

Rothamsted Repository Download

A - Papers appearing in refereed journals

Xu, D., Carswell, A. M., Zhu, Q., Zhang, F. and De Vries, W. 2020. Modelling long-term impacts of fertilization and liming on soil acidification at Rothamsted experimental station. *Science of the Total Environment*. 713 (15 April), p. 136249.

The publisher's version can be accessed at:

- <https://dx.doi.org/10.1016/j.scitotenv.2019.136249>
- <https://www.sciencedirect.com/science/article/pii/S004896971936245X?via%3Dihub>

The output can be accessed at:

<https://repository.rothamsted.ac.uk/item/97785/modelling-long-term-impacts-of-fertilization-and-liming-on-soil-acidification-at-rothamsted-experimental-station>.

© 26 December 2019, Please contact library@rothamsted.ac.uk for copyright queries.

Supporting information

Table S1 Chalk applications for Park Grass during 1965-2009.

Year	Chalk applications (t CaCO ₃ ha ⁻¹)	
	N ₁ Ca*	N ₂ PKSCa*
1965	6.3	8.8
1967	3.1	4.4
1968	3.1	4.4
1990	6.7	4.3
1994	0.75	5.1
1997	1.5	2.1
2000	0.75	3.0
2003	0.75	3.0
2006	0.75	1.0
2009	0.75	2.0

* N₁, N₂: 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 (CaCO₃) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.

Table S2 Crop types and fertilizer nitrogen application rates for Sawyers Field during 1962-1972.

Year	Crop*	Variety	Fertilizer N** (kg ha ⁻¹)
1962-1963	Soybeans	Tick 30B	0
1964	Soybeans	Spring Tick	32
1965-1966	Barley	Maris Badger	63
1967	Barley	Maris Badger	94
1968	Potatoes	Majestic	188
1969	Fallow	None	0
1970-1971	Barley	Julia	94
1972	Barley	Julia	90

*: The previous crop is Sugar beet in 1961 with no record, assuming no fertilizer input;

** : Applied as calcium ammonium nitrate with 8% calcium and 24% nitrogen, assuming NO₃: NH₄ =1:1.

Table S3 Average dry matter yields and element contents in the removed herbage under different treatments during 1964-2012 in the Park Grass experiment.

Treatments †	Yield in dry matter (t ha ⁻¹ yr ⁻¹)#	Element contents in herbage (%) §					
		N	P	K	Ca	Mg	S
Control	2.8±0.2	1.7	0.14	1.1	0.88	0.21	0.22
N ₁	1.5±0.2	2.2	0.13	1.2	0.39	0.16	0.33
N ₁ Ca	2.8±0.2	2.0	0.12	0.95	0.98	0.16	0.34
PKS	4.6±0.3	1.8	0.31	2.3	0.73	0.17	0.24
N ₂ PKS	5.6±0.3	2.0	0.25	2.1	0.24	0.13	0.25
N ₂ PKSCa	6.5±0.3	1.7	0.30	2.2	0.62	0.13	0.27

Data presented are mean values, no replicates;

†Control: no manure or fertilizer input; N₁, N₂: 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 (CaCO₃) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965;

#Average values and standard error for yields, which have been recorded every year since 1965 (except the second cut in 2003). Since in 1964, the plot c and d had not been divided and lime was not applied, the yields of which were assumed to equal to the yields in plot d in 1965;

§ Average values for the two cuts during 2000-2012 according to e-RA (the electronic Rothamsted Archive, see more details in <http://www.era.rothamsted.ac.uk/>).

Table S4 Average yields of different crops, lime input and estimated N fixation rates under different treatments at Sawyers Field between 1962-1972.

Treatment*	Lime input (t ha ⁻¹)	Yields of different crops in rotation period (t ha ⁻¹ yr ⁻¹)#				N fixation§ (kg ha ⁻¹ yr ⁻¹)
		1962-1964	1965-1967	1968	1970-1972	
		Soybean	Barley	Potato	Barley	
N	0	1.6±0.4	2.8±1.6	21±0.7	0.4±0.30	360
NCa ₁	5.0	2.7±0.2	4.6±0.6	23±0.9	2.8±1.4	604
NCa ₂	10	2.6±0.3	4.3±1.1	20±1.7	3.3±1.0	579
NPK	0	1.6±0.2	2.9±2.0	31±2.6	1.2±1.1	369
NPKCa ₁	5.0	2.7±0.1	5.2±0.2	37±1.9	4.3±0.7	618
NPKCa ₂	10	3.0±0.1	5.2±0.2	36±0.5	4.5±0.7	684

Data presented are mean values of two replicates

* 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; Ca₁: 5 t CaCO₃ ha⁻¹ and Ca₂: 10 t CaCO₃ ha⁻¹, applied in 1962;

Average values and standard error of all yields in the period from two replicates. The yields for the soybean (grown in 1962-1964, yields in 1962 was missing) and barley are grain yields at 85% dry matter; for potatoes (grown only in 1968) are the fresh weight of tubers at field moisture content. There was a fallow in 1969 and yields for soybean in 1962 were assumed equal to those in 1963. We assumed that there were only inputs by atmospheric deposition and no removal by crops before 1962.

§ Estimation of N fixation rate was calculated by dividing the total amount of N fixed during soybean growth period. The total amount of N fixed for different treatment was estimated based on the yields of soybeans, assuming that approximately 75 kg N ha⁻¹ was fixed under 1 t ha⁻¹ grain yield production, according to Herridge et al. (2008).

Table S5 Element contents in harvested crops in Sawyers Field.

Crop	Element concentration in harvested part (%)					
	N	P	K	Ca	Mg	S
Soybeans	4.5	0.20	0.93	0.89	0.40	0.22
Soybeans (crop residue)	1.5	0.11	1.0	0.49	0.15	0.20
Barley (grain)	1.8	0.34	0.43	0.05	0.10	0.16
Barley (straw)	0.67	0.10	1.1	0.36	0.09	0.18
Potatoes	0.30	0.07	0.44	0.02	0.02	0.02

Data sources: Roy et al. (2006) and Nijhof (1987);

Table S6 Simulated NH₄ and NO₃ budgets for the long-term liming experiments.

Treatment	Sources and fate of NH ₄ (keq ha ⁻¹ yr ⁻¹)					
	Input *	Fixation**	Net mineralization	Uptake	Nitrification	Leaching
<i>Park Grass</i> †						
Control	1.0	0.71	0.85	2.2	0.07	0.29
N ₁	4.4	0	0.44	1.8	0.58	2.4
N ₁ Ca	4.4	0.71	0.54	3.1	0.48	2.0
PKS	1.0	3.6	0.72	4.4	0.18	0.75
N ₂ PKS	7.7	0	0.96	6.0	0.51	2.2
N ₂ PKSCa	7.7	1.4	0.46	6.3	0.63	2.7
<i>Sawyers Field</i> #						
N	3.2	0	0.58	1.4	0.19	2.1
NCa ₁	3.2	0	0.71	2.7	0.12	1.1
NCa ₂	3.2	0	0.73	2.7	0.12	1.1
NPK	3.2	0	0.58	2.1	0.14	1.5
NPKCa ₁	3.2	0	0.91	3.2	0.09	0.87
NPKCa ₂	3.2	0	0.95	3.1	0.09	0.93
Treatment	Sources and fate of NO ₃ (keq ha ⁻¹ yr ⁻¹)					
	Input *	Nitrification	Uptake	Denitrification	Leaching	
<i>Park Grass</i> †						
Control	1.2	0.07	0.51	0.03	0.70	
N ₁	1.2	0.58	0.04	0.01	1.7	
N ₁ Ca	1.2	0.48	0.07	0.06	1.5	
PKS	1.2	0.18	0.27	0.01	1.1	
N ₂ PKS	1.2	0.51	0.50	0.01	1.2	
N ₂ PKSCa	1.2	0.63	0.21	0.03	1.6	
<i>Sawyers Field</i> #						
N	3.6	0.19	0.35	0.00	3.3	
NCa ₁	3.6	0.12	1.1	0.00	2.5	
NCa ₂	3.6	0.12	1.1	0.00	2.6	
NPK	3.6	0.14	0.25	0.00	3.3	
NPKCa ₁	3.6	0.09	2.0	0.00	1.7	
NPKCa ₂	3.6	0.09	2.0	0.00	1.6	

* Input is atmospheric deposition plus fertilization. In Park Grass, there is no NO₃ input by fertilizers since all is applied in the form of ammonium sulphate application (100% NH₄);

** Here we assumed that the N fixation rate was 0% for the N₁ and N₂PKS in Park Grass. In Sawyers Field, N fixation was assumed to be zero since it only occurred during the soybean growth period, which was treated to compensate for N uptake in that period.

† Control: no manure or fertilizer input; N₁, N₂: 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 (CaCO₃) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.

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; Ca₁: 5 t CaCO₃ ha⁻¹ and Ca₂: 10 t CaCO₃ ha⁻¹, applied in 1962.

Table S7. Sulphate (SO₄-S), phosphate (H₂PO₄-P), base cation (BC) and aluminium (Al) inputs and leaching losses for Park Grass (1965-2012) and Sawyers field (1962-1972).

Treatment	Input (keq ha ⁻¹ yr ⁻¹)			Leaching (keq ha ⁻¹ yr ⁻¹)			
	SO ₄	H ₂ PO ₄	BC	SO ₄	H ₂ PO ₄	BC	Al
<i>Park Grass</i> †							
Control	1.6	0.08	1.2	1.3	0.00	2.2	0.00
N ₁	5.1	0.08	1.2	4.8	0.00	0.99	3.4
N ₁ Ca	5.1	0.08	11	4.5	0.00	4.5	0.01
PKS	9.3	1.2	7.8	8.6	0.68	5.2	4.0
N ₂ PKS	16	1.2	7.8	15.3	0.62	4.1	10
N ₂ PKSCa	16	1.2	24	15	0.54	14	0.37
<i>Sawyers Field</i> #							
N	2.0	0.06	2.4	1.7	0.11	3.4	0.00
NCa ₁	2.0	0.06	11	1.4	0.11	3.3	0.00
NCa ₂	2.0	0.06	20	1.4	0.11	3.5	0.00
NPK	2.0	0.93	5.1	1.6	0.15	4.1	0.00
NPKCa ₁	2.0	0.93	14	1.2	0.14	2.7	0.00
-NPKCa ₂	2.0	0.93	22	1.2	0.14	2.7	0.00

* Fluxes of HCO₃ are not included in this table but in the acidity budgets. Na and Cl are assumed to have no interactions with the mineral soil in the VSD+ model and all input of them were leached;

† Control: no manure or fertilizer input; N₁, N₂: 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 (CaCO₃) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.

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; Ca₁: 5 t CaCO₃ ha⁻¹ and Ca₂: 10 t CaCO₃ ha⁻¹, applied in 1962.

Table S8. Acidity production (keq H ha⁻¹ yr⁻¹) for treatments in Park Grass (1965-2012) and Sawyers field (1962-1972). Note that net Cl retention or release is not included.

Treatment	N transformations	Net H input	Net BC [¶] uptake	Net S uptake	Net P uptake	Net HCO ₃ leaching	Total production
<i>Park Grass</i> [†]							
Control	0.28	1.2	2.5	-0.38	-0.13	0.04	3.5
N ₁	2.5	1.1	0.93	-0.31	-0.06	0.00	4.2
N ₁ Ca	2.7	-8.9	2.4	-0.59	-0.11	0.03	-4.4
PKS	0.17	2.5	5.0	-0.69	-0.46	0.00	6.5
N ₂ PKS	5.5	2.6	4.3	-0.86	-0.46	0.00	11
N ₂ PKSCa	5.4	-13	6.4	-1.1	-0.62	0.01	-2.9
<i>Sawyers Field</i> [#]							
N	0.84	0.53	1.5	-0.36	-0.13	0.02	2.4
NCa ₁	1.0	-8.2	2.7	-0.71	-0.24	0.06	-5.3
NCa ₂	1.1	-17	2.6	-0.70	-0.24	0.14	-14
NPK	1.5	-1.3	1.4	-0.42	-0.16	0.02	1.1
NPKCa ₁	0.44	-10	3.3	-0.87	-0.30	0.07	-7.4
NPKCa ₂	0.36	-19	3.4	-0.90	-0.31	0.18	-16

[†] Control: no manure or fertilizer input; N₁, N₂: 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 (CaCO₃) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.

[#] 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; Ca₁: 5 t CaCO₃ ha⁻¹ and Ca₂: 10 t CaCO₃ ha⁻¹, applied in 1962;

§ Note that this is consumption due to added lime;

* Liming impacts were included; for N₁Ca and N₂PKSCa in Park Grass, they were -10.2 and -17.1 keq H ha⁻¹ yr⁻¹, respectively and for Ca₁ and Ca₂ treatment in Sawyers Field, they were -7.5 and -15.1 keq H ha⁻¹ yr⁻¹.

Table S9. Acidity consumption ($\text{keq H ha}^{-1} \text{ yr}^{-1}$) for Park Grass experiment (1965-2012) and Sawyers field (1962-1972).

Treatment	BC release	Al exchange	S adsorption	P adsorption	Total consumption¶
<i>Park Grass</i> †					
Control	3.5	0.00	0.02	-0.04	3.5
N ₁	0.78	3.4	-0.02	0.02	4.2
N ₁ Ca	-4.4	0.01	-0.01	-0.03	-4.4
PKS	2.5	4.0	-0.01	0.07	6.5
N ₂ PKS	0.64	10	-0.03	0.13	11
N ₂ PKSCa	-3.3	0.37	-0.02	0.05	-2.9
<i>Sawyers Field</i> #					
N	2.5	0.00	0.03	-0.18	2.4
NCa ₁	-5.0	0.00	-0.04	-0.29	-5.3
NCa ₂	-14	0.00	-0.03	-0.29	-14
NPK	0.44	0.00	-0.01	0.63	1.1
NPKCa ₁	-7.8	0.00	-0.07	0.49	-7.4
NPKCa ₂	-16	0.00	-0.05	0.48	-16

† Control: no manure or fertilizer input; N₁, N₂: 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 (CaCO₃) addition; note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965.

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; Ca₁: 5 t CaCO₃ ha⁻¹ and Ca₂: 10 t CaCO₃ ha⁻¹, applied in 1962;

¶ The total H consumption is calculated by the sum of BC release and Al exchange.

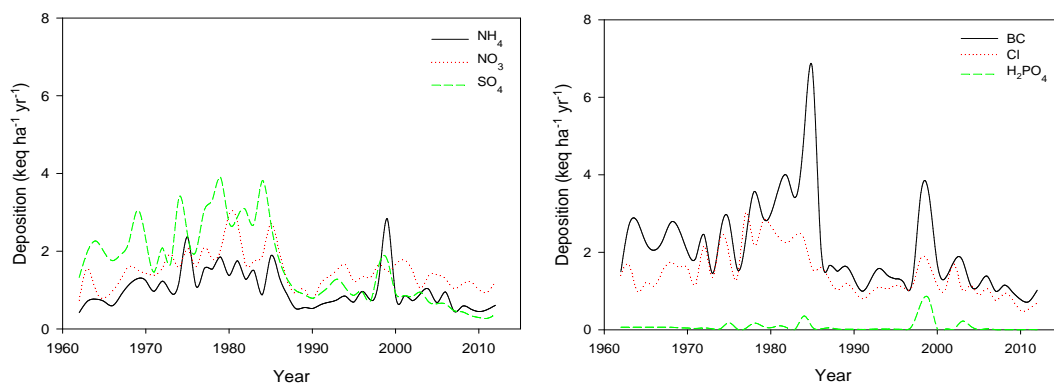


Fig. S1 Reconstruction of total atmospheric deposition of sulphate (SO₄), nitrogen (NH₄ and NO₃), chloride (Cl), phosphorus (H₂PO₄) and base cations (BC, sum of K, Na, Ca and Mg) at Rothamsted Research (1962-2012). Total deposition values were estimated by multiplying wet deposition with a total:wet deposition ratio of 2.2 for NH₄ and 2 for SO₄, BC, Cl and H₂PO₄. For NO₃, the ratio was set at 4.2 in 1962-1990 and 5.0 in 1990-2012. Wet deposition was derived from e-RA (1962-1991; <http://www.era.rothamsted.ac.uk/>) and ECN (1992-2012; <http://www.ecn.ac.uk>).

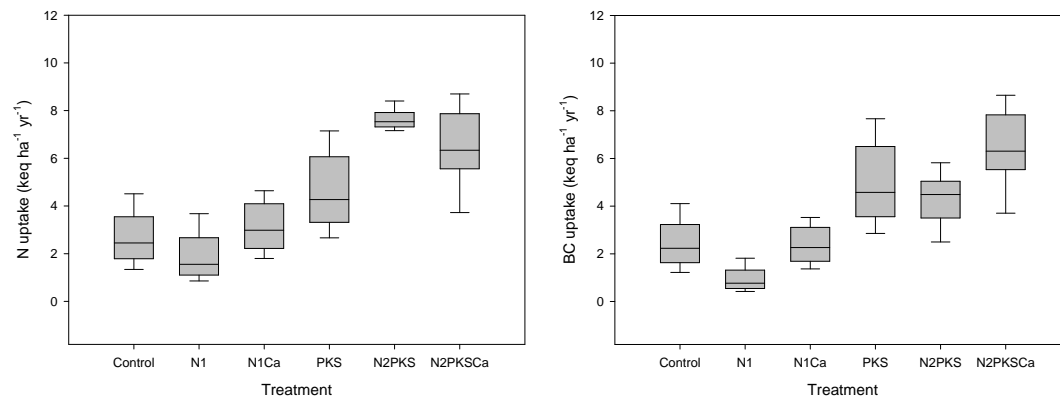


Fig. S2 Variation of N and BC uptake for different fertilizer and lime treatments in Park Grass during 1965-2012. The line within the box represent the median values; the bottom and top edges of the box represent 25 and 75 percentiles of all data, respectively; and the bottom and top bars represent 10 and 90 percentiles, respectively.

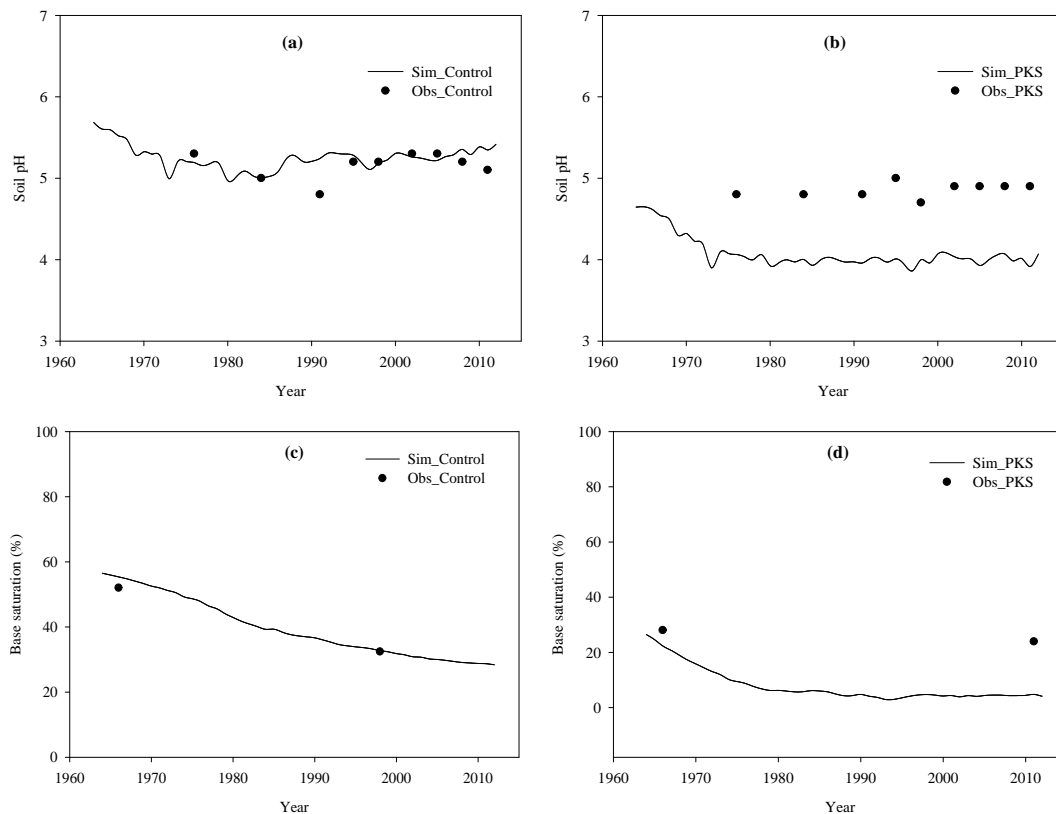


Fig. S3 Reconstruction of soil pH (a and b) and base saturation (c and d) changes by the VSD+ model for the Park Grass experiment (1965-2012). Control is no manure or fertilizer input; PKS: 35 kg P ha⁻¹ yr⁻¹, 225 kg K ha⁻¹ yr⁻¹, 10 kg Mg ha⁻¹ yr⁻¹, 15 kg Na ha⁻¹ yr⁻¹ and 122 kg S ha⁻¹ yr⁻¹. Note that the inputs of N and of PKS in Park Grass were already given since 1856, while liming started in 1965. The observed base saturation data after 1990 were estimated according to the observed soil pH (which is relatively constant in that 10 years, see a and b) and the observed pH-BS relationship (see Fig. 3) because of the missing measurement in this period.

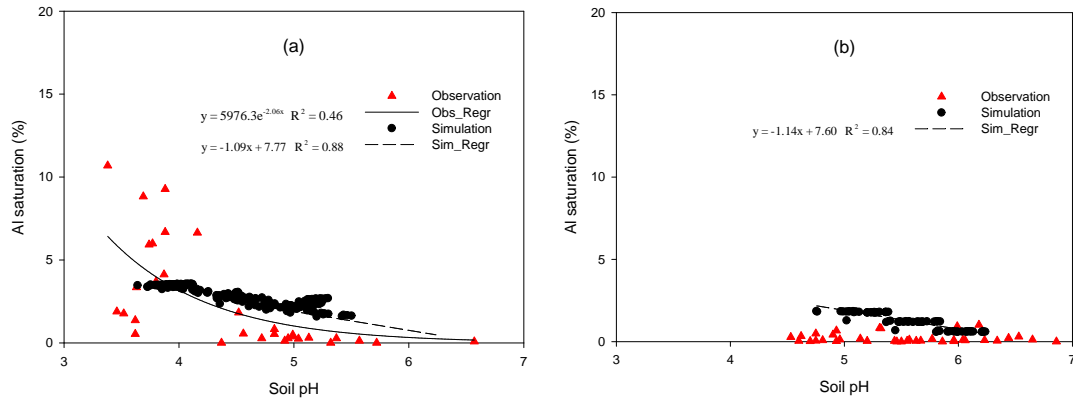


Fig. S4 The relation between aluminium (Al) saturation and Soil pH as simulated by the VSD+ model (●, Simulation) and the trendline (----, Sim_Regr) in Park Grass (a; period 1965-2012) and Sawyers Field (b; period 1962-1972) compared to the observations (▲, Observation) and the trendline (—, Obs_Regr). Note that Al saturation in Sawyers Field was close to zero and thus no regression could be made.

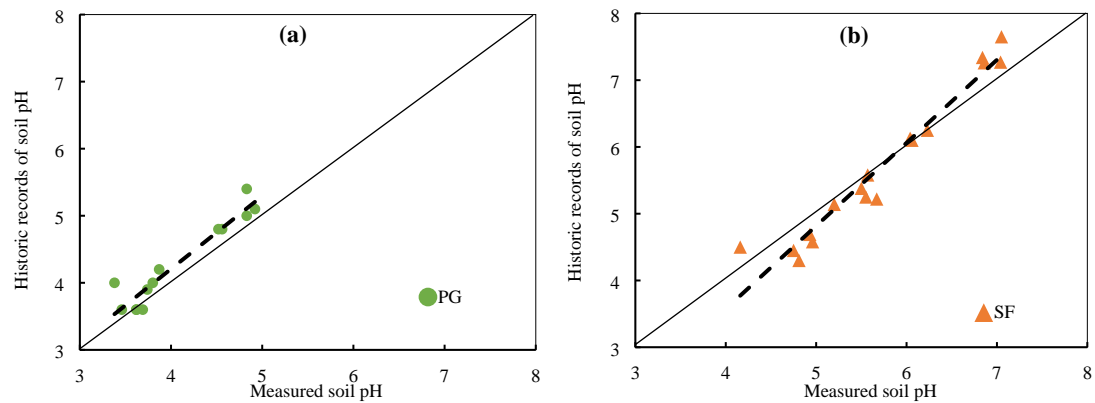


Fig. S5 Comparison of historic records of soil pH from e-RA and recent measured soil pH in the two long-term liming experiments (1965-2011 for Park Grass (a); 1971 for Sawyers Field (b)). Solid lines in the figures represent the 1:1 line and dashed lines are fitted lines for the relationships.