 5.53% to 19.46% across the 50 soils.

The variation in soils used is further evidenced by the different soil classifications including Brown Earths, Luvisols, Alluvial Gleys, Surface Water Gleys and Brown Podzols. These soils would be typical of the majority of mineral soils under agronomic activity in Ireland (O'Sullivan et al., [2018\)](#page-13-13). These classifications offer insights into the soil's broader characteristics and behaviour, which can influence lime requirements such as drainage status, OM content, fertilizer use offtakes and CEC.

3.2 | **Twenty-eight-day lime incubation study**

The analysis of lime requirements for different soils, derived from a 28-day incubation study with calcium

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carbonate, is detailed in Table [2.](#page-8-0) In literature, lime incubation studies can range from 3days (Liu et al., [2008\)](#page-12-19) to over 60days (Godsey et al., [2007\)](#page-12-20) and will depend on the liming material, for example, its neutralizing value (NV). The time for the lime incubation study described here (4weeks) was chosen based on the reaction of a range of soils to lime after 2, 4, 6 and 8weeks of incubation. Based on this study (results not shown) it was seen that the pH of soil (and the slope of the lime–reaction curve; Table [2](#page-8-0)) did not appreciably change with the additional incubation time after 4weeks. This finding agrees with other lime incubation studies (Van der Berg, [2017\)](#page-13-7).

In general, there was an identifiable linear response to additional amounts of lime with the majority of r^2 values exceeding .9, suggesting that >90% of the variance in LR can be explained by the linear regression model. The graphs (Figure [1a–d](#page-9-0)) illustrate the relationship between lime application (in tonnes per hectare) and soil pH for four random soils.

In order to reach a target pH of 6.3 (recommended for grassland, Teagasc.ie [\(2020](#page-13-14))) the lime requirement varied from 0 tonnes of lime per hectare (for Soils 40 and 45) to 20.4 tonnes for soil 34. One of the main factors determining the lime requirement according to this incubation study is not the starting soil pH, but the slope of the lime–response curve (a lower slope value illustrates a slower response), as evidenced by soils 12 ($m = 0.0311$) and 13 ($m = 0.0380$), both had the same starting pH of 6.27 but required 3.15 and 1.18 tonnes of lime per hectare, respectively, to reach a pH of 6.3. Table [1](#page-6-0) details the differences between these two soils, with Soil 12 having over 3.5% more clay than Soil 13 (both loam). However, Soil 12 had over three times the amount of OM at 19.26% and was designated a gley soil based on water retention being a dominant feature of its formation. Soils with higher OM tend to contain acidic organic compounds, potentially necessitating more lime for pH adjustment (Kumar et al., [2012](#page-12-4); Sims, [1996\)](#page-13-15).

Table [2](#page-8-0) also shows how soil textures and CEC influence LR; for example, Soil 44, which is rich in clay (38%), requires a lime addition of 21.1t/ha to reach the target pH of 6.3, highlighting the influence of soil texture on lime demand (Stiles, [2004\)](#page-13-16), while Soil 38 with the highest CEC at 34.30 requires 20.74 tonnes of lime per hectare to achieve the target pH of 6.3, potentially caused by its higher clay content (34%; OM of 9.2%), indicating the complex interaction among CEC, texture, OM and LR (Goulding, [2016\)](#page-12-10). The combination of these factors is crucial for accurate lime application. These results highlight the necessity of considering OM, soil textures and CEC collectively when determining LRs for specific soils, exemplifying the difficulty involved in soil pH management (Bönecke et al., [2021\)](#page-12-21).

TABLE 1 General properties of 50 grassland mineral soils.

TABLE 1 (Continued)

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3.3 | **Correlation with the lime incubation study**

Table [3](#page-10-0) examines the correlations between the various lime requirement methods and values obtained from a 28-day lime incubation study for all soils and soils in lower (7% to 23%) and higher clay (24% to 38%) categories. Table [3](#page-10-0) presents Pearson correlation coefficients (Pearson correlation) and coefficients of determination $(r^2 \text{ values})$ for each method, along with corresponding *p*-values and correction equations as predicted by linear regression.

For all methods, apart from the SMP buffer method, there is a dis-improvement in r^2 value as the clay content increases to the higher category (7%–23% and 24%–38%); this is most stark for the TSM buffer that goes from an r^2 value of .488 to .284 in the higher clay amounts. The SMP buffer bucks this trend with a slight improvement in *r* 2 from .442 to .514 for the higher clay soils.

The clay content of the soils has been shown to have a significant impact on the lime requirement according to a lime incubation study (Makepeace et al., [2022](#page-12-22)). The clay components of soils will retain multi-charged cations such as Fe and Al, in the interlayer spaces of phyllosilicates and will have a profound effect on both the LR of these soils and their interaction with other cations and anions (Kumari & Mohan, [2021](#page-12-23)). The SMP buffer contains four separate chemicals that contribute to its buffering

capacity – triethanolamine, para-nitrophenol, potassium chromate and calcium acetate. Sikora details the individual and sum of these components to act as a soil pH buffer, as a function of acidity neutralized in an effort to find an alternative buffer (Sikora, [2006\)](#page-13-6). Para-nitrophenol in particular with a pKa of 7.5 is essential to the buffering capacity of the SMP buffer along with other well-known buffers such as the Adams–Evans and Woodruff buffers (Hoskins & Erich, [2008\)](#page-12-12). Both the TSM and Sikora buffers contain imidazole and MES to replace para-nitrophenol and potassium chromate, respectively, as described by Sikora. McLean et al. [\(1966\)](#page-12-24) found that the SMP buffer was more suitable for soils requiring more than 4.5 tonnes of lime per hectare and having a pH lower than 5.8. A similar finding was found with South African soils where soils requiring less than 4 tonnes of lime per hectare had an *r* 2 value of .28 when correlated with an incubation experiment, but this r^2 value rose to .98 for soils requiring over 4 tonnes per hectare of lime (Van der Berg, [2017](#page-13-7)).

The overall r^2 value between the SMP pH and LR according to the incubation study was .497 (a Pearson value of −.705; the minus sign is a result of soils with a lower pH requiring additional lime). This r^2 value was slightly lower than the .6 value obtained by Godsey et al. [\(2007\)](#page-12-20) for 97 Ohio soil samples, however, the target pH here was 6.8; in addition, the majority of these soils only required between 2 and 6 tonnes of lime per hectare in comparison to the

Soil number Incubation equation

Soil 1 $y=0.0474x+5.719$ Soil 2 $y=0.0569x+5.538$ Soil 3 $y=0.0397x+5.965$ Soil 4 $y=0.0405x+6.096$ Soil 5 $y=0.0449x+5.659$ Soil 6 $y=0.0765x+5.634$ Soil 7 $y=0.1116x+5.289$ Soil 8 $y=0.102x+4.832$ Soil 9 $y=0.0407x+5.799$ Soil 10 $y=0.0768x+5.455$ Soil 11 $y=0.0472x+6.150$ Soil 12 $y=0.0311x+6.302$ Soil 13 $y=0.038x+6.355$ Soil 14 $y=0.0351x+6.192$ Soil 15 $y=0.0297x+6.141$ Soil 16 $y=0.0345x+6.187$ Soil 17 $y=0.039x+5.971$ Soil 18 $y=0.0715x+6.139$ Soil 19 $y=0.0991x+5.158$ Soil 20 $y=0.1025x+5.4027$ Soil 21 $y=0.0632x+5.184$ Soil 22 $y=0.0724x+5.619$ Soil 23 $y=0.0824x+5.750$ Soil 24 $y=0.1137x+5.358$ Soil 25 $y=0.0772x+6.260$ Soil 26 $y=0.0399x+6.106$ Soil 27 $y=0.0751x+4.999$ Soil 28 $y=0.046x+6.245$ Soil 29 $y=0.0301x+5.991$ Soil 30 $y=0.0772x+6.189$ Soil 31 $y=0.0428x+5.817$ Soil 32 $y=0.0298x+6.064$ Soil 33 $y=0.0796x+5.251$ Soil 34 $y=0.0678x+4.915$ Soil 35 $y=0.0789x+5.299$ Soil 36 $y=0.0756x+5.785$ Soil 37 $y=0.032x+5.989$ Soil 38 $y=0.0309x+5.659$ Soil 39 $y=0.0513x+5.890$ Soil 40 $y=0.0467x+6.508$

Soil 41 $y=0.0568x+6.210$.94 6.12 6.12 1.58 Soil 42 *y*=0.0711*x*+5.218 1.00 5.20 15.22

TABLE 2 (Continued)

Note: y = The lime response in tonnes ha⁻¹, while *x* is the pH measured following a 0.02 M CaCl₂ extraction.

FIGURE 1 (a–d) Scatter graphs representing the relationship between lime application and soil pH.

wide LRs displayed by Table [2](#page-8-0). The same study also investigated the correlation between the calcium hydroxide titration method and the lime incubation study in two trials: 16 soils in a lab incubation trial and 12 soils in a field incubation trial, with the r^2 value moving from .95 for the lab trial to .76 for the field trial. In another field incubation study across 14 sites (but with a total *n* value of 437), the r^2 values for MM, Sikora and SMP decreased from .28 to .18 and .12, respectively (Pagani & Mallarino, [2012\)](#page-13-17), highlighting the additional variability in a field incubation trial.

Using seven soils all with medium levels of OM (4.3 to 7.1), Hoskins and Erich [\(2008\)](#page-12-12) saw r^2 values from .87

to .96 comparing the SMP buffer to the lime incubation study. The increase in r^2 values was seen when the LR pH was increased from 6.0 to 7.0. In the same study, the MM buffer had slightly better r^2 values of .91 to .96—again the increases see when the LR pH was raised from 6.0 to 7.0. In a similar lime incubation study conducted over 3weeks with 22 soils from Pennsylvania in the United States, the opposite trend was seen with the r^2 values when the LR requirement was raised from 6.5 to 7.0 with the SMP buffer having values of .87 and .82 while the MM had values of .92 and .87, respectively (Wolf et al., [2008\)](#page-13-18). Again, these improved correlations may be explained by the textures of the soil as well as its OM content, with the clay content

varying from 16% to 26% and the OM varying from 2.2% to 4.8%.

The Rothlime method provided the strongest correla tion in the lower clay category (r^2 value of .576), however, this was reduced to .379 in the higher clay category. The Rothlime method was designed for simple on-farm calcu lations and thus uses rounded figures from broad variable inputs, for example, arable versus grassland, along with five types of soil from peats to sand. This ease-of-use ap proach (although it still requires the inputters to have a water–soil pH) thus will affect accuracy and it has been shown to overestimate the LR, particularly with more acidic soils (Boyko et al., [2023\)](#page-12-25).

3.4 | **Correlations with the SMP buffer**

Table [4](#page-11-0) describes the correlations between the SMP buffer method and other LR determination methods. The corre lation is evaluated for different clay content ranges, low clay (7%–23%) and high clay (24%–38%), which empha sizes the effect of this factor on lime prediction. The goal of these correlations was to find an alternative LR method to the SMP buffer method for Irish grassland mineral soils. The Ca(OH)₂ titration method had the highest r^2 (.816) values across all soils with little difference seen between the two clay categories (.882 for low clay and .848 for high clay soils), while the Sikora buffer method r^2 values improved from .496 to .724 from the low to high clay soils. Of the buffer methods, the MM buffer had the highest r^2 value of .763, again with little difference in correlations from low to high clay soils (.800 to .771). Liu, Warneke, and Jacobsen [\(2004](#page-12-7)), Liu, Kissel, et al. ([2004](#page-12-8)) carried out a study to establish the equilibrium pH of saturated $Ca(OH)$ ₂ solution with 17 diverse soils and assess the titration procedure's ability to predict LR compared with standard incubation methods. The findings indicated that LR estimates were accurate when a 30-min equilibration time between base additions was employed with r^2 values of .99.

In an interlaboratory trial, Tunney et al. [\(2010](#page-13-19)) found strong agreements across 57 mineral grassland soils be tween the SMP buffer pH and Sikora, MM and the $\rm Ca(OH)_2$ titration pH, with Pearson values of .98, .96 and .97, re spectively. Pearson values for this study were quite simi lar .822, .873 and −.903 for the same techniques. Tunney's study, however, did not calibrate the various methods against a lime incubation trial (Table [2\)](#page-8-0). Another study on arable soils in Iowa, USA ($n = 481$), found $r²$ values correlating the SMP buffer pH to Sikora buffer pH and the original Mehlich buffer pH of 0.85 and 0.72, respectively (Pagani & Mallarino, [2012](#page-13-17)). After calibrating both the SMP and MM buffer method against a lime incubation study,

Hoskins and Erich found a significant difference between their LR predictive values, with the SMP buffer showing a higher bias for soils with a low LR, while MM biased towards soils with a higher LR; however, these differences were found to be within the limit of resolution according to local testing guidelines (Hoskins & Erich, [2008\)](#page-12-12).

In Ireland, soils tend to have a higher OM content as a result of higher rainfall and the fact that almost 80% of the area under grassland can be considered permanent grassland owing to not having been ploughed in a num ber of years (Rath & Peel, [2022;](#page-13-20) Tunney et al., [2010\)](#page-13-19). The level of OM will have a significant influence on the buffering capacity of the soil and ultimately the LR of the soil (Kumar et al., [2012](#page-12-4)). The higher OM levels are often as sociated with soils with a higher clay content caused by the water retention properties of this fine-earth material, thus the impact on the buffering capacity may be synergis tic. The range of soils used here appears to have a much wider range of % OM and clay content and thus LR (as seen from the incubation study; Table [2\)](#page-8-0) than currently seen in similar studies across literature. It is likely this di versity of traits had an impact on the predictive powers of these tests. This impact is seen by the superior correla tions between the SMP buffer method and other LR tests (Table 4), that is, not seen in the comparisons with the individual LR tests and the lime incubation study (Table [3](#page-10-0)).

4 | **CONCLUSION**

The SMP buffer test, despite the need to find a suitable re placement, was the most accurate predictor of LR accord ing to a lime incubation study for Irish mineral grassland soils. Any choice of alternative methods must consider a number of factors, as well as accuracy, and include ease of use, throughput and safety for technicians and disposal. The buffer methods allow for a high throughput of sam ples as a result of their relatively quick reaction time. After the SMP method, of the other buffer methods described, the MM was the next best predictor of LR based on the in cubation study; however, the accuracy of the MM was re duced in the higher clay category. The MM buffer was also the closest alternative buffer method to the SMP buffer method in terms of correlations (after the $Ca(OH)_{2}$ titration method). Finally, this study highlighted the impact of soils with a higher OM and clay contents on the accuracy of current methods for determining LRs.

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CONFLICT OF INTEREST STATEMENT

All authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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