Article

Predicting the Base Neutralization Capacity of Soils Based on Texture, Organic Carbon and Initial pH: An Opportunity to Adjust Common Liming Recommendation Approaches to Specific Management and Climate Conditions

Joerg Ruehlmann [1,*], Eric Bönecke [1], Robin Gebbers [2], Felix Gerlach [3], Charlotte Kling [4], Katrin Lück [3], Swen Meyer [5], Anne Nagel [6], Stefan Palme [4], Golo Philipp [7], Dirk Scheibe [8], Ingmar Schröter [6], Sebastian Vogel [9] and Eckart Kramer [6]

[1] Leibniz-Institute of Vegetable and Ornamental Crops, Theodor-Echtermeyer-Weg 1, 14947 Grossbeeren, Germany; boenecke@igzev.de

[2] Institute of Agricultural and Nutritional Sciences, Martin-Luther University Halle-Wittenberg, Karl-Freiherr-von-Fritsch-Straße 4, 06120 Halle (Saale), Germany; robin.gebbers@landw.uni-halle.de

[3] Land- und Forstwirtschaft Komturei Lietzen GmbH & Co. KG, Lietzen Nord 38, 15306 Lietzen, Germany; felix.gerlach@komturei-lietzen.de (F.G.)

[4] Gut Wilmersdorf GbR, Wilmersdorfer Str. 23, OT Wilmersdorf, 16278 Angermünde, Germany; kling@gut-wilmersdorf.de (C.K.)

[5] Faculty of Agricultural and Environmental Sciences, University of Rostock, Justus-von-Liebig-Weg 6, 18059 Rostock, Germany; s.meyer@uni-rostock.de

[6] Landscape Management and Nature Conservation, Eberswalde University for Sustainable Development, Schicklerstraße 5, 16225 Eberswalde, Germany; ischroeter@hnee.de (I.S.); eckart.kramer@hnee.de (E.K.)

[7] Landwirtschaft Petra Philipp, Berliner Str. 36B, OT Booßen, 15234 Frankfurt/O., Germany; golo-philipp@t-online.de

[8] LAB Agricultural Consultation of Agricultural Unions Brandenburg GmbH, Eberswalder Str. 84H, 15374 Müncheberg, Germany; scheibe@lab-agrarberatung.de

[9] Leibniz Institute for Agricultural Engineering and Bioeconomy, Agromechatronics, Max-Eyth-Allee 100, 14469 Potsdam, Germany; svogel@atb-potsdam.de

* Correspondence: ruehlmann@igzev.de

Abstract: Liming is an effective measure to increase the soil pH and to counterbalance soil acidification. Therefore, the liming recommendations (LRs) for agricultural practice consider two aspects: changing the initial pH to the desired pH and compensating for all pH decreases taking place within the liming interval. The separation of these aspects is essential to optimize LRs and to minimize lime losses to the environment. Therefore, we developed a pedotransfer function (PTF) to calculate the lime demand to change the initial pH to the desired pH and compared the results with the LRs for agricultural practice. Applying this PTF to a set of 126 soil samples that were analyzed for base neutralization capacity could explain approximately 78% of the variability in the pH changes after the addition of different amounts of $Ca(OH)_2$. Consequently, the lime demand to change the initial pH to the desired pH increased by approximately one-sixth compared to the lime demand proposed by the liming recommendation scheme, which is commonly used in Germany. From the numerical difference between the lime demand according to the LRs and the PTF, we calculated the annual acidification rates based on the soil texture, organic matter content and initial pH. Decoupling the abovementioned two aspects of LRs might be helpful to optimize the LRs by adapting to different regions, diverse management strategies and a changing climate.

Keywords: acidification; organic carbon; lime; pedotransfer function; pH; soil; texture

1. Introduction

Liming has been well known to be an important agricultural measure since the roman times [1]. Thus, lime fertilization recommendation schemes in many countries have

been developed over decades and are well established in particular regions, e.g., in Germany, the Netherlands, Scotland, Sweden, the United Kingdom and the United States (California) [2–8]. In all countries, the corresponding look-up tables determine the lime requirement that is necessary to change a currently measured soil pH to an optimum pH value, which depends on the estimates of the soil texture (e.g., by hand texturing) and soil organic matter (SOM) content (e.g., by loss on ignition). Here, we refer mainly to the recommendation scheme that is commonly used in Germany. This scheme was applied to classify the results of the recent German national soil survey: only 35% of the arable soils and 24% of the grassland soils were in the optimum pH range [9]. In contrast, approximately 42% of the mineral soils under arable farming and 57% of the grassland soils had too low pH values. The pH-BB project "Precision liming in Brandenburg" (http://ph-bb.com, accessed on 30 August 2023) was initiated to improve the lime management and the first results were provided [10–14]. All of these studies refer to the lime fertilization recommendation schema provided by the Association of German Agricultural Investigation and Research Institutions (VDLUFA). Over the last 40 years, the VDLUFA look-up table system has served the needs of lime fertilization in agricultural practice [12]. It is based on 30 years of fertilization experiments, which have investigated the influences of the soil pH (estimated in 0.01 molar $CaCl_2$ solution), the soil texture and the SOM content on the optimum lime rate [15,16].

The recommended amount of lime has to fulfill two tasks:

Task A Change the initial pH (pH_0) to the desired pH (pH_{target}), which depends on the soil's pH buffer capacity to resist pH changes upon the addition of H^+ or OH^- ions [15].

Task B Compensate for all pH changes taking place within the liming interval—typically a crop rotation over three to four years—caused by acidification processes such as plant nutrient uptake, calcium leaching from soils and the mineralization of organic matter as well as acidic atmospheric deposition [17].

Whereas the soil buffer capacity is mainly affected by the clay content, mineralogy and SOM content [18], the intensity of soil acidification processes is modified by the management of fertilization, cropping, by the environmental conditions and by climate and acidic atmospheric deposition. The management- and climate-dependent annual acidification rates (ARs) vary globally in a wide range. We express hereafter the ARs in lime equivalents to compensate for the annual acidification (kg CaO ha^{-1} yr^{-1}), whereas the AR varies globally between 0 and approximately 850 kg of CaO ha^{-1} yr^{-1} [1,19–22]. These variations are mainly affected by fertilizer additions, the Ca removal by crops, leaching via drainage and the soil pH [19]. The ARs differentiate according to the soil texture group; the land use and annual precipitation [23] are presented in Table 1.

Table 1. Lime equivalents (kg CaO ha^{-1} yr^{-1}) to compensate acidification due to neutralization and leaching as dependent on soil texture, land use and annual precipitation (after [23]).

Soil Texture	Land Use	Lime Equivalents to Compensate Acidification (kg CaO ha^{-1} yr^{-1})		
		Annual Precipitation		
		<600 mm	600–750 mm	>750 mm
sandy	Arable land	300	400	500
	Grass land	150	250	350
loamy	Arable land	400	500	600
	Grass land	200	300	400
clayey	Arable land	500	600	700
	Grass land	250	350	450

Regarding nitrogen fertilization, compared to previous predictions, an approximate doubling of the AR was reported, reflecting the greater quantities of inorganic N fertilizer applied to agricultural land [1]. The following lime equivalents to compensate for acidification were given by Goulding [17]:

- 10 kg acid deposition ammonium-N: 56 kg ha^{-1} CaO;
- 10 kg fertilizer ammonium-N: 40 kg ha^{-1} CaO;
- 10 kg fertilizer urea-N: 11 kg ha^{-1} CaO;
- 10 kg elemental S: 18 kg ha^{-1} CaO.

The lime losses via crop Ca offtakes are likely to have been relatively small in comparison with the acidifying fertilizer inputs and leaching losses with the following crop-specific values [24]:

- Potatoes yielding 40 t ha^{-1}: 10 kg ha^{-1} CaO;
- Cereal grain plus straw yielding 7 t ha^{-1}: 30 kg ha^{-1} CaO;
- Grass (silage) yielding 40 t ha^{-1}: 65 kg ha^{-1} CaO.

Lime losses via leaching occur in areas and periods where rainfall exceeds evapotranspiration, where the annual ARs vary from approximately 135 to 210 kg CaO ha^{-1} [21,25]. Additionally, the ARs are positively correlated to the added lime amount and, consequently, the higher the soil pH, the more the ARs decrease exponentially during the decrement of the soil pH [20].

When the rules of lime fertilization recommendations were created, as the VDLUFA approach used herein, both the abovementioned Tasks A and B should be considered. In particular, it is important to adapt the respective lime fertilization recommendations to the regional climate and management conditions to accomplish Task B. Decoupling the lime demand for both tasks might be essential to adapt the LR to the changing climate and management conditions. Unfortunately, these two aspects cannot be separated from the VDLUFA look-up tables. However, Vogel et al. [13] published the first approach, which compares the outputs of their base neutralizing capacity (BNC) investigations with the relatively rough recommendations of the VDLUFA look-up tables to exclusively predict the direct pH changes per unit base application. Furthermore, these look-up tables consider the three pH-relevant soil parameters, pH, texture and class-based SOM. This system was adapted to the requirements of precision farming by transferring it into a continuous, stepless approach [12], hereinafter called the "VDLUFA approach".

Hence, the objective of the present paper is to separate the VDLUFA-based calculated lime requirement into the proportions that are necessary to (i) change the initial pH to the target pH (Task A) and to (ii) compensate for the acidification processes that take place during the liming interval (Task B). For Task A, we will generate a pedotransfer function (PTF) that quantifies the pH change through the lime application as a continuous function of the initial soil pH as well as of its texture and soil organic carbon (SOC) content. For that, we will use data from laboratory experiments published by Vogel et al. [13]. They measured the soil pH change after Ca(OH)$_2$ application using the BNC method. We call this PTF hereinafter the "BNC approach". The remaining proportion of the lime demand needed to fulfill Task B as calculated using the VDLUFA approach will then be discussed in relation to the annual lime loss rates as given in the literature.

2. Materials and Methods

2.1. Site Description

In this contribution, we refer to agricultural fields in a quaternary landscape of the northeast German Plain that were already described in detail by Vogel et al. [13,14]. The fields are part of three farms: Farm I, Lat: 52.376035, Long: 14.461919; Farm II, Lat: 53.110092, Long: 13.909461; and Farm III, Lat: 52.483766, Long: 14.333079 of the federal state of Brandenburg (Germany). A total of 126 soil samples were taken and analyzed for soil texture, SOC and pH (Figure 1, Table 2).
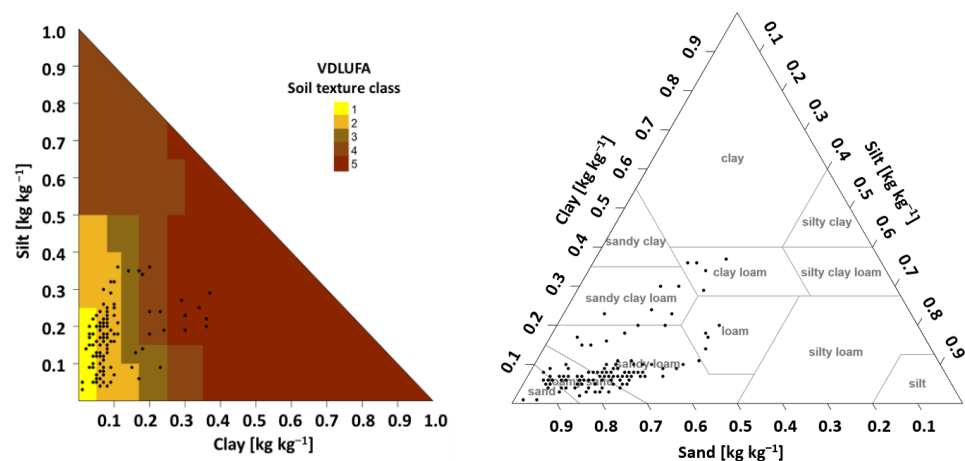
Figure 1. Clay, silt and sand contents (black dots) of the used soil samples as classified according to the German VDLUFA classification [16] (**left**) and the USDA system [26] (**right**).

Table 2. MPD, SOC and initial pH values of the five test fields of the three farms.

	Farm I	Farm II	Farm III
MPD [10^{-3} m]			
Min	0.01	0.05	0.01
Max	0.21	0.15	0.29
SD	0.05	0.03	0.09
SOC (g kg^{-1})			
Min	4.40	6.40	5.75
Max	32.30	12.60	26.2
SD	5.11	1.25	6.66
Initial pH			
Min	5.24	5.71	4.51
Max	7.55	7.32	7.24
SD	0.49	0.34	0.77

Because the geological maps for the abovementioned region of Brandenburg are only available in resolutions of 1:100,000 and 1:25,000 [27], they can be used solely for an overview but not to characterize the geological substrates that are present exactly on the coordinates of the 126 soil samples. However, in this region, fine- to coarse-grained sands are mainly melt-water deposits, whereas loamy and clayey soils are deposits of creek and river valleys (flood plains) or ground moraine formations (tills and boulder clays) [27].

To compile soil texture into one variable, the clay, silt and sand fractions were aggregated to the mean particle diameter (MPD) according to Shirazi et al. [28] (Table 2).

2.2. Soil Analyses

The base buffering was determined as described by Vogel et al. [13]. From each of the 126 soil samples, 6 subsamples of 25 g were taken. Different concentration levels of Ca(OH)$_2$ were added to five of these subsamples, namely 0.25, 0.5, 1.25, 2.5 and 5 mmol$_c$ (25 g soil)$^{-1}$, while the sixth sample was just mixed with deionized water (pH$_0$). The pH values were measured with a glass electrode (WTW SenTix® 81, Xylem Analytics, Weilheim, Germany) in the supernatant solution after 18 h of mechanical shaking. SOC was predicted via elementary analysis using the dry combustion method [29]. The particle distribution of the fraction <2 mm was determined via wet sieving and sedimentation after removal of the organic matter using hydrogen peroxide (H$_2$O$_2$) and dispersion with 0.2 N sodium pyrophosphate (Na$_4$P$_2$O$_7$) after removing inorganic carbon with hydrochloric acid according to the German standard in soil science [30]. The ranges of the three particle size fractions are clay (0–0.002 × 10^{-3} m), silt (0.002–0.063 × 10^{-3} m) and sand (0.063–2 × 10^{-3} m).

Our "BNC dataset" contains the results of 630 soil samples treated with Ca(OH)$_2$ and 126 control soil samples mixed with deionized water, which were divided into a calibration dataset (two-thirds) and a validation dataset (one-third) using a random number generator.

2.3. Creating the BNC Approach

The lime amount, as recommended by the VDLUFA look-up table system, depends on the initial soil pH before CaO application, the soil texture (clay content) and the SOM content [12], while the BNC approach uses these three variables as a lime requirement predictor, too.

From Vogel et al. [13], it is known that the soil pH reacts with a saturation effect to the application of increasing quantities of Ca(OH)$_2$ and that an exponential model is commonly used in soil science to describe such a relationship [31,32]. The curvature of this exponential model depends on the difference (ΔpH) between a given initial pH (pH$_0$) and the maximum pH (pH$_{max}$), which is the pH of the saturated base solution.

The functional dependency of ΔpH on the soil texture cannot be derived from the literature because texture is given in this context in a non-scaled form but classified, e.g., as sand, loam and clay soil [17]. Therefore, we applied the MPD as an aggregated soil texture measure also on the BNC approach, as used in the VDLUFA approach [12].

Consequently, pH$_0$ and pH$_{max}$ as well as the SOC and the MPD are considered in the BNC approach to predict the soil pH changes after base application, whereby the ΔpH per unit of applied base decreases exponentially if the difference in pH$_{max}$ − pH$_0$ decreases. We parameterized and validated the BNC approach using the corresponding parts of the BNC dataset.

2.4. Comparison of the CaO Amounts Necessary to Change pH$_0$ to pH$_{target}$ as Calculated Using Both the VDLUFA and the BNC Approaches

To test the outputs of both the VDLUFA and the BNC approaches, we created an independent test dataset covering the texture, SOC and pH$_0$ ranges of the BNC dataset. To obtain valid regression results, we divided the ranges of input parameters in the following steps: SOC: 5, 10, 20 and 30 (g kg^{-1}); pH$_0$: 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0 and 7.5; and MPD: 0.005, 0.017, 0.042, 0.091 and 0.203 (10^{-3} m). The MPD values correspond to the MPDs of the five VDLUFA mineral soil texture classes [12]. The results of the 160 combinations were used to calculate the CaO amounts that are required to change the pH from the pH$_0$ to the pH$_{target}$. Then, we applied the BNC approach to calculate the Ca(OH)$_2$ amount necessary to obtain the same pH changes as calculated using the VDLUFA approach [12]. We fitted this Ca(OH)$_2$ demand via least square optimization between the pH$_{target}$ values as predicted using both approaches, the VDLUFA and the BNC. Finally, we converted 1 mmol$_c$ Ca(OH)$_2$ (25 g soil)$^{-1}$ to 1 Mg CaO (ha^{-1} × 0.1 m^{-1}) stoichiometrically by applying Factor 1.12 [33]. Multiplying this factor by the bulk density (1.5 mg m^{-3}) and the topsoil depth (3 × 0.1 m) gives the final conversion factor, f$_c$ = 5.05.

2.5. Statistics

The above-mentioned Ca(OH)$_2$ demand—as calculated using the BNC approach necessary to obtain the same pH changes calculated using the VDLUFA approach—was predicted using the GRG least square optimization method of the Solver Add-In of Microsoft® Excel® LTSC MSO (16.0.14332.20579) (Microsoft, Redmond, WA, USA). The coefficient of determination R^2 (Equation (1)) and the root mean square error (*RMSE*) (Equation (2)) were used as statistical measures to validate the quality of the predictions, with the R^2 calculated according to Kvalseth [34]:

$$R^2 = 1 - \frac{\sum_{i=1}^{n} (y - \hat{y})^2}{\sum_{i=1}^{n} (y - \overline{y})^2} \tag{1}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} (y - \hat{y})^2}{n}} \tag{2}$$

where $\hat{y}$ is the fitted value of the observed y, $\bar{y}$ is the arithmetic mean of the sample, and n is the number of observations.

3. Results and Discussion

Our preliminary investigations to create the BNC approach showed that we have to apply a nonlinear function to describe the relationship between the pH change (ΔpH) per unit of hydroxide application when the pH_0 increases and apply a linear function to consider both the texture and the SOC effect (Equation (3)):

$$\Delta pH = (pH_{max} - pH_0) \times (1 - \exp(-\alpha \times Ca(OH)_2)) + \beta \times MPD - \gamma \times SOC \quad (3)$$

where $pH_{max} = 12.45$ according to the pH of saturated calcium hydroxide [35]; $Ca(OH)_2$ ($mmol_c$ $(25\ g\ soil)^{-1}$); MPD (10^{-3} m); SOC (g kg^{-1}); and α, β and γ are dimensionless fitting parameters.

This mathematical model reflects the following well-known relationships where the ΔpH per unit of applied base:

- Decreases exponentially if the $pH_{max} - pH_0$ decreases because of the abovementioned saturation effect [31,32];

- Decreases if the SOC increases because the buffer capacity is linearly related to the SOC [36];
- Increases if the MPD increases because the buffer capacity is linearly related to the clay content [18] (which is inversely related to the MPD).

To parameterize the BNC approach, we applied Equation (3) to the calibration dataset. The predicted values of the three dimensionless fitting parameters are $\alpha = 0.685$ (0.017), $\beta = 2.642$ (0.211) and $\gamma = 0.054$ (0.004), with the standard errors in parentheses. The regression between the measured and predicted ΔpH has $R^2 = 0.781$ and $RMSE = 0.19$. Thereafter, we applied the parameterized BNC approach to the validation dataset, resulting in $R^2 = 0.778$ and $RMSE = 0.25$. The results of both the model calibration and validation are separately visualized for the three test sites (Figure 2).

The application of different $Ca(OH)_2$ concentrations led to pH changes between 0.1 and 7.6 pH units. For the calibration, the mathematical model (Equation (3)) was able to explain approximately 94% of the variability in the pH changes after $Ca(OH)_2$ addition. Also, the slopes of the regression functions for the predicted vs. observed pH changes (Figure 1) were close to 1. The intercepts were close to zero, which implies that the systematic errors in shift and scale are negligible. When the model was applied to the validation data set, the model performance indices are in the same range. From these results, it can be concluded that the variables pH_0, MPD and SOC are the main predictors of pH changes after $Ca(OH)_2$ addition. Considering that we used soils of different origin (compare Section 2.1), the effects of different geological substrates and the resulting differences in the mineral-specific buffer capacities [37,38] seem to be less effective within the mentioned soil selection compared to the three factors included in the BNC approach. The test dataset described in Section 2.4 was used to compare the outputs of both the VDLUFA and the BNC approaches. The total test dataset was first used to calculate the CaO amounts necessary to change the given pH_0 values to the pH_{target} as calculated using the VDLUFA approach. Second, we excluded 70 data points from further calculations, where these calculated CaO amounts were negative because $pH_0 > pH_{target}$. Then, we applied the BNC approach to the remaining 90 data points to calculate the $Ca(OH)_2$ amount necessary to obtain the same pH changes as calculated using the VDLUFA approach.
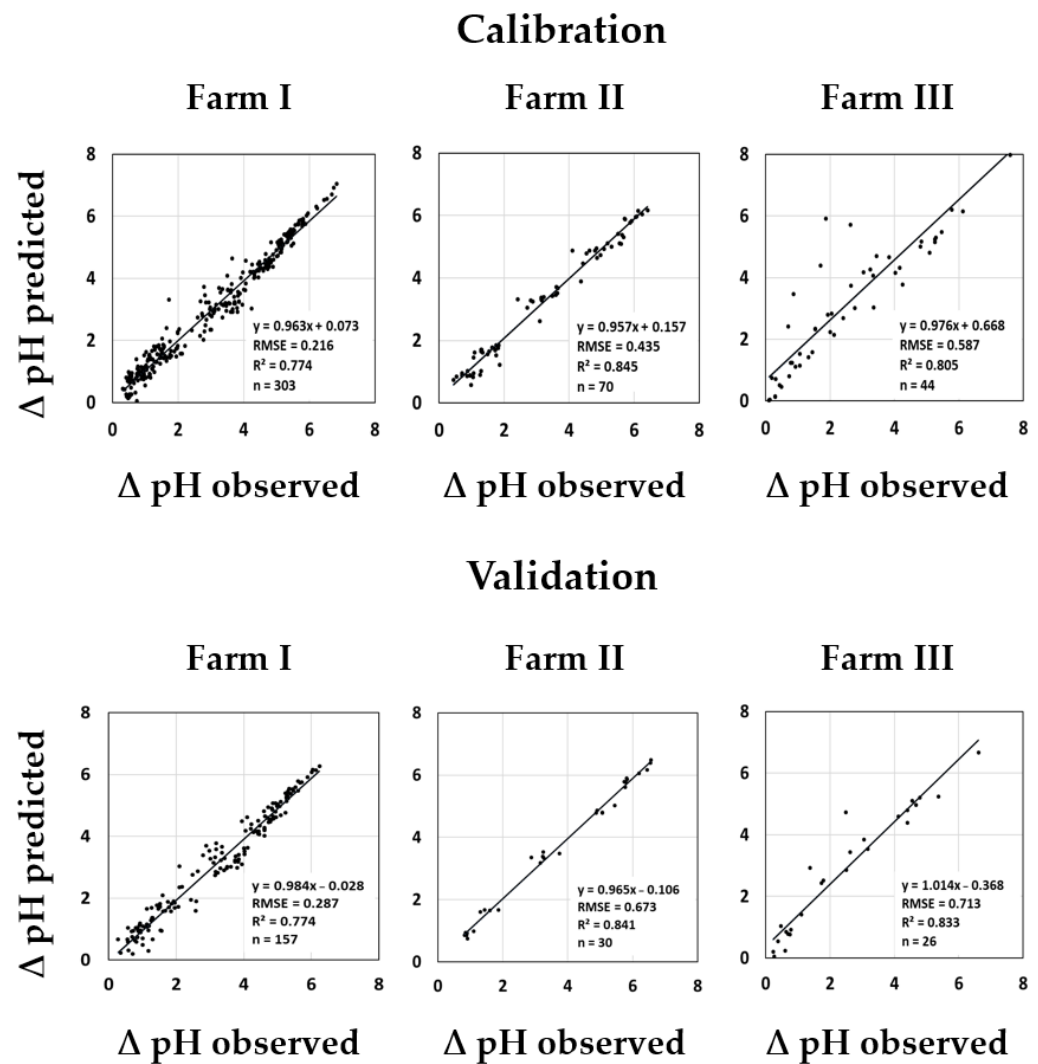
Figure 2. Predicted pH changes after $Ca(OH)_2$ addition vs. pH changes observed according to Equation (3) as applied to the calibration (**top**) and validation datasets (**bottom**) and as separately visualized for the three test sites.

As mentioned in the introduction section, the LR for farmers, e.g., the VDLUFA approach, considers both the lime amount required to change the pH_0 to pH_{target} (Task A) and the lime amount that is necessary to compensate for the pH changes during one liming interval, e.g., 3 years (Task B). Consequently, the liming recommendation according to the VDLUFA should generally show higher CaO demands for the abovementioned pH change. In Figure 3, the results of applying both the BNC and the VDLUFA approaches to the created test dataset are shown separately for the four SOC levels. The required CaO amounts calculated using the BNC approach (CaO_{BNC}) increases when the SOC also increases. This is because the soil's buffer capacity is linearly related to the SOC [36]. The CaO amounts calculated using the VDLUFA approach (CaO_{VDLUFA}) showed an inverse behavior as exemplified for a clayey soil (MPD = 0.005) and a loamy (MPD = 0.017) soil. This happens because the SOM counteracts Al toxicity by forming complexes with the Al ions [39,40]. This results in lower VDLUFA pH_{target} values and accordingly lower recommended lime amounts.

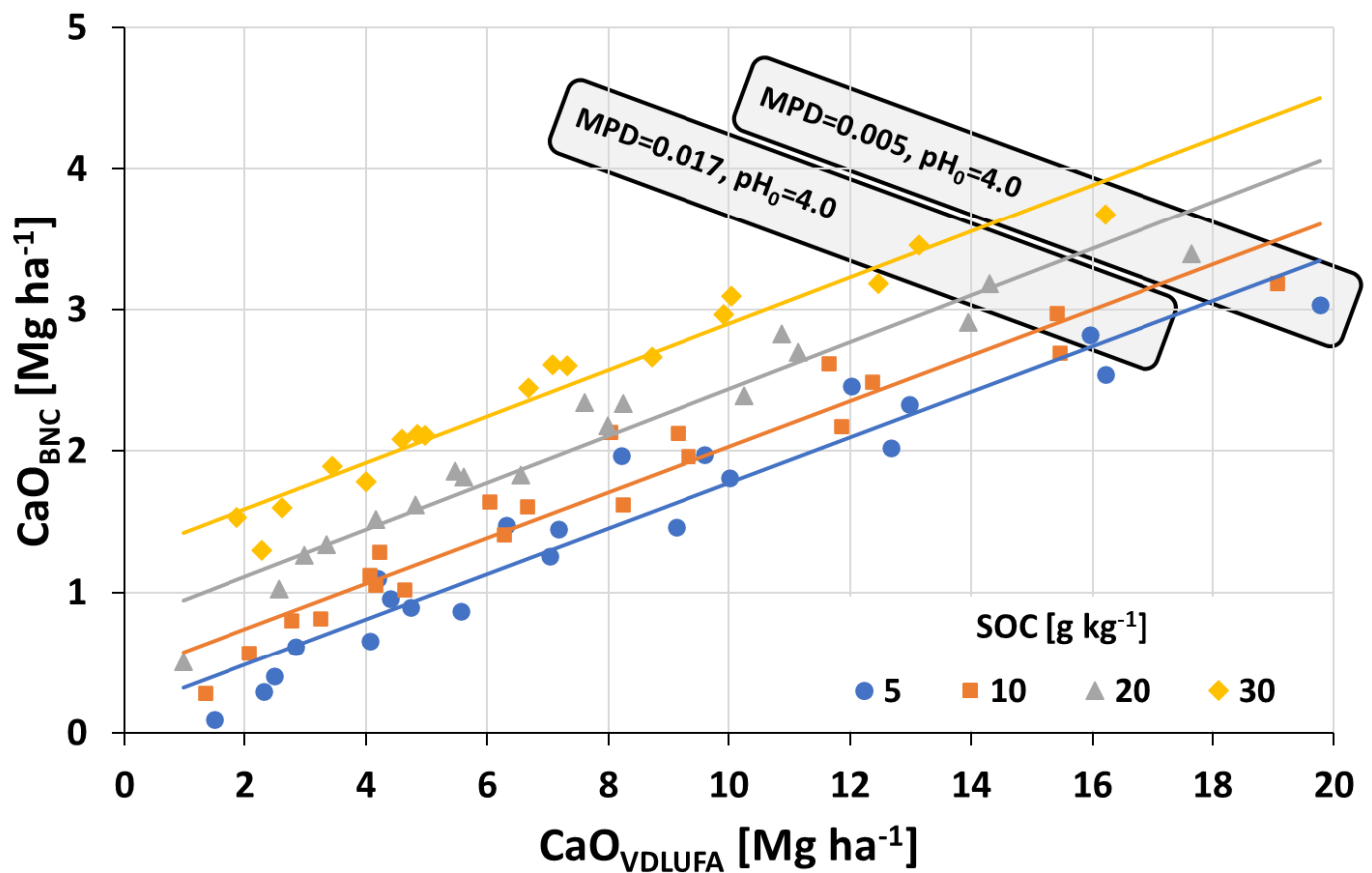**Figure 3.** Lime amounts required to change the pH from pH_0 to pH_{target} as calculated using the BNC (CaO_{BNC}) and the VDLUFA (CaO_{VDLUFA}) approaches (dots), respectively, and grouped based on SOC levels as mentioned in Section 2.4. The specifications of corresponding linear regression functions (lines) are given below. Within the gray shaded fields, two different mean particle diameter (MPD) groups with the same initial pH (pH_0) value (see Section 2.4) are indicated. Linear regression lines are colored corresponding to the SOC level with following specifications: SOC = 5 g kg^{-1}: y = 0.161x + 0.164, R^2 = 0.320, *RMSE* = 0.225; SOC = 10 g kg^{-1}: y = 0.162x + 0.414, R^2 = 0.493, *RMSE* = 0.200; SOC = 20 g kg^{-1}: y = 0.166x + 0.735, R^2 = 0.942, *RMSE* = 0.183; SOC = 30 g kg^{-1}: y = 0.161x + 1.2658, R^2 = 0.798, *RMSE* = 0.141.

The slopes of the regression functions presented in the caption of Figure 3 show that CaO_{BNC} has an increase of approximately one-sixth that of the CaO_{VDLUFA}. This is lower than the required lime amount estimated by Vogel et al. [13], who predicted a corresponding slope of 1/10 by applying the class-based VDLUFA look-up table values. However, their dataset had a lower CaO_{VDLUFA} recommendation range with a maximum of approximately 5 mg ha^{-1}.

The reader should bear in mind that the VDLUFA approach considers both the amount of lime required to change the pH_0 to the pH_{target} and the amount of lime that is necessary to compensate for the pH changes during one liming interval. However, the BNC approach solely considers the amount of lime needed to raise the pH from the pH_0 to the pH_{target}. The numerical difference between both approaches yields the acidification rate during the liming interval. In Figure 4, the annual AR, considering 3 years per liming interval, is shown as being dependent on the MPD and pH_0.
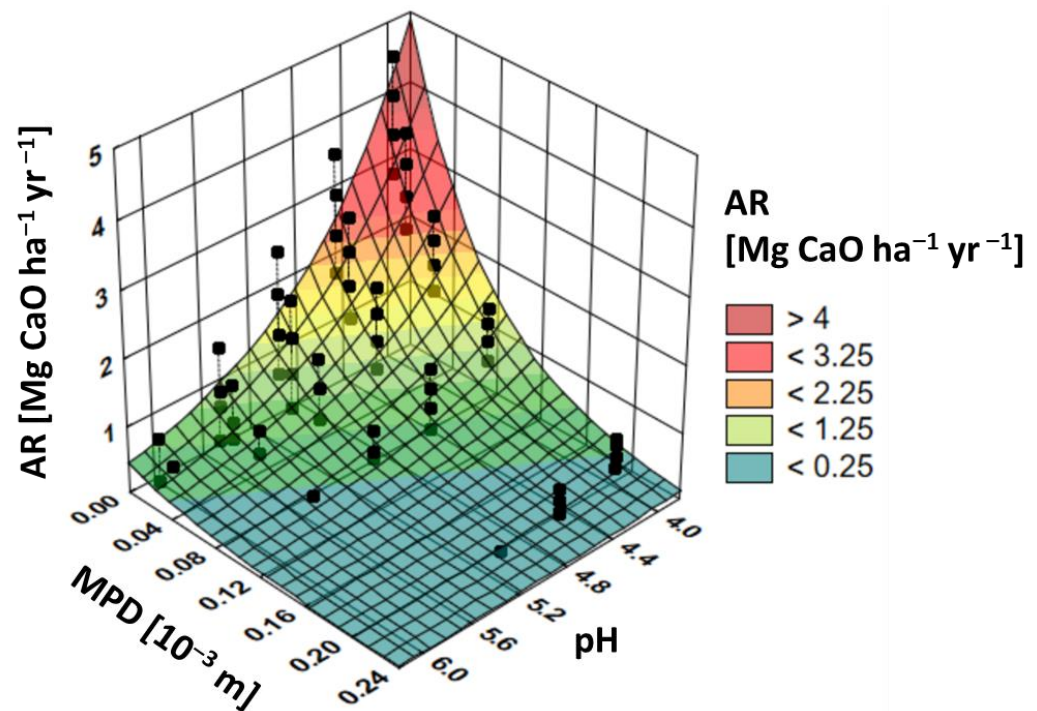
Figure 4. Annual acidification rate (AR) (Mg CaO ha^{-1} yr^{-1}) dependent on mean particle diameter (MPD) and initial soil pH (pH$_0$). Per MPD–pH$_0$ combination, up to four AR values are shown, resulting from the four SOC contents of 5, 10, 20 and 30 (g kg^{-1}), as mentioned in the created dataset (Section 2.4).

The AR was predicted using the following model (Equation (4)):

$$AR = a \times \exp(-b \times pH_0) \times \exp(-c \times MPD) \tag{4}$$

with a = 226.82 (90.96), b = 1.008 (0.093) and c = 15.14 (1.92).

Generally, the calculated AR is related to the applied CaO amount as recommended by the VDLUFA, which increases when the MPD and pH$_0$ decrease. Relatively low AR values < 0.25 Mg ha^{-1} were estimated for a broad range of MPD-pH$_0$ combinations but mainly for sandy soils (MPD > 0.042 × 10^{-3} m) (compare Section 2.4). However, excessive AR values up to approximately 4 Mg CaO ha^{-1} yr^{-1} were predicted for loamy and clayey soils (MPD < 0.042 × 10^{-3} m) in combination with lower pH$_0$ values. These values clearly exceed the maximum AR of approximately 0.85 Mg CaO ha^{-1} yr^{-1} [1,19–22].

Since up to four AR values per MPD–pH$_0$ combination are related to different SOC values, as explained in the caption of Figure 3 and in Section 2.4, we extended Equation (4) via an SOC term (Equation (5)).

$$AR = a \times exp(-b \times pH_0) \times exp(-c \times MPD) - d \times SOC \tag{5}$$

where a = 83.46 (14.18), b = 0.736 (0.040), c = 8.33 (0.61) and d = 0.036 (0.003).

Including the SOC term improves the model performance from R^2 = 0.722 (Equation (4)) to R^2 = 0.918 while reducing the *RMSE* from 0.502 Mg CaO ha^{-1} yr^{-1} to 0.308 Mg CaO ha^{-1} yr^{-1} (Equation (5)) (Figure 5).

Finally, we want to focus on Ca leaching as a relevant lime loss process considered in several lime loss regression models [1,21]. The global relationship between water balance and the soil pH was evaluated by Slessarev et al. [25]. They observed an abrupt transition from an alkaline to acidic soil pH that occurs at the point where the mean annual precipitation begins to exceed the mean annual potential evapotranspiration. The VDLUFA look-up tables were developed based on field experiments in the eastern part of Germany [15] in regions with a mean annual climatic water balance (precipitation–potential evapotranspi-

ration) of -100 to 100 mm [41]. However, the VDLUFA look-up tables are more or less uniformly applied in Germany, neglecting that the climatic water balance ranges between -250 and 1200 mm yr^{-1} as estimated at 40 selected climate stations [42]. Consequently, using the climatic water balance as a site-dependent factor might further improve the efficiency of liming and allow for it to be adapted to a changing climate.
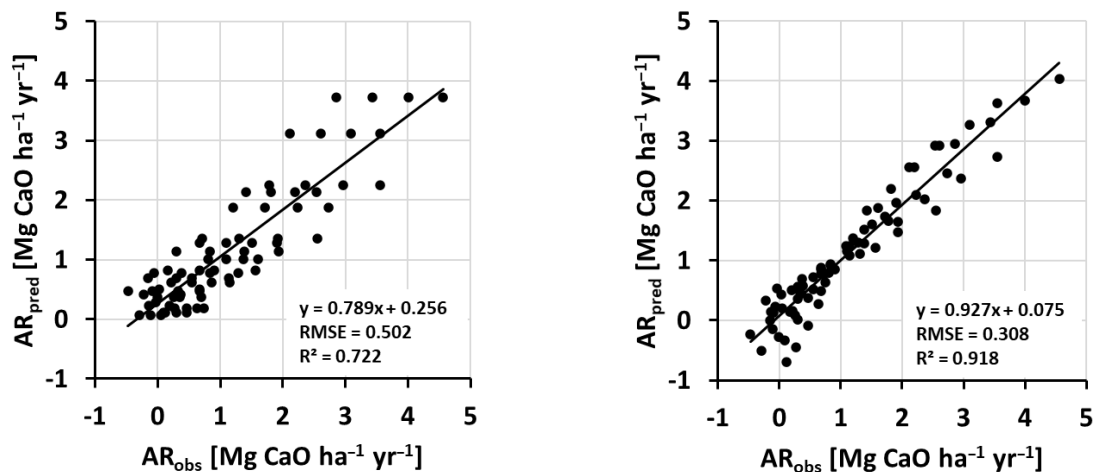
Figure 5. Acidification rates (ARs) estimated via the difference between the VDLUFA and the BNC approaches. AR_{obs} vs. AR_{pred} according to Equation (4) without SOC term (**left**) and according to Equation (5) with SOC term (**right**).

4. Conclusions

A new pedotransfer function for quantifying the liming-induced pH changes dependent on the pH_0, MPD and SOC was established. For future research, we strongly recommend testing and recalibrating the BNC approach (Equation (3)) on the data of soils with a larger variety, especially in the geological parent material.

Comparing the outputs of both the VDLUFA and the BNC approaches enabled an estimation of the annual acidification rate as being dependent on the pH_0, soil texture and SOC for site conditions in eastern Germany. The predicted above-average acidification rate values of up to approximately 4 Mg CaO ha^{-1} yr^{-1} raise questions for the main acidification process responsible. Since the acidification process depends on the climate conditions, management practices and other factors, the acidification rate varies in space and time. Therefore, we suggest a decoupling of the lime rate calculation, i.e., to separately calculate the amount of lime required to change the pH from the pH_0 to the pH_{target} and the amount of lime that is necessary to compensate for acidification. This might be helpful to optimize LRs adapted to different regions, varying management strategies and a changing climate.

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