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Modelling long-term impacts of fertilization and liming on soil acidification at Rothamsted experimental station

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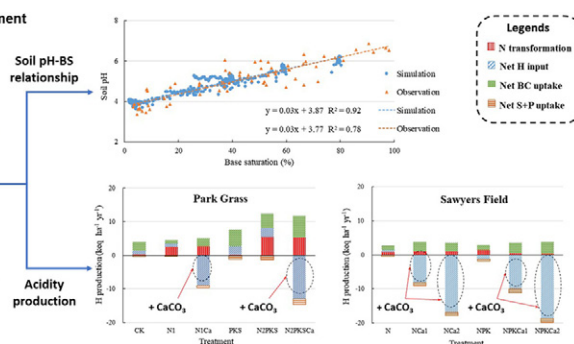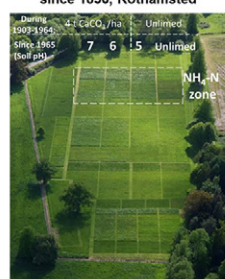[d] *Wageningen University and Research, Environmental Research, PO Box 47, 6700AA Wageningen, the Netherlands*

HIGHLIGHTS

- The soil acidification model VSD+ was tested for two long-term fertilization and liming experiments.
- VSD+ was capable of simulating observed soil pH and base saturation changes over time.
- Crop removal contributed most to acidity production followed by nitrogen transformations.
- VSD+ can be used to predict liming requirements and liming intervals in response to management.

GRAPHICAL ABSTRACT

ABSTRACT

Liming is widely used to reduce the impacts of soil acidification and optimize soil pH for agricultural production. Whether models can simulate the effect of liming on soil pH, and base saturation (BS), and thereby guide lime application, is still largely unknown. Long-term experimental data from a grassland (Park Grass, 1965–2012) and arable land (Sawyers Field, 1962–1972) at Rothamsted Research, UK, were thus used to assess the ability of the VSD+ model to simulate the effects of long-term fertilization and liming on soil acidification. The VSD+ model was capable of simulating observed soil pH and BS changes over time in the long-term liming experiments, except for a treatment in which sulphur (S) was added. Normalized Mean Absolute Errors (NMAE) and Normalized Root Mean Square Errors (NRMSE) of simulated and observed pH values, averaged over the observation periods varied between 0.02 and 0.08 (NMAE) and 0.01–0.05 (NRMSE). The acidity budget results for Park Grass suggest that nitrogen (N) transformations contributed most to acidity production, causing predominantly aluminium (Al) exchange in the topsoil (0–23 cm) followed by base cation (BC) release, but in the treatment with S addition, BC uptake had a nearly similar effect on acidity production. However, in Sawyers Field, the acidity budget suggested that BC uptake was the dominant cause of soil acidification, while the impacts of N transformations were limited. Liming was found to sufficiently replenish BC and decrease Al exchange in the topsoil layer. Overall, the VSD+ model can adequately reconstruct the impacts of fertilizer and liming applications on acid neutralizing processes and related soil pH and BC changes at the soil exchange complex.

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1. Introduction

Soil acidification reduces food production and agricultural sustainability worldwide. It is estimated that acidic soils (topsoil pH < 5.5) cover nearly 30% of the global ice-free land area, with most of the potential arable land composed of acidic soils (Sumner and Noble, 2003; Von Uexküll and Mutert, 1995). Soil acidification is associated with various conditions restricting crop growth. This includes a decrease in the availability of base cations (BC, including calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K)) due to enhanced leaching, which leads to soil fertility degradation and potential yield decline (Zhang et al., 2016). At low pH, generally below 4.5, the release of toxic aluminium (Al) and manganese (Mn) may cause root damage and further reduce yields (Hue et al., 2001; Zhou, 2015). Furthermore, the availability of toxic heavy metals, especially cadmium (Cd), increases with decreasing soil pH (De Vries et al., 2007a; De Vries and McLaughlin, 2013; Groenenberg et al., 2010), implying that soil acidification leads to a potential risk of Cd accumulation in crops, animals and humans through bioaccumulation (De Vries et al., 2007b; Mok et al., 2015).

Soil acidification is a natural process which has been enhanced by human activities. Growing industrial activities, leading to enhanced nitrogen oxide (NO_x) and sulphur dioxide (SO_2) emissions in the last century have caused severe atmospheric acid deposition, and enhanced acidification of forest soils in many regions, including Europe, North America and China (Reuss et al., 1987; Van Breemen et al., 1982; Zhu et al., 2016). In addition, soil acidification rates in terrestrial ecosystems have been accelerated by elevated ammonia (NH_3) emissions in response to increased N inputs to agriculture all over the world (Galloway et al., 2008; Tian and Niu, 2015; Vitousek et al., 1997). Long-term N application has greatly increased crop yields (Erisman et al., 2008), but this has been accompanied with increased removal of BC from the soil, within the harvested crops, and leaching of BC with excess nitrate (NO_3) (Hao et al., 2019; Zhu et al., 2018a), since the NO_3 ions are not strongly adsorbed by the soil. Net generation of acidity (H) caused by N fertilizers is induced by an uncoupling of the N cycle (De Vries and Breeuwsma, 1987). For instance, it is estimated that approximately 1.72 and 5.24 kg of lime are required to neutralize the acidity production from the application of 1 kg of N as urea and ammonium sulphate, respectively (Hedley and Bolan, 2003).

To ensure food security and agricultural sustainability, it is fundamental to ameliorate soil acidification. A recent study shows that approximately 13% of the considered croplands in China may suffer from Al toxicity in 2050, if the nutrient management remains unchanged (Zhu et al., 2018b). Data suggest that nearly 40% of arable soils and 57% of grassland soils in the UK are below the recommended pH level (Goulding, 2016). Liming is a long-established and widely used soil management practice to ameliorate soil acidity and improve crop yields (Fageria and Baligar, 2008). Adequate lime input can elevate the soil pH to an appropriate level, which eliminates the toxicity of Al and Mn, reduces the uptake of heavy metals such as Cd and nickel (Ni) (Hooda and Alloway, 1996) and counteracts leaching losses of BC. By increasing the pH, liming also enhances the plant availability of N, P, Ca, Mg and molybdenum (Mo) (Holland et al., 2018).

The standard method for assessing lime requirements is to multiply the required pH increase, from a measured initial value to a target value (such as pH 6–6.5 in Goulding (2016)), by the acid buffering capacity to increase the pH by one unit value. Several analytical methods have been developed to determine the acid buffering capacity, e.g. soil incubation, direct titration and the use of buffer solutions (Eckert and Sims, 1995; Pagani and Mallarino, 2012). The problem with these methods is that the required time for equilibrium is several weeks, which can be impractical for routine testing of soil. Direct titration methods can provide a more rapid alternative, although they tend to underestimate the lime requirements (Pagani and Mallarino, 2012).

Based on these methods, various lime requirement calculators have been developed. One example is RothLime (Goulding et al., 1989), which calculates lime requirements based on data of measured pH changes in long-term liming experiments at Rothamsted. Based on these empirical data, the model calculates the lime requirement for a given soil type, land use (arable/grass), the difference between initial and required pH and the amount of acidity that the liming materials to be used will neutralize (see http://www.rothamsted.ac.uk/rothlime for details). However, results are based on empirical data, and are lacking insight into buffering mechanisms. Furthermore, both laboratory methods and existing lime calculators do not give dynamic insight as to when the soil can be buffered by the added lime. This requires information on the ongoing soil acidification rate at the field scale, due to acid deposition and fertilization, along with the buffering rate. In this context, a process-based soil acidification model could be an appropriate tool.

This study applies the soil acidification model Very Simple Dynamic Model Plus (VSD+) (Bonten et al., 2016) to simulate fertilization and liming impacts on soil acidification in two long-term liming experiments. The VSD+ model was originally developed to predict trends in forest-soil acidification in response to changes in atmospheric deposition of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3) across Europe (Posch and Reinds, 2009). Recently, VSD+ has been further developed and validated for croplands in China and has proven appropriate for the simulation of soil acidification rates in intensive agricultural systems (Zeng et al., 2017). The aim of this study is to evaluate predictions of liming impacts from VSD+ and to assess the potential of VSD+ to calculate lime requirements at field and regional scale without laborious laboratory assessments.

2. Materials and methods

2.1. Model description

The VSD+ (Bonten et al., 2016), is an extension of the VSD model (Posch and Reinds, 2009), which simulates soil acidification processes in a single-layer. It includes a set of mass balance equations and equilibrium equations to simulate changes in soil and soil solution chemistry, including changes in soil base saturation (BS) and pH. Soil and soil solution chemistry is determined by elemental input of inorganic and organic fertilizers, N fixation and deposition, net uptake by plants, net mineralization/immobilization, nitrification and denitrification, as well as soil buffering processes. Plant removal is derived from annual growth rates (forests) or crop yields (agriculture) multiplied with elemental contents of harvested biomass. The uptake of N is divided over NH_4 and NO_3. The VSD+ model assumes preferential uptake of NH_4, by including a specified high fraction of available NH_4 that is taken up, while the remainder is NO_3 uptake. This implies that even in cases where nitrification is limited, the concentration of NO_3 is generally higher than that of NH_4. The net mineralization or immobilization of N is calculated from the turnover of carbon (C) pools, distinguishing decomposable plant material (DPM), resistant plant material (RPM), microbial biomass (BIO), humified organic matter (HUM) and inert organic matter (IOM), using the RothC model and the C:N ratios of those C pools. Nitrification and denitrification are modelled as first-order rate constants times the total available amounts of NH_4 and NO_3, respectively. The rates of mineralization, nitrification and denitrification are calculated as a maximum value multiplied by reduction functions for the effect of temperature and soil moisture (see Bonten et al. (2016) for details).

Key soil buffering processes include weathering, cation exchange (Gaines-Thomas equation or Gapon equation) and dissolution of Al hydroxides according to a gibbsite equilibrium (Bonten et al., 2016). In this study, we chose the Gapon equation to model cation exchange, in which Ca, Mg and K are summed as BC. In VSD+, interaction between Na on the adsorption complex and in solution is neglected and Na on the adsorption complex is lumped with K, which is treated as a divalent cation. In the adapted agricultural version, element inputs by fertilizers, P and S

adsorption-desorption, and N losses by NH_3 emission are also included (Zeng et al., 2017). Within this approach, it is assumed that applied fertilizer dissolves within a year, implying that the elements in chemical fertilizer can be summed with element deposition in ionic form. NH_3 emission from N fertilizers is included as a fraction of the N fertilizer input. Wet and dry deposition, weathering and uptake rates are given as annual fluxes for each ion. In addition, the input parameters comprise soil cation exchange capacity (CEC), BS, CO_2 pressure in the soil solution and the amount of C and N. Annual water flux is a crucial input for the VSD+ model, which is calculated with a pre-processor, called the MetHyd model, on the basis of daily data on rainfall, air temperature, sunshine hours and soil texture (Bonten et al., 2016).

2.2. Experimental design and site data

The model simulations were based on data from two long-term experiments at Rothamsted Research, Hertfordshire, UK, (1) Park Grass (PG): permanent grassland, and (2) Sawyers Field (SF): an arable field under a variety of crops; both received varying lime and fertilizer applications (see http://www.era.rothamsted.ac.uk/ for further information). The PG experiment (51°48′14″N, 0°22′21″W), began in 1856, at a permanent pasture site (Hopkins et al., 2009). The topsoil (refers to 0–23 cm depth) had a pH of 5.5 at the beginning of the experiments. Annual applications of various combinations of N, P, K, Mg, Na and S were made to investigate their effects on hay yields (Silvertown et al., 2006). After several decades, the long-term application of inorganic fertilizer resulted in significant differences in soil pH among treatments. Hence, after 1905, nearly all plots were divided into two subplots, limed and unlimed, to examine the effect of liming. After 1965, the limed subplots were further divided to allow for lime additions that maintained soil pH at 7 or 6, and the unlimed subplots were further divided to allow lime addition that maintained soil pH at 5 and a remaining unlimed subplot (White et al., 2012).

At SF (51°48′58″N, 0°22′29″W), a long-term liming experiment started in 1962 to study the interaction between soil pH, P and K on crop yields in a rotation of beans, barley and potatoes. Different rates of lime were applied in 1962 to fields with a topsoil pH of ~5 before lime application (Bolton, 1971; Bolton, 1977). Soil samples were taken from the topsoil after harvest and before ploughing every year from each plot, except for 1965 and 1969 (Bolton, 1977). Significant increases in soil pH and exchangeable Ca under lime application were observed, with pH values ranging 4.4 to 7.6 (Bolton, 1977).

The model was initialized one year before liming started, at 1965 for PG and 1962 for SF. In most of the results, we focus on the period 1965–2012 for PG and 1962–1972 for SF.

2.3. Fertilizer and liming rates, and ammonia emissions

Eight treatments from the PG experiment were selected during 1965–2012, including six inorganic fertilizer application treatments and two lime application treatments, in which the fertilization started in 1856 and liming in 1965. Details of the elemental input by fertilization and the lime ($CaCO_3$) inputs in the two experiments are shown in Table 1. For the PG experiment, six treatments from different combinations of N, P, K, S, Mg and Na fertilizers and lime application were selected, focusing on the effects of the following factors on soil acidification processes:

(i) N fertilizer input: 48 kg N ha^{-1} yr^{-1}, denoted as N_1, and 96 kg N ha^{-1} yr^{-1}, denoted as N_2;
(ii) the application of P, K and S: no fertilizer or manure application in control plot and no N input, but 35 kg P ha^{-1} yr^{-1}, 225 kg K ha^{-1} yr^{-1}, 10 kg Mg ha^{-1} yr^{-1}, 15 kg Na ha^{-1} yr^{-1} and 122 kg S ha^{-1} yr^{-1} for PKS; 55 and 110 kg more S ha^{-1} yr^{-1} for N_1, N_2, respectively.

Table 1
Fertilizer and lime inputs for the grassland (Park Grass, 1965–2012) and the arable (Sawyers Field, 1962–1972) site.

Treatments	Total element additions in fertilizer (kg ha^{-1} yr^{-1})							$CaCO_3$ input[a]
	NH_4-N	NO_3-N	SO_4-S	H_2PO_4-P	K	Mg	Na	(t)
Park Grass[b]								
Control	0	0	0	0	0	0	0	0
N_1	48	0	55	0	0	0	0	0
N_1Ca	48	0	55	0	0	0	0	24
PKS	0	0	122	35	225	10	15	0
N_2PKS	96	0	232	35	225	10	15	0
N_2PKSCa	96	0	232	35	225	10	15	38
Sawyers Field[c]								
N	0–94[d]	0–94[d]	0	0	0	0	0	0
NCa_1	0–94[d]	0–94[d]	0	0	0	0	0	5.0
NCa_2	0–94[d]	0–94[d]	0	0	0	0	0	10
NPK	0–94[d]	0–94[d]	0	27	105	0	0	0
$NPKCa_1$	0–94[d]	0–94[d]	0	27	105	0	0	5.0
$NPKCa_2$	0–94[d]	0–94	0	27	105	0	0	10

Data presented are mean values for the years 1965–2012 for Park Grass (no replicate), and for the years 1962–1972 for Sawyers Field (two replicates for each treatment).
[a] Application rates of chalk ($CaCO_3$) in Park Grass were given between 1965 and 2009 (see Table S1), with variable amount depending on the severity of soil acidification. In Sawyers Field, $CaCO_3$ was applied in 1962 only. Note that 1 t $CaCO_3$ contains 363 kg Ca and 2 kg Mg, in equal to 18.1 keq Ca and 0.2 keq Mg. It is assumed that no HCO_3^- input under lime application.
[b] Control: no manure or fertilizer input; N_1, N_2: ammonium sulphate supplying 48, 96 kg ha^{-1} yr^{-1} N and 55, 110 kg ha^{-1} yr^{-1} S; PKS: triple superphosphate supplying 35 kg P, potassium sulphate supplying 225 kg K and 99 kg S; sodium sulphate supplying 15 kg Na and 10 kg S and magnesium sulphate supplying 10 kg Mg and 13 kg S; Ca: with lime ($CaCO_3$) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.
[c] N: applied as calcium ammonium nitrate in variable amount; PK: superphosphate supplying 27 kg P ha^{-1} yr^{-1} and muriate of potash supplying 105 kg K ha^{-1} yr^{-1}; Ca_1: 5 t $CaCO_3$ ha^{-1} and Ca_2: 10 t $CaCO_3$ ha^{-1}, applied in 1962.
[d] Amount of N fertilizer varied depending on the crops. See Table S2.

(iii) lime (as $CaCO_3$) application: lime application since 1965, with amounts dependent on the severity of soil acidification (see Table S1 in Supporting Information), and unlimed.

At SF, three lime application rates (0, 5 and 10 t ha^{-1}, applied in 1962) were selected combined with and without annual dressings of triple superphosphate and potassium chloride (27 kg P ha^{-1} yr^{-1} and 105 kg K ha^{-1} yr^{-1}), giving a total of 12 plots with two replicates during 1962–1972. The crops grown during the observation period were beans (1962–4), barley (1965–7), potatoes (1968) and barley (1970–2). All plots received the same amount of N fertilizer, as calcium ammonium nitrate, which were applied according to crop requirements (see Table S2).

Emission of NH_3 from N fertilizer was assessed as a fraction of the N fertilizer input. For ammonium sulphate applications, the emission factor was set at 3.2% of the N applied (Misselbrook et al., 2000; Whitehead and Raistrick, 1990). Under the treatments with calcium ammonium nitrate applications, the NH_3 emission from fertilizer was set at 1.1% of N applied (Goebes et al., 2003; Misselbrook et al., 2000). We assumed that there were no NH_3 emissions from plots without N addition.

2.4. Atmospheric deposition and N fixation

Precipitation and deposition data for Rothamsted are available from 1853 onwards (Sverdrup et al., 1995). Continuous total (wet plus dry) deposition for the period 1962–2012 were estimated based on wet deposition data, multiplied by a ratio of total: wet deposition ratio. Wet deposition of NH_4 and NO_3, sulphate (SO_4), chloride (Cl), BC and P during 1962–1991 were derived from e-RA (the electronic Rothamsted Archive, providing a permanent managed database for secure storage of data from Rothamsted's Long-term Experiments; http://www.era.

rothamsted.ac.uk/). From 1992 onwards, estimations of wet deposition of those elements were derived from (i) precipitation chemistry data reported by Rennie et al. (2017) for the UK Environmental Change Network (ECN), a long-term environmental monitoring and research program (Morecroft et al., 2009) and (ii) daily rainfall extracted from Rothamsted daily meteorological data from e-RA.

Total deposition of all elements, shown in Fig. S1, was calculated based on the wet deposition, derived from e-RA and a total:wet ratio (total deposition of NO_3 between 1994 and 2012 was available in e-RA). Total:wet ratios used for NH_4 and SO_4 during 1962–2012 were 2.2 and 2.0, respectively, while for NO_3, the ratio was 4.2 for 1962–1993, based on Goulding and Blake (1993). For BC, Cl and P, we used a total: wet ratio of 2.0 during 1962–2012. The ratio for Na, K, Ca and Mg was based on: (i) ratios of Na and SO_4 in throughfall and bulk deposition of forests in Europe and (ii) average model results for the Netherlands (Van Jaarsveld et al., 2010). The ratio for Cl and P was based on ratios of Cl and P in throughfall and bulk deposition of forests in Europe (Kopáček et al., 2011; Talkner, 2009).

Biological N fixation can be an important N source when legumes are present. In the PG experiment N input from fixation was assessed by multiplying an estimated percentage of legumes (mainly clover) under different fertilizer treatments by an average N fixation rate of 200 kg N ha^{-1} yr^{-1} (Carlsson and Huss-Danell, 2003; Ledgard, 2001). The estimated percentages for PG were 0% for the N_1 and N_2PKS plots; 5% for the control and N_1Ca plots; 10% for the N_2PKSCa plots and 25% for the PKS plot, with related N fixation rates of 0, 10, 20 and 50 kg N ha^{-1} yr^{-1}, respectively (Macdonald, 2018). For SF it was assumed that N fixation only occurred during the springbean growth period (1962–1964, see Table S2), which was calculated based on srpingbean yields, with approximately 75 kg N ha^{-1} fixed with 1 t ha^{-1} grain yield production (Herridge et al., 2008).

2.5. Element removal by crops

The element removal by crop harvesting in PG (1965–2012) and SF (1962–1972) is shown in Table 2. In the grassland PG experiment, it was calculated based on recorded herbage yields (1965–2012) and the mineral (N, P, K, Ca, Mg and S) contents in herbage (2000−2012) for each treatment (see Table S3 for details). Herbage yields were originally estimated by weighing the produce from the whole plot, either as hay (first harvest) or green crop (second harvest), and dry matter yield was subsequently determined in the laboratory. It is assumed that the herbage yields reflect net plant uptake for all elements. The elemental contents of herbage were mean values, based on annual data between 2000 and 2012, obtained from e-RA. Since Jenkinson et al. (2004) reported that approximately 20% of N returned to soil during haymaking, the net N uptake for all treatments was thus calculated by multiplying the total N removal in herbage by a reduction ratio of 0.8 for the first harvest (see variation of N and BC uptake in Fig. S2).

For SF, element removal by crops and straw were calculated based on harvested biomass and nutrient content of crops and straw, see Table S4 for details. Since only grain yields were recorded every year from 1963 (Bolton, 1971), the straw production was derived by multiplying grain yields by a straw: grain ratio of 1.6 for springbean (Zhu et al., 2018b) and 1.0 for barley (Scarlat et al., 2010). The nutrient contents of crop grain and straw (see Table S5) were based on Roy et al. (2006) and Nijhof (1987).

Organic C input from crop growth were also considered. According to Coleman et al. (1997), it was assumed that the annual C input to the control plot is 3.0 t C ha^{-1} and for the fertilized is 2.7 t C ha^{-1} for PG, while for SF it was set at 0.7 t C ha^{-1} for all plots.

2.6. Soil properties

Soil properties for PG and SF are included in Table 3. All data were derived from e-RA and applied to the topsoil (0-23 cm) for all

Table 2
Plant removal rates for the selected experiments in Park Grass (1965–2012) and Sawyers Field (1962–1972).

Treatments	Net crop or herbage removal rate (kg ha^{-1} yr^{-1})					
	N	P	K	Ca	Mg	S
Park Grass[a]						
Control	39	4.0	31	24	5.9	6.0
N_1	27	1.9	18	6.0	2.4	5.2
N_1Ca	45	3.4	27	27	4.6	9.6
PKS	66	14	107	34	7.7	11
N_2PKS	90	14	118	14	7.2	14
N_2PKSCa	91	19	145	40	8.6	18
Sawyers Field[b]						
N	33	4.3	20	10	4.4	8.5
NCa$_1$	92	8.4	36	19	8.5	16
NCa$_2$	90	8.1	34	19	8.4	16
NPK	43	5.3	25	11	5.2	9.6
NPKCa$_1$	102	11	46	23	10	19
NPKCa$_2$	110	11	47	24	11	20

Data presented are mean values for the years 1965–2012 for Park Grass ($n = 1$), and for the years 1962–1972 for Sawyers Field ($n = 2$).
  [a] Control: no manure or fertilizer input; N_1, N_2: 48, 96 kg N ha^{-1} yr^{-1} and 55, 110 kg S ha^{-1} yr^{-1}; PKS: 35 kg P ha^{-1} yr^{-1}, 225 kg K ha^{-1} yr^{-1}, 10 kg Mg ha^{-1} yr^{-1}, 15 kg Na ha^{-1} yr^{-1} and 122 kg S ha^{-1} yr^{-1}; Ca: with lime (CaCO$_3$) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.
  [b] N: applied as calcium ammonium nitrate in variable amount; PK: 27 kg P ha^{-1} yr^{-1} and 105 kg K ha^{-1} yr^{-1}; Ca$_1$: 5 t CaCO$_3$ ha^{-1} and Ca$_2$: 10 t CaCO$_3$ ha^{-1}, applied in 1962.

treatments. Soil analyses were carried out on historical samples for a combination of plots, with or without lime input, during 1903–2011 for PG and SF to determine soil pH, CEC and BS. Historic data shows that the soil pH varied 3.8–7.0 among all plots. Soil pH was measured in a 1:2.5 soil: water suspension using a combined calomel reference/ glass electrode and pH meter. The CEC and exchangeable cations were measured in a buffered (pH = 7) ammonium acetate solution according to Sikora et al. (2014). Results of soil analysis for the initial data used in modelling are given in Table 4.

Parameters in VSD+ describing the amounts of S and P adsorbed (meq kg^{-1}) are the maximum adsorption capacity of the soil (X_{admax}, meq kg^{-1}; X is S or P), the dissolved concentration (meq l^{-1}) and the half-saturation constant (X_{half}, meq l^{-1}), included in the Langmuir adsorption isotherm (Zeng et al., 2017). For P, the maximum adsorption capacity P_{admax} was set at 35 and the half-saturation adsorption capacity P_{half} at 0.20 according to Zhu et al. (2018b). The maximum adsorption capacity for S was assumed 25 times lower than P, while S_{half} was assumed equal to P_{half} based on De Vries et al. (1994) and Schoumans (2013), S_{admax} was thus set at 1.4 and S_{half} at 0.20. Since Park Grass has received high P and S inputs since 1856 (by deposition in the control plot and fertilization in the treated plots), we assumed that the initial absorbed amounts were in equilibrium with the net inputs (input minus cop removal), implying very limited P and S ad- or desorption.

Land use greatly affects nitrification and denitrification of applied inorganic N. These processes play an important role in soil acidity production. In this study, the uptake efficiency of available N (N_{upeff}) and the maximum nitrification rates (k_{ni}) for PG and SF were calibrated by a measured ratio of NH_4:NO_3 in the surface 0–23 cm soil layers by Blake et al. (1999) and 0–10 cm by Kemmitt et al. (2006), respectively. Maximum denitrification rates (k_{denit}) in PG were calibrated using the N_2O emission rate of Goulding et al. (1998) and the same value assumed for SF. Details of the approach can be found in the footnotes of Table 3.

2.7. Meteorology and hydrology

Soil water contents and precipitation surpluses were derived by running the hydrological model MetHyd as a pre-processor for VSD+ (Bonten et al., 2016). Required input data for MetHyd include soil texture and daily observation of precipitation, sunshine hours and temperature, which were derived from e-RA. Vegetation albedo was set at 0.25

Table 3
Soil properties and model parameters used as model input data for Park Grass and Sawyers field.

Parameters	Unit	Park Grass	Sawyer Field
Soil depth	m	0.23	0.23
Soil bulk density	g cm^{-3}	1.1	1.2
Clay content	%	21	21
CO_2 pressure	mbar	10	10
Initial C pool in soil[a]	g m^{-2}	6992	3409
Initial C:N ratio in soil[a]	g g^{-2}	15	11
Initial $CaCO_3$ content	%	0.00	0.00
Ca weathering rate	keq ha^{-1} yr^{-1}	0.70	0.70
K weathering rate	keq ha^{-1} yr^{-1}	0.20	0.20
Mg weathering rate	keq ha^{-1} yr^{-1}	0.05	0.05
Na weathering rate	keq ha^{-1} yr^{-1}	0.10	0.10
S_{half}[b]	meq L^{-1}	0.20	0.20
S_{admax}[b]	meq kg^{-1}	1.4	1.4
P_{half}[b]	meq L^{-1}	0.20	0.20
P_{admax}[b]	meq kg^{-1}	35	35
Maximum nitrification rate (k_{nit})[c]	yr^{-1}	0.20	0.10
Maximum denitrification rate (k_{denit})[c]	yr^{-1}	4.0	4.0
Uptake efficiency of available N (N_{upeff})[c]	–	0.60	0.90
Reduction factor mineralization (rf_miR)	–	0.89	0.76
Reduction factor nitrification (rf_nit)	–	0.84	0.71
Reduction factor denitrification (rf_denit)	–	0.84	0.71
K_{AlBC}[d]	(meq l^{-1})$^{1/6}$	−0.67	−0.01
K_{HBC}[d]	(meq l^{-1})$^{-1/2}$	3.7	3.8
K_{Alox}[d]	(meq l^{-1})$^{-2}$	8.9	7.0

[a] The values of C pool and C:N ratio for Park Grass are the averages of plots 1, 3, 7, 9, 14 and 17, which were measured in 1959;

[b] S_{admax} and P_{admax} are the maximum adsorption capacity of the soil for S or P, respectively; S_{half} and P_{half} are the half-saturation constant for S or P.

[c] The combinations of N_{upeff} and maximum nitrification rates (k_{ni}) for Park Grass and Sawyers Field were calibrated by measured approximate ratio of NH_4:NO_3 at 1 in the surface 0–23 cm soil layers by Blake et al. (1999) and 0–10 cm by Kemmitt et al. (2006).; k_{denit} was calibrated by the measured nitrous oxide emission by Goulding et al. (1998).

[d] Values for the constants here are given as decadic logarithms.

for PG and 0.17 for SF according to Page (2012) and Zhu et al. (2018b). The reduction functions for mineralization (rf_miR), nitrification (rf_nit) and denitrification (rf_denit) of N, due to temperature and/or

Table 4
Data of pH, cation exchange capacity (CEC) and base saturation (%) used for Park Grass in 1964 and Sawyers Field in 1961.

Treatment[a]	Soil pH[b]	CEC[b] (meq kg^{-1})	Base saturation[b] (%)
Park Grass[a]			
Control	5.0	181	52
N_1	3.9	203	4.0
N_1Ca	3.9	203	4.0
PKS	4.4	184	28
N_2PKS	3.5	264	8.0
N_2PKSCa	3.5	264	8.0
Sawyers Field[c]			
N	5.0	136	40
NCa_1	5.0	136	40
NCa_2	5.0	136	40
NPK	5.0	136	40
$NPKCa_1$	5.0	136	40
$NPKCa_2$	5.0	136	40

[a] Control: no manure or fertilizer input; N_1, N_2: 48, 96 kg N ha^{-1} yr^{-1} and 55, 110 kg S ha^{-1} yr^{-1}; PKS: 35 kg P ha^{-1} yr^{-1}, 225 kg K ha^{-1} yr^{-1}, 10 kg Mg ha^{-1} yr^{-1}, 15 kg Na ha^{-1} yr^{-1} and 122 kg S ha^{-1} yr^{-1}; Ca: with lime ($CaCO_3$) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.

[b] The soil pH, CEC and BS measured in Park Grass are from 0 to 15 cm samples in 1956 for plot 1, 7, 9 and 0–23 cm samples in 1966 for plot 3 (assumed equal for the starting year 1964). In Sawyers Field, the CEC was estimated, according to Helling et al. (1964), based on historic data of soil pH in 1962, organic carbon content, clay content and bulk density from e-RA. The % BS data was derived by measured exchangeable base cation contents in 1967 from e-RA under unlimed treatment (N and NPK in this study), assumed to be equal for the starting year 1961.

[c] N: applied as calcium ammonium nitrate in variable amount; PK: 27 kg P ha^{-1} yr^{-1} and 105 kg K ha^{-1} yr^{-1}; Ca_1: 5 t $CaCO_3$ ha^{-1} and Ca_2: 10 t $CaCO_3$ ha^{-1}, applied in 1962.

soil moisture, were computed with MetHyd and typically varied between 0.7 and 0.9 (see Table 3).

2.8. Weathering rates and exchange constants

Data used for weathering rates are given in Table 3, based on the results of Sverdrup et al. (1995). Selectivity constants for H/BC exchange (K_{HBC}) and Al/BC exchange (K_{AlBC}), and the Al equilibrium constant (K_{Alox}), which mainly determine the changes in pH and BS, were initialised based on De Vries and Posch (2003), are given as decadic logarithms in Table 3. In this study, they were calibrated based on observed changes in soil pH, BS and Al saturation (EAl) available in some years for PG (between 1965 and 2012) and for SF (between 1962 and 1972), using a Bayesian calibration routine as described in Zeng et al. (2017). The range in possible exchange rates was based on reported ranges in De Vries and Posch (2003) and Al equilibrium constants were assumed to vary between 7 and 9 (see Table 3).

2.9. Model evaluation

The model was evaluated by comparing measured and predicted soil pH using the Normalized Mean Absolute Error (NMAE) and the Normalized Root Mean Square Error (NRMSE) according to Janssen and Heuberger (1995):

$$NMAE = \frac{\sum_{i=1}^{N} | P_i - O_i |}{N \bar{O}} \tag{1}$$

$$NRMSE = \sqrt{\frac{\sum_{i=1}^{N} (P_i - O_i)^2}{N \bar{O}^2}} \tag{2}$$

where P_i and O_i are the predicted and observed values for site i, $\bar{O}$ is the average of the observations and N is the number of observations.

2.10. Calculation of acidity budgets

The acidity budget, which is the key budget for identifying soil acidification, was calculated by aggregating the various proton/acidity production and consumption processes according to De Vries and Breeuwsma (1987) and De Vries et al. (1989). Acidity budgets were calculated using land input and output rates (keq ha^{-1} yr^{-1}) according to Zeng et al. (2017). The total H production from net inputs and outputs of elements (H_{pro}) was calculated as:

$$H_{pro} = (NH_{4in} - NH_{4out} + NO_{3out} - NO_{3in}) + (HCO_{3out} - HCO_{3in}) \\ + (Cl_{out} - Cl_{in}) + (H_{in} - H_{out}) + BC_{upt} - S_{upt} - P_{upt} \tag{3}$$

where input (X_{in}) is the amount of deposition of element X from atmosphere and fertilizer and outputs (X_{out}) represent the amount leached out of soil layer, which were determined by VSD+ outputs.

The included H production processes are N transformations ($NH_{4in} - NH_{4out} + NO_{3out} - NO_{3in}$), net HCO_3 leaching ($HCO_{3out} - HCO_{3in}$), net Cl leaching ($Cl_{out} - Cl_{in}$) and net BC uptake (BC_{upt}) while net H input ($H_{in} - H_{out}$) also contributes to H production, while net P and S uptake ($S_{upt} + P_{upt}$) consume H. The potential effect of net Cl leaching was neglected by assuming that Cl output by leaching equals Cl input and that Cl uptake is negligible.

Lime inputs at Rothamsted were in the form of calcium carbonate ($CaCO_3$), which contains 36.3% Ca and 0.2% Mg soluble in HCl, according to Bolton (1977). Hence, 1 t $CaCO_3$ contains 363 kg Ca and 2 kg Mg, equal to 18 keq Ca and 0.16 keq Mg. It is assumed that all C in applied lime is emitted as CO_2 in the year of application, according to IPCC (Eggleston et al., 2006), suggesting no HCO_3 input under lime application.

There can also be consumption when H_{in} is less than H_{out}, which rarely occurs. The included H consumption processes are the S

adsorption ($S_{in} - S_{upt} - S_{out}$), the P adsorption ($P_{in} - P_{upt} - P_{out}$), and BC release by weathering and Al exchange, which was calculated according to:

$$H_{con} = (S_{in} - S_{upt} - S_{out}) + (P_{in} - P_{upt} - P_{out}) \\ + (BC_{upt} + BC_{out} - BC_{in}) + (Al_{out} - Al_{in}) \quad (4)$$

S is in form of SO_4 and P is in form of H_2PO_4. Al uptake was ignored in this study.

3. Results

3.1. Reconstruction of acidification history by the VSD+ model

The simulated and observed soil pH for the liming experiments of PG (1965–2012) and SF (1962–1972) correlated reasonably well (Fig. 1). Observed liming effects on soil pH in PG and SF showed larger variations than the simulations. In the N_1 and N_2PKS treatments of PG, soil pH increases, in response to liming, were observed approximately 5 years after the first application in 1965. In this period, the increase in simulated soil pH was higher than the observations between 1965 and 1970. The simulated decrease in soil pH between 1975 and 1990 was also higher than observed in the N2PKS treatment, but comparable in the N1 treatment. The simulated increase in pH after liming in 1990 (amount of lime applied was 6.7 t ha^{-1} in N_1Ca and 4.3 t ha^{-1} in

N_2PKSCa), was more comparable with observations (Fig. 1b). The simulated soil pH changes in the control plot compared well with observations, with a slight overestimation, while VSD+ underestimated the soil pH in PKS plot (see Fig. S3). In SF, VSD+ slightly underestimated soil pH in several years after liming (for Ca_1 treatments during 1962–1964 and for Ca_2 during 1962–1968; Fig. 1c and d). After 1970, simulations correlated well with observations for the limed plots, while VSD+ slightly overestimated soil pH for the unlimed plots.

Averaged over the whole observation periods, the deviation between simulated and observed pH values was low for all treatments, as shown by the NRMSE (0.01–0.05) and NMAE (0.02–0.08), except for the PKS plot, with values of 0.15 for NRMSE and 0.18 for NMAE, respectively (Table 5). This indicates that VSD+ well reconstructed both trends and absolute values of soil pH in the grassland and arable experiments. The mean difference between simulations and observations, over the observation period was 3–8% in PG (except for PKS: 18%) and 2–7% in SF (Table 5).

The VSD+ model was able to simulate the long-term liming impacts on soil BS changes reasonably well for PG and very well for SF (Fig. 2). Sharp increases of BS after lime input were observed in 1965 for PG and 1962 for SF. In PG, BS rapidly declined once lime additions were stopped. In PG, VSD+ overestimated BS compared to the 1970 observation, whereas it underestimated BS compared to the 2000 and 2010 observations. VSD+ predicted BS changes on the PG control plot well but not for the PKS plot (see Fig. S3).
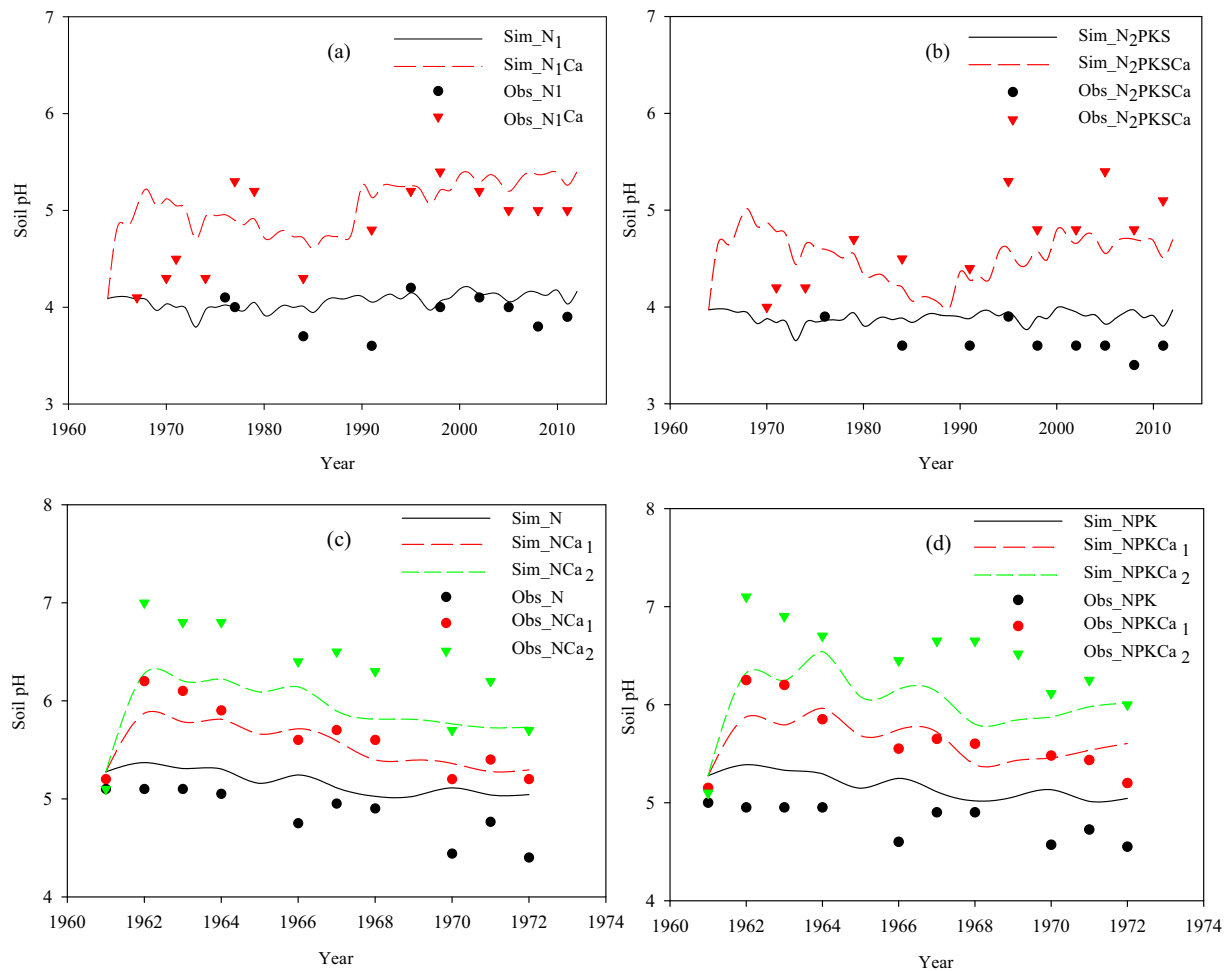

Fig. 1. Reconstruction of soil pH by the VSD+ model in the topsoil (0–23 cm) under different fertilization treatments and liming treatments in the Park Grass experiment (a and b 1965–2012) and Sawyers Field (c and d, 1962–1972). N_1, N_2: 48, 96 kg N ha^{-1} yr^{-1} and 55, 110 kg S ha^{-1} yr^{-1}; PKS: 35 kg P ha^{-1} yr^{-1}, 225 kg K ha^{-1} yr^{-1}, 10 kg Mg ha^{-1} yr^{-1}, 15 kg Na ha^{-1} yr^{-1} and 122 kg S ha^{-1} yr^{-1}; Ca: with lime (CaCO$_3$) addition; N: applied as calcium ammonium nitrate in variable amount; PK: 27 kg P ha^{-1} yr^{-1} and 105 kg K ha^{-1} yr^{-1}; Ca_1: 5 t CaCO$_3$ ha^{-1} and Ca_2: 10 t CaCO$_3$ ha^{-1}, applied in 1962; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.

Table 5
Normalized Root Mean Square Error (NRMSE) and Normalized Mean Absolute Error (NMAE) of the simulated soil pH as compared to the measured pH for Park Grass (1965–2012) and Sawyers field (1962–1972) at Rothamsted.

Treatment	NRMSE	NMAE
Park Grass		
Control	0.01	0.03
N_1	0.01	0.04
N_1Ca	0.05	0.08
PKS	0.15	0.18
N_2PKS	0.02	0.07
N_2PKSCa	0.05	0.08
Sawyers Field		
N	0.03	0.06
NCa$_1$	0.01	0.02
NCa$_2$	0.03	0.05
NPK	0.03	0.07
NPKCa$_1$	0.01	0.03
NPKCa$_2$	0.03	0.05

3.2. Soil pH, base saturation and Al saturation

Fig. 3 shows the comparisons of simulated and observed relationships between soil pH and BS for PG and SF. Soil sample analyses data from 1903 to 2011 showed a linear relationship between soil pH and BS in the two long-term liming experiments at Rothamsted, which was well fitted by the VSD+ simulation. These results suggest that VSD+ can predict soil pH and BS changes under long-term fertilizer and lime application in non-calcareous soil, although there is a tendency to overestimate the soil pH at a given BS by about 0.4 units in PG and to underestimate it by about 0.1 unit in SF (see the regression equations for the simulations and observations in Fig. 3).

Fig. S4 shows the comparisons of simulated and observed relationships between soil pH and Al saturation for PG and SF. In the grassland (PG), an exponential relationship was observed between soil pH and Al saturation, with exchangeable Al increasing exponentially when soil pH < 4.5. In the arable experiment (SF), Al saturation was close to zero. The predicted Al saturation by VSD+ was slightly higher than observed above pH 4.5, but lower than observed below pH 4.5, indicating that Al exchange is less well described than BC exchange.

3.3. Soil acidification rates and impacts of liming

3.3.1. N budgets and element fluxes

The acidity production in soil is mainly determined by N transformations and furthermore by net H input, net HCO_3 leaching and net BC uptake (see Eq. (3)). To quantify the contribution of N transformations ($NH_{4in} - NH_{4out} + NO_{3out} - NO_{3in}$) to the acidity production, we explored the fate of NH_4 and NO_3 by quantifying the N budgets for PG treatments for 1965–2012 and SF treatments for 1962–1972 (Fig. 4).
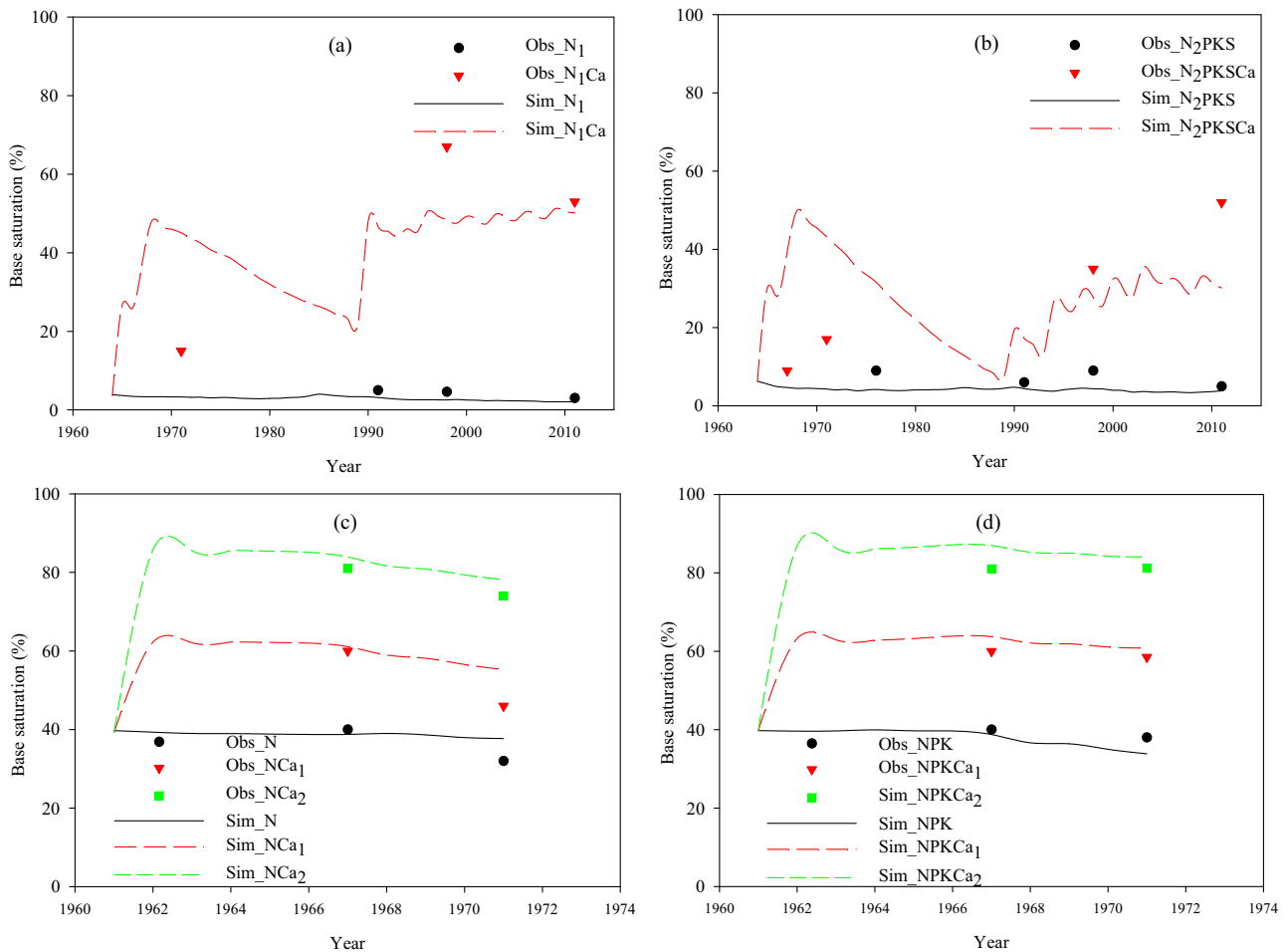

Fig. 2. Base saturation (BS, %) changes simulated by the VSD+ model in the topsoil (0–23 cm) under different fertilization treatments and liming treatments in the Park Grass experiment (a and b 1965–2012) and Sawyers Field (c and d, 1962–1972). N_1, N_2: 48, 96 kg N ha^{-1} yr^{-1} and 55, 110 kg S ha^{-1} yr^{-1}; PKS: 35 kg P ha^{-1} yr^{-1}, 225 kg K ha^{-1} yr^{-1}, 10 kg Mg ha^{-1} yr^{-1}, 15 kg Na ha^{-1} yr^{-1} and 122 kg S ha^{-1} yr^{-1}; Ca: with lime (CaCO$_3$) addition; N: applied as calcium ammonium nitrate in variable amount; PK: 27 kg P ha^{-1} yr^{-1} and 105 kg K ha^{-1} yr^{-1}; Ca$_1$: 5 t CaCO$_3$ ha^{-1} and Ca$_2$: 10 t CaCO$_3$ ha^{-1}, applied in 1962; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965 and the observed base saturation of treatments of Sawyers Field in 1967 were derived from Bolton (1971).
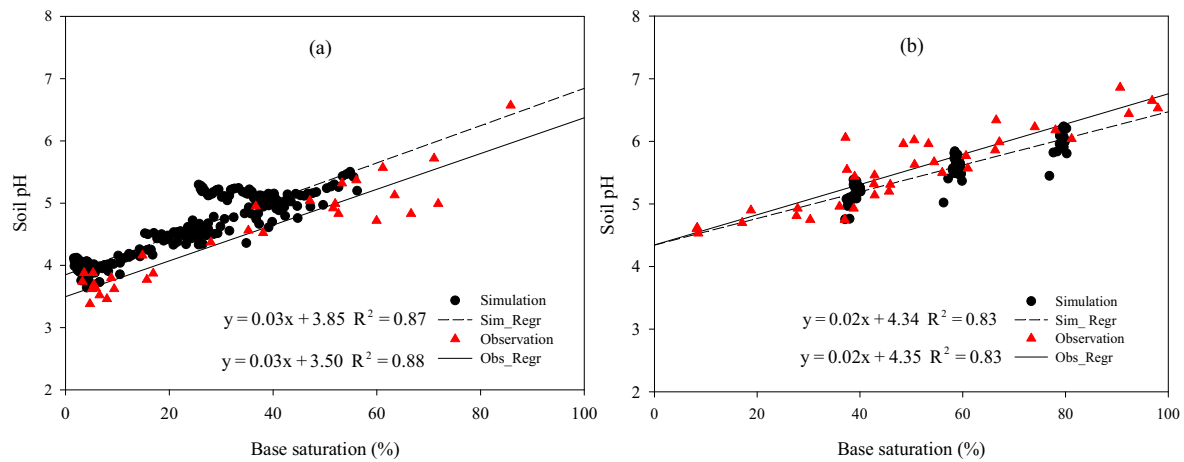
Fig. 3. Soil pH and base saturation simulated by the VSD+ model (●, Simulation) and the trendline (––, Sim_Regr) in Park Grass (a; period 1965–2012) and Sawyers Field (b; period 1962–1972) compared to the observations (▲, Observation) and the trendline (––, Obs_Regr).
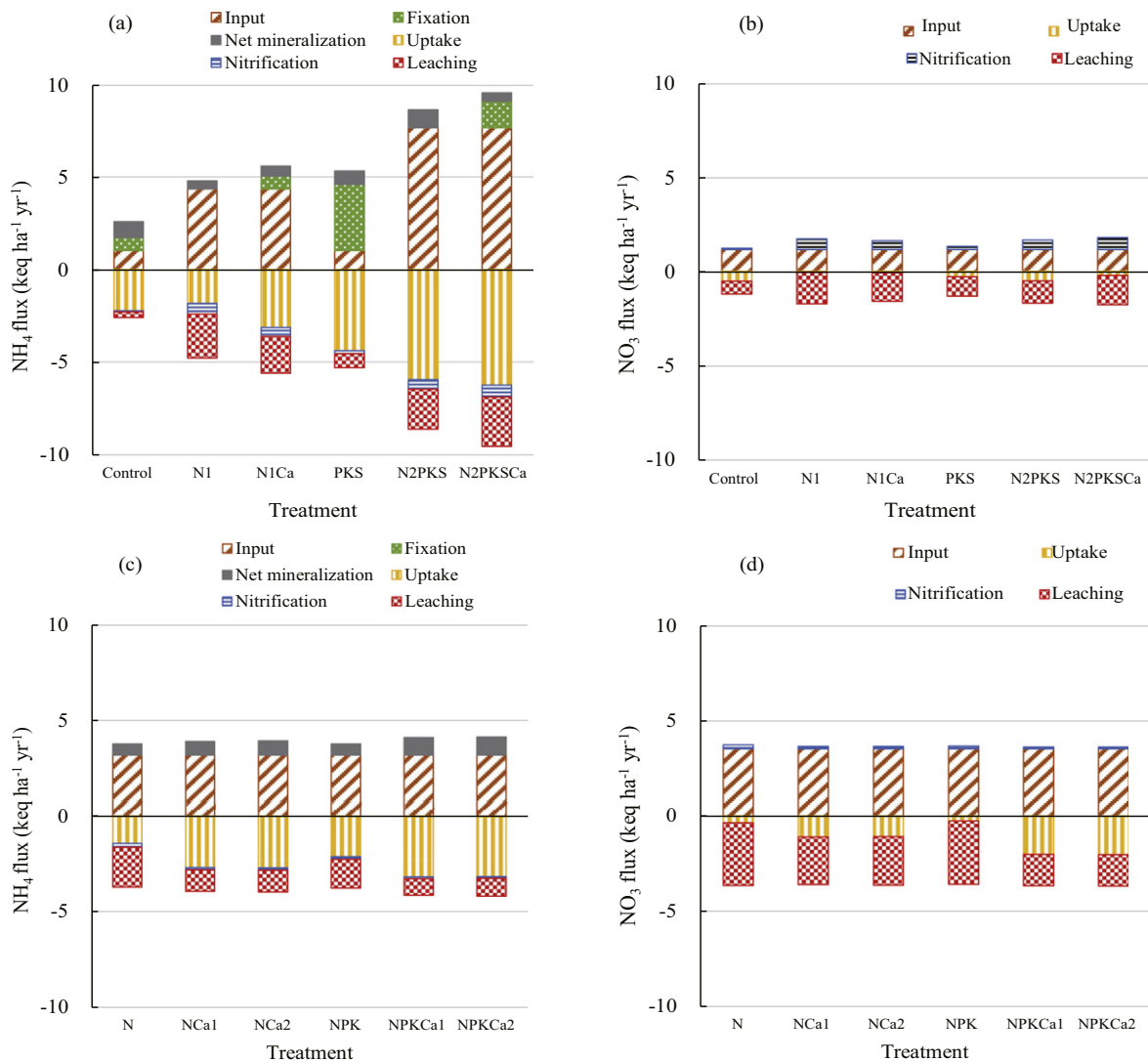

Fig. 4. N budgets simulated by VSD+ for all treatments in Park Grass (a and b; period 1965–2012) and Sawyers Field (c and d; period 1962–1972). Control is no manure or fertilizer input; N_1, N_2: 48, 96 kg N ha^{-1} yr^{-1} and 55, 110 kg S ha^{-1} yr^{-1}; PKS: 35 kg P ha^{-1} yr^{-1}, 225 kg K ha^{-1} yr^{-1}, 10 kg Mg ha^{-1} yr^{-1}, 15 kg Na ha^{-1} yr^{-1} and 122 kg S ha^{-1} yr^{-1}; Ca: with lime (CaCO$_3$) addition; N: applied as calcium ammonium nitrate in variable amount; PK: 27 kg P ha^{-1} yr^{-1} and 105 kg K ha^{-1} yr^{-1}; Ca$_1$: 5 t CaCO$_3$ ha^{-1} and Ca$_2$: 10 t CaCO$_3$ ha^{-1}, applied in 1962; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965. Note that denitrification rates were too low in the two experiments, according to VSD+, to show in this figure, but see Table S6 for details.

In PG, NH_4 input was much higher than NO_3 and most NO_3 was leached. The N_1 and N_2PKS plots, with high NH_4 fertilizer inputs, had greater NH_4 and NO_3 leaching compared to the control plot in PG, but the leaching amount of NH_4 was irrespective of the N input rate. The uptake of NH_4 in the N_1 treatment was lower than in the control plot, in accordance with the lower crop yields (see Table S3), which is likely due to the strong N induced soil acidification (soil pH was ~4) in this plot. The addition of PKS, especially in combination with N, caused a great increase in NH_4 uptake, along with greater crop yields than the control plot (see Table S3). Lime input in PG also increased NH_4 uptake, which had nearly no effect on NH_4 or NO_3 leaching, by comparing N_1Ca and N_2PKSCa to N_1 and N_2PKS, respectively. In SF, addition of P and K fertilizer did not influence N transformations, while lime input increased both NH_4 and NO_3 uptake, leading to less leaching of those N forms. Details of N budgets can be found in Table S6.

The consumption of soil acidity is determined by fluxes of SO_4, H_2PO_4, BC and Al (see Eq. (4)), shown in Table S7. In PG, SO_4 leaching was high in the treatments with SO_4 fertilizer input (Table 1), such as N_1, PKS and N_2PKS, accompanied by at least 70% of the sum of BC and Al leached. Under the N_2PKSCa treatment, the SO_4 leaching rate (16 keq ha^{-1} yr^{-1}) was equivalent to a BC leaching rate of 15 keq

ha^{-1} yr^{-1}, indicating that the high SO_4 input led to severe BC loss from the soil. No Al exchange was found in the control plot in PG, while Al leaching was found in the N_1, PKS and N_2PKS treatment, where the soils were very acidic (soil pH~4 according to the simulations). Unlike PG, for the SF treatments there was surplus BC (input minus leaching) because SO_4 fertilizer inputs were absent, leading to less BC leaching. Al leaching was absent in SF because of the relatively high soil pH.

3.3.2. Acidity production and consumption

Fig. 5 shows the acidity budgets in PG and SF. In PG with NH_4 input from fertilizer, most of the acidity production came from N transformations (64% for N_1 and 48% for N_2PKS), followed by net BC uptake and then net H input, which accounted for 32% and 20% of the total acidity production in N_2PKS, respectively. Long-term addition of NH_4 fertilizer under the N_1 treatment led to decreased BC uptake compared to the control, due to severe soil acidification. In the N fertilized and limed plots (N_1Ca and N_2PKSCa), acidity production from N transformations and net BC uptake was comparable, while net BC uptake dominated acidity production for the control and PKS treatments. Increased BC uptake, due to enhanced crop yield, occurred with lime inputs in the PG
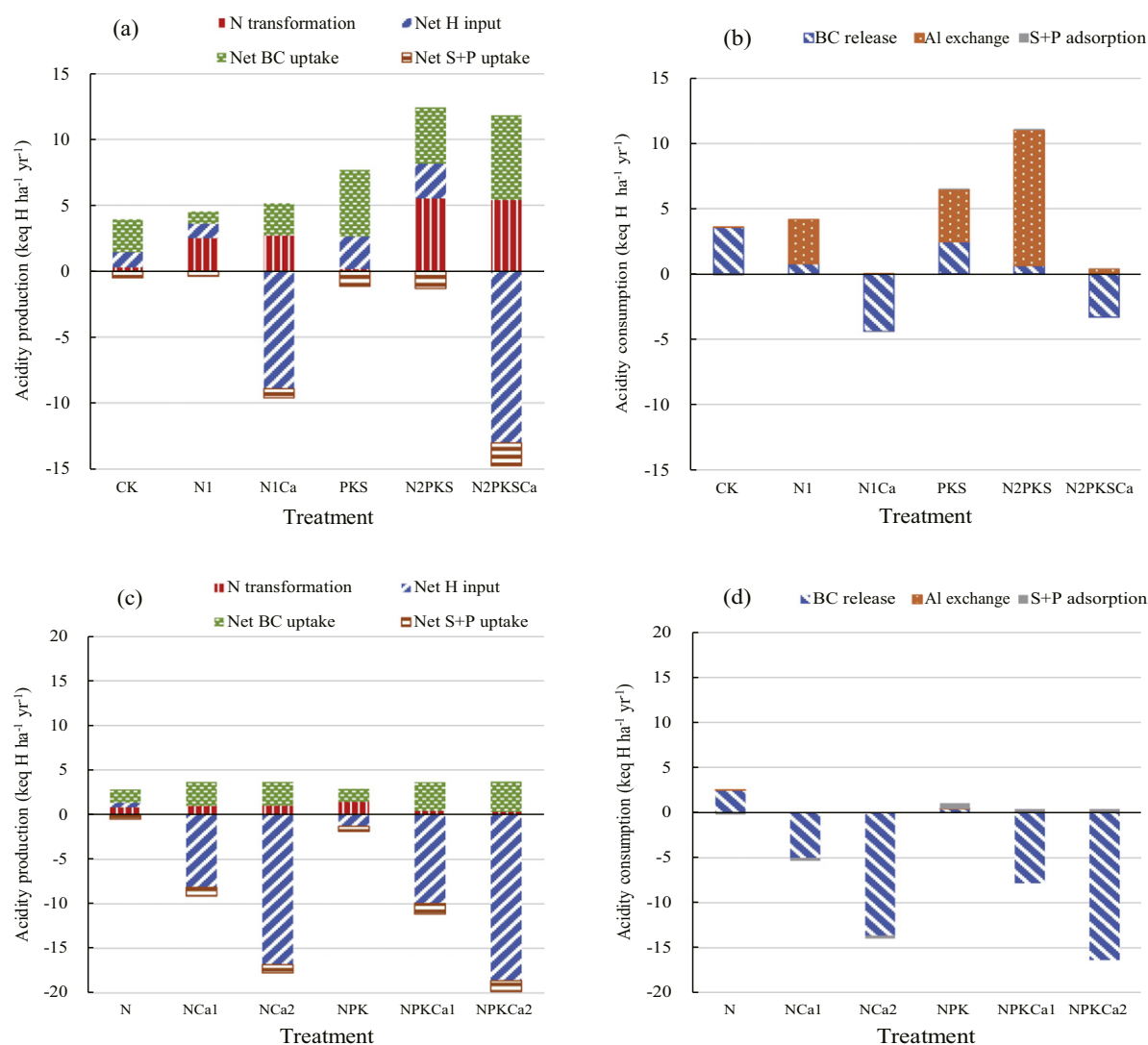

Fig. 5. Acidity budgets simulated by VSD+ for all treatments in Park Grass (a and b; period 1965–2012) and Sawyers Field (c and d; period 1962–1972). Control is no manure or fertilizer input; N_1, N_2: 48, 96 kg N ha^{-1} yr^{-1} and 55, 110 kg S ha^{-1} yr^{-1}; PKS: 35 kg P ha^{-1} yr^{-1}, 225 kg K ha^{-1} yr^{-1}, 10 kg Mg ha^{-1} yr^{-1}, 15 kg Na ha^{-1} yr^{-1} and 122 kg S ha^{-1} yr^{-1}; Ca: with lime ($CaCO_3$) addition; N: applied as calcium ammonium nitrate in variable amount; PK: 27 kg P ha^{-1} yr^{-1} and 105 kg K ha^{-1} yr^{-1}; Ca_1: 5 t $CaCO_3$ ha^{-1} and Ca_2: 10 t $CaCO_3$ ha^{-1}, applied in 1962; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965. Note that net HCO_3 leaching were too low in the two experiments, according to VSD+, to show in this figure, but see Table S8 for details.

treatments. The negative values for net H input under liming at PG were due to neutralization of soil acidity by lime. Simulated soil acidification rates for the PKS and N_2PKS treatments relative to the control were higher due to S fertilizer input and greater BC uptake. For all PG treatments, net HCO_3 leaching was negligible.

In contrast to PG, BC uptake dominated acidity production (about 48% in N treatment) in the SF plots, and N transformations were less important due to the N form applied (calcium ammonium nitrate). In the SF-NPK treatment, the addition of K led to a negative net H input, reducing soil acidification compared to the N treatment. Liming significantly increased net BC uptake, compared to unlimed plots, and decreased acidity in SF (see Table S8 for more details of acidity production of PG and SF in).

As to the acidity consumption, much higher Al exchange was found under NH_4 fertilized treatments (N_1 and N_2PKS) in PG, while lime application decreased Al exchange and reversed BC release in the two liming experiments (Fig. 5). For example, for the PG- N_1Ca treatment, the acidity production from N transformations was 3.8 keq ha^{-1} yr^{-1}, net H input was 1.2 keq ha^{-1} yr^{-1} and BC uptake was 2.4 keq ha^{-1} yr^{-1}, which was counteracted by lime inputs of 10 keq ha^{-1} yr^{-1}, leading to an increase of 2.7 keq ha^{-1} yr^{-1} BC at the exchange complex against H (see Table S8). Under all treatments for both PG and SF, except the N treatment in SF, soil SO_4 adsorption was slightly negative, implying S release and related acidity production (Table S9). Soil P adsorption, however, contributed considerably to acidity consumption in the P treated plots in SF (NPK, NPKCa$_1$ and NPKCa$_2$) and to a lesser extent in the P treated plots in PG (PKS, N_2PKS and N_2PKSCa). In the remaining (zero P) treatments P desorption was simulated and was considerable in SF and low in PG with N_1 in PG being slightly positive.

4. Discussion

4.1. Accuracy of simulated soil acidification by VSD+

4.1.1. Simulated pH trends and acidity budgets in sulphur and phosphors treated plots

The VSD+ model was able to simulate soil pH changes for the two long-term liming experiments and was consistent with the observed changes under fertilizer and lime application, except for the PG treatments including additional fertilizer S inputs (PKS, N_2PKS and N_2PKSCa treatments, with S fertilizer inputs of 122 and 232 kg ha^{-1} yr^{-1}, respectively). For example, observations showed no decrease in soil pH for the PKS treatment in PG from 1965 to 2012, while the VSD+ simulation suggested significant soil acidification. This was caused by a simulated high SO_4 leaching accompanied with BC leaching. The pH behaviour could only be reproduced when using extremely (implausibly) high SO_4 adsorption parameters, but this is not in line with literature information (Foster et al., 1986; Johnson and Todd, 1983; Singh and Johnson, 1986). In soils, SO_4 adsorption is mostly limited and enhanced S inputs lead to increased concentrations of SO_4 in soil solution, enhancing SO_4 leaching from the soil, accompanied with soil BC loss (Reuss et al., 1987). In the control plot, SO_4 leaching was thus calculated at 1.3 keq ha^{-1} yr^{-1} (or 21 kg S ha^{-1} yr^{-1}), accompanied with 40% of the total BC leached, while for the treatments receiving 55 kg S ha^{-1} yr^{-1} (N_1 and N_1Ca), SO_4 leaching increased up to three times (see Table S7). Even a tenfold increase in the SO_4 adsorption constant used (see Table 3) hardly changed those results (not displayed). These results correspond with those reported by McGrath et al. (2003) in England, which suggests 35 kg S ha^{-1} yr^{-1} loss from untreated soil and 83 kg S ha^{-1} yr^{-1} loss from soils receiving 50 kg S ha^{-1} yr^{-1}, in line with the limited S adsorption of soils thus suggesting that the simulated SO_4 leaching in PG by VSD+ is plausible. Hence, it is currently unclear why the observed soil pH under PKS treatment did not decrease considering the high S inputs, both by fertilization and deposition during 1965–2012.

We assumed equilibrium between long-term S deposition and the adsorbed S pool in both PG and SF, since high S deposition from the atmosphere had historically occurred prior to 1960–1985. We made the same assumption for the S treated plots in PG (N_1, N_1Ca, PKS, N_2PKS and N_2PKSCa; see Table 1) since the elevated S inputs took place for >100 years before liming took place in 1965 (from 1856 to 1965). Consequently, we predicted minimal interaction between S in the soil and the soil solution (even a slight S desorption) leading to high S leaching in the S treated plots in PG (see Table S7). For SF the S input was less and, thus, so was S leaching.

There was significant soil P adsorption in the P treated plots in SF. This is because the initial P pool was assumed to be in equilibrium with atmospheric P deposition since P fertilization started in 1962. Unlike SF, adsorption was much lower in the P treated plots in PG since P fertilization had occurred for over 100 years and we assumed an adsorbed soil P pool in equilibrium with these inputs minus crop P uptake. In the untreated P plots, there was significant P desorption to meet the crop P demand. Unfortunately, we did not have data on adsorbed soil P pools (oxalate extractable P). However, measured concentrations of Olsen P (Sodium bicarbonate extractable P, which is widely used to denote the soil available P pools) in the 0–7.5 cm layer in Park Grass in 1992 varied widely under various quantities of mineral P fertilizer application, ranging from 4.0 mg P kg^{-1} in unfertilized plots to 196 mg P kg^{-1} in fertilized plots (McDowell and Condron, 2000).

4.1.2. Simulated and observed pH trends after liming

In general, VSD+ simulated soil pH changes under liming treatments well in PG and SF. One cause for the deviations might be the occurrence of limited lime dissolution rates. Dampney (1985) reported nearly no observed soil pH changes on grassland below 7.5 cm soil depth under a single 20 t ha^{-1} lime application on the surface soil. This indicates that the dissolution rate of lime, buffering the acid production, is likely lower than the simulated instantaneous dissolution of lime. This might be the reason that during 1965–1975, soil pH was not obviously raised by liming in the topsoil (0–23 cm) under grassland in PG. A higher exchange of BC against H than simulated on soil organic matter in the topsoil may also be a reason for a lower soil pH increase (Ritchie and Dolling, 1985) Another cause might be the uncertainty in soil pH measurements. In this study, soil pH was measured in a 1:2.5 soil: water suspension, which tends to be unstable in practice (Kissel et al., 2009; Sumner, 1994). Furthermore, historic soil pH records from e-RA tend to be higher than measured in PG, while in SF, the pH records were lower than the recent measured pH when soil pH is relatively low (~5) but higher if soil pH reached 7 (see Fig. S5). This might be the reason that VSD+ tended to overestimate soil pH in PG and in SF in the N and NPK treatments at low pH (soil pH ~5) and underestimate soil pH at high pH (soil pH >6.5) after liming.

4.1.3. Simulated and observed relationships between pH and base saturation and Al saturation

Simulated BS shows a significant linear relationship with soil pH, which is highly consistent with the analysis of historic soil samples from the two long-term liming experiments. Linear relationships were also reported by Beery and Wilding (1971) on 64 soils from the Great Lakes region, USA, comprising three soil types that vary widely in their physical, chemical, and mineralogical properties. The model could thus simulate long-term fertilization and liming impacts on BS and soil pH quite well in non-calcareous soils. The linear relationships of BS against soil pH proves that soil pH is mainly affected by exchange of BC with protons (H) between pH 4 and 7 (De Vries et al., 1989).

Overall, the simulated Al behaviour was also in line with reported mechanisms in literature. In the PG control treatment, with soil pH > 4.5, no Al exchange was found and BC release mainly consumed soil acidity, in accordance with soil buffer mechanisms (Ulrich, 1991). Thus, Al leaching did not occur in the SF treatments because soil pH remained above 4.5. However, there was a difference in the observed and simulated relationship between Al saturation and pH. In our analyses of the historic soil samples, a significant exponential relationship

was found between Al saturation and soil pH, with Al saturation increasing rapidly below a soil pH of 4.5. Similar patterns in exchangeable Al content with decreases in soil pH were also reported by Blake et al. (1999) at the Park Grass experiment. However, the simulations from VSD+ produced a linear relation between soil pH and Al saturation, highlighting the need for improving Al exchange in VSD+.

4.2. Role of VSD+ in evaluating the potential of agricultural management on acidification

While VSD+ has already been proven to be appropriate for simulating changes in soil pH and BS in three long-term experiments, of various intensive agricultural croplands in China (Zeng et al., 2017), this study showed that the model is also suitable to simulate the liming effects in two long-term fertilization and liming experiments in the UK. In all experiments, the model simulates well with the major buffer mechanisms in soil (De Vries et al., 1989; Ulrich, 1991), and can thus reproduce soil acidification rates at sites with differences in soil/geology, climate and land use in China and the UK. In non-calcareous agricultural soils, with pH values between 4.5 and 6.5, BC exchange is the major buffering mechanism and VSD+ can well simulate the balance of exchangeable cations, considering inputs by fertilization, atmospheric deposition, lime, and removal by plant uptake. Keys for an accurate assessment at a given site are accurate site data on those inputs and on measurements of the CEC and exchangeable cations composition of the soil.

The VSD+ model enables users to assess the main drivers of soil acidification, including N transformations, BC uptake and net H input, under different fertilization regimes and cropping systems. Consequently, VSD+ allows the evaluation of mitigation measures at a regional scale, e.g. in response to changed policies that might cause a risk of BC deficiency. This includes the impacts of changed agricultural management, such as changes in the N fertilizer type (changes in the proportion of NH_4 and NO_3 affecting soil acidification) and replacement of N-fertilizer with manure rich in Ca and Mg. In addition, it can assess the required rate and frequency of lime application, i.e. the required liming amounts and liming intervals in view of the soil acidification rates of for different management approaches, based on a required raise in soil pH and BS.

5. Conclusions

The application of the soil acidification model VSD+ on historic data from two long-term liming experiments at the Rothamsted Research, Harpenden, UK showed a good reconstruction of soil pH and base saturation changes, except for soils with high S fertilization. Furthermore, there was a significant linear relationship between simulated base saturation and soil pH, which is consistent with observations from historic soil samples. Overall, the simulated Al behaviour was also in line with reported mechanisms in literature, but there was a difference in the observed and simulated relationship between Al saturation and pH. In the grassland experiment, N transformations most contributed to acidity production, followed by base cations uptake. The dominant buffering mechanism in this system was Al exchange in the topsoil (0-23 cm), followed by BC release. In the arable rotation experiment BC uptake was the primary cause of soil acidity production, followed by N transformations. Liming was found to supplement BC and decrease Al exchange in the 0-23 cm soil layer. The combination of acidity budgets and robust predictions of soil pH changes indicate that VSD+ can accurately simulate liming impacts on acid neutralizing processes, specifically BC exchange at the soil exchange complex, suggesting a potential use of VSD+ for lime recommendations at regional scale to mitigate soil acidification.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.136249.

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