



Ecochemical effects of phonolite rock powder, dolomite and potassium sulfate in a spruce stand on an acidified glacial loam

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Abstract

In a field experiment, the ecochemical effects of soil amelioration with dolomite, phonolite rock powder and fertilization with potassium sulfate were compared. By dolomite and phonolite the acid-neutralizing capacity of the soil and the pH level should be stabilized. In addition, the correction of a latent potassium deficiency in spruce stands at acidified glacial loams was intended. In comparison to fertilizing with potassium sulfate liming as well as the application of phonolite rock powder showed a prominent improvement of the soil chemical status already within the first 4–5 years. Both treatments increased the base saturation, the dolomite to a depth of 60 cm, the phonolite to a depth of 30 cm. At the limed plot, strong nitrate leaching occurred with peaks at 80 cm soil depth higher than the EU threshold for drinking water. In the phonolite plot this also occurred, but the nitrate concentrations remained lower. The silicate rock powder reacted more slowly than dolomite. Thus, we can state that silicate rock powder can be an alternative to conventional liming in regions where the risk of nitrate mobilization is high and especially at water preservation areas where special care has to be observed. But the phonolite which was used in this experiment released a considerable amount of sodium, which disturbed the amelioration effect. In practice, it would be better to use a silicate rock powder with a low sodium content. Fertilization with potassium sulfate provided a fast nutritional effect but displayed no potential for soil chemical amelioration.

Introduction

At the glacial loams in the pre-mountainous area of Oberschwaben, Southwest Germany, a latent deficiency of potassium supply occurs in spruce stands (Zöttl and Hüttl 1985; von Wilpert and Hildebrand 1994). The potassium supply shows a certain fluctuation with weather conditions. In dry seasons, the potassium supply decreases and in rainy periods it recovers. The pool of plant available potassium is normally sufficient, but its spatial distribution in the soil matrix limits the uptake (Hildebrand 1994). In dry periods, the diffusive transport of potassium from the inner parts of soil aggregates to their surfaces is interrupted. The roots of trees live in macropores on

the surface of soil aggregates, because they need oxygen. This is the reason why they cannot reach the potassium stock in the soil aggregates, especially in dry periods. Even mycorrhiza hyphae with their small diameter do not penetrate soil aggregates because of the oxygen deficiency inside the aggregates, as von Wilpert et al. (1996) have demonstrated in laboratory experiments.

A fertilization experiment was set up at Ochsenhausen to test the potential of various chemical forms of potassium and of lime for long-term improvement of the potassium supply, as well as their potential for chemical soil amelioration. The conventional way of managing disturbances of forest nutrition is to provide the deficient element in a soluble

form. This would be a neutral salt such as potassium sulfate. But the application of neutral salts would have no potential for soil chemical amendment aside from their nutritional effect, because the cation of a strong base is bound to an anion of a strong acid so that the alkalinity of the soil solution is not altered by introducing a neutral salt into the ecosystem. Thus, it has to be expected, that fertilization with neutral salts will have a more or less short-term ecological effect. Another, more sustainable strategy would be the stabilization of the soil chemical status by introducing buffer substances, that are bound to anions of weak acids (H_2CO_3 or H_4SiO_4). Because carbonates or silicates have a comparatively low solubility, they would cause a slow increase of soil pH and a slow release of substances with a nutritional and buffering effect. The increase of soil pH would gradually ameliorate the living conditions of soil organisms. Thus, the rate of bioturbation would increase, improving the ability of roots and mycorrhiza to access the potassium reserves contained in soil aggregates (Hildebrand 1994).

Buffer substances can be introduced into forest ecosystems by liming or by application of silicate rock powder. In this paper we compare the effects of the application of a silicate rock powder, liming and potassium sulfate fertilizing on the soil solution chemistry, on the composition of the exchangeable ion pool, and on tree nutrition. The hypothesis is, that both, the dolomite and the phonolite rock powder, cause a long-term increase of soil pH and base saturation. The effect of silicate rock powder is expected to be slower than that of dolomite liming, so that side effects, e.g. a surplus in nitrification, will be lower. Silicate rock powder contains potassium, so a certain nutritional effect can be expected, whereas by liming, no additional potassium is introduced into the system. In the context of potassium deficiency, liming is not the usual procedure, since it is only the deblocking and release of intra-aggregate potassium that is intended. We expected, that the fertilization with potassium sulfate would have a fast nutritional effect. It shall be clarified by the trial, how severe side effects caused by its high solubility would be.

Material and methods

The fertilization trial was installed in a homogeneous, 65 year old spruce stand. The substrate consists of Riss moraine loams on which gleyic luvisols have

developed. The soil varies from an acidic luvisol to gleyic luvisol. The humus layer is characterized as between moder and raw-humus with a thickness between 4 and 10 cm (Ol 0.5–2 cm, Of 1–4 cm, Oh 0.5–5 cm). The $\text{pH}(\text{H}_2\text{O})$ value ranges between 3.7 and 4.1 in the Ah and Al-horizons. In the Sw-Bt-horizon, at the depth of 30–60 cm, the $\text{pH}(\text{H}_2\text{O})$ increases to values of 4.2–4.3. The regional climate is cool-humid with an average precipitation of 950 mm/a and a mean temperature of 7.2°C.

Both the dolomite and the phonolite rock powder were finely ground to increase the rate of dissolution which occurs at the particle surface. The grain size <0.1 mm amounted to more than 90 weight-percent. The geologic origin of the fertilizers are Jurassic dolomite with a carbonate content >90% and volcanic phonolite originating from the Kaiserstuhl mountain in the upper Rhine valley. A special characteristic of the phonolite is its content of hydrothermal minerals like zeolites (e.g. natrolite), which provide an ion exchange capacity (Wimmenauer 1989). The content of nutritional and the most important ecochemical elements of the dolomite and the phonolite is referred to in Table 1. The chemical composition of the phonolite was characterized by two extracts, the digestion in HNO_3 under pressure which did not crack the stable silica lattices, and the digestion in HF, which was a total extract dissolving the silicates completely. Moreover the content of water soluble elements was determined by a cold water pre-extract (2.5 g solid substance, percolated with 100 ml deionized water), and then the cation exchange capacity (CEC) of the phonolite was determined by percolation with 100 ml 1M NH_4Cl .

The dolomite was characterized by high contents of calcium and magnesium and very little potassium. In the phonolite, the neutral cations calcium, potassium and sodium are dominant; magnesium was nearly lacking. In comparing the extracts of the phonolite material, we found that potassium, magnesium and calcium fractions display different solubilities. The calcium content was predominantly soluble, whereas potassium and magnesium were obviously bound in stable crystalline lattices. The content of water soluble elements was low in the phonolite rock powder. It amounts to about 0.1% of the total element content. In contrast, the CEC, that was calculated as sum of the exchangeable cations in Table 1, was with 833 $\mu\text{mol}_\text{c} \text{ g}^{-1}$ ($c_v = 2.7\%$) comparatively high (Table 1). Blum et al. (1989a) found in volcanic ashes a CEC of 459 $\mu\text{mol}_\text{c} \text{ g}^{-1}$ and in diabas rock powder, 176

Table 1. Chemical composition of the dolomite and phonolite used for the experimental fertilization. In the phonolite were water soluble salts (cold water preextract), the exchangeable ion pool (percolation with 1M NH₄Cl) and the total element content in two different solubilities (digestion in HNO₃ and HF) distinguished.

	Dolomite		Phonolite				
	(weight %)		(weight %)				
		***		*	**	***	****
pH	9.4		10.1				
Ca		22.4		0.024	0.91	5.4	5.9
Mg		10.5		0.00049	0.012	0.32	0.6
K		0.1		0.0018	0.024	0.11	4.23
Na		n.m.		0.041	0.83	n.m.	4.37
P		0.64		n.m.	n.m.	0.02	0.04
S		3.71		n.m.	n.m.	1.28	n.m.

n.m. : not measured; * Preextract in cold water; ** Exchangeable cations (percolation with 1M NH₄Cl); *** digestion in HNO₃ under high pressure; **** Digestion in HF, total element content n.m. not measured

$\mu\text{mol}_c \text{ g}^{-1}$. In the phonolite rock powder used in our trial, about 15% of the total calcium content and nearly 20% of the sodium content were exchangeable.

The fertilization trial was established in April 1994. The doses were 10 Mg ha⁻¹, at the dolomite plot as well as at the phonolite plot. The potassium sulfate plot was fertilized with 1 Mg ha⁻¹. These doses met the order of magnitude which is used in the amelioration practice, where the normal dose in South Germany is 3–4 Mg ha⁻¹ for liming and 0.5 Mg ha⁻¹ for potassium sulfate fertilizing (Evers 1991; Schüler 1992; Beese and Meiwes 1995). In the present fertilizing experiment, one to two times higher doses were chosen compared to the current practices, because in the experiment the effects of the fertilizer application should be slightly increased for better interpretation of the characteristic effects that the different fertilizers display. Thus, in the experiment the ecological risks of overdoses – which lie in the range of realistic variations such as irregularities caused by fertilizer distribution in the forest – can be assessed.

The total input of neutral cations summed up to 10.6 kmol_c ha⁻¹ at the potassium sulfate plot, to 65.4 kmol_c ha⁻¹ at the phonolite plot and to 217.4 kmol_c ha⁻¹ at the dolomite plot. The potassium input was about 11 kmol_c ha⁻¹ at both, the potassium sulfate and the phonolite plots.

The dissolution rate of dolomite is independent of the dolomite pool at high doses. It is limited mainly by the availability of CO₂ for formation of hydrogen carbonate (Hildebrand and Schack-Kirchner 1995). Little interactions with soil processes, such as the impact of strong acids, influence the dissolution of dolomite, because the dolomite is applied onto the surface of the humus layer. According to model

experiments of Hildebrand and Schack-Kirchner (1995), we can assume a more or less constant ion flux caused by the dissolution of dolomite within the first 5 to 6 years at the dolomite plot. At the phonolite plot the low solubility of silicates controls the ion flux in the long-term.

The experimental plots were 0.25 ha in area for long-term inventory work concerning changes in ground vegetation and in structure of the humus layer. In each plot, an intensively equipped 16 m² subplot was established at which the fertilizer was distributed as exactly as possible on the basis of single square meters. The intensively equipped subplots of each treatment were grouped in the center of the experimental site. The soil solution was collected by suction lysimeters at 14 day intervals. The lysimeter cups (ceramic cups with pores <0.45 μm) were inserted immediately below the humus layer and in the mineral soil at a depth of 20 cm and 80 cm. The soil solution was quasi continuously sampled by pumping every 8 hours for half an hour to maintain a suction between 300–400 hPa and the surrounding matrix potential. At each depth, three replications were installed at a spacing of 30–50 cm. The soil solutions from the three replications were combined in one duran bottle as a mixed sample for each depth. Thus, the soil solution samples represent a “pedon” with an 1–2 m² area. On the same subplots, tensiometers (3 in each depth as well) were installed, which, in combination with meteorological data, allowed calculation of the soil water flux using the water-flux model WHNSIM (Huwe and Totsche 1995). Sodium fluxes were calculated by multiplication of measured sodium concentrations in the soil solution with the water fluxes that we calculated by use of the water model.

At each experimental plot, three to five randomized soil profiles were dug in autumn 1998 and spring 1999. This was four to five years after the fertilizer application. At each soil profile, at the depth intervals 0–5 cm, 5–10 cm, 10–30 cm and 30–60 cm in the mineral soil, soil samples were collected from three profile walls (about 50 cm length). From these soil samples the exchangeable ions were extracted by percolation with 1M NH_4Cl in a soil/solution ratio of 2.5 g/100 ml. The differences between treatments were tested by an unpaired t-test procedure of the SAS statistical package (SAS Institute Inc., SAS/STAT 1990).

In winter 1996/1997 at each plot from 5 trees the needles from the upper crown (7th – 9th whorl) were sampled. One and three year-old needles were collected separately. For each age group samples were combined over the five trees.

Soil solutions were filtered (0.45 μm) before chemical analysis. In the soil solutions, the cations were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP), dissolved organic carbon (DOC), phosphate and ammonium by photometry and the anions sulfate and nitrate by ion chromatography (IC); pH was measured with a glass electrode. In soil samples, the pH was measured in H_2O and in 1M KCl with a soil/solution ratio of 1/2.5 shaken for 4 hours. The needles were digested in HNO_3 under pressure, cations and P were assayed by ICP. The total N content was analyzed with the Kjeldahl method. All analytical methods were used according to the analytical manual for the German soil survey (Federal Ministry of Food, Agriculture and Forestry 1990).

Results

Even at the early stage of the experiment, four to five years after fertilizer application, the composition of the soil solutions of all fertilized plots, as compared to the untreated plot, showed a pronounced shift in the chemical characteristics. Time series of element concentrations in the soil solution showed initial solution effects caused by the fertilizers. Here we have focused on the uppermost soil layer to show the initial solution processes in the most sensitive and biological active compartment of the soil. Some risks for the groundwater like leaching of aluminum or nitrate could be assessed at 80 cm soil depth, below the rooting zone. Longer-term chemical changes could be presented by the composition of the exchangeable cations (Table

2). Moreover initial nutritional effects could be presented.

Effects of potassium sulfate application on soil solution

The high solubility of potassium sulfate induced an intense transport pulse of potassium in the soil solution which exceeded the uptake capacity of tree roots (Figure 1). The high ionic strength in the soil solution caused heavy exchange processes such as the release of high amounts of aluminum (Figure 2) within the rooting zone (20 cm) which is potentially toxic for roots and can be interpreted as a transfer of acidity into the subsoil because it releases protons by hydrolysis and thus causes an acidification risk for the groundwater. After potassium sulfate fertilization, the Al concentrations in the soil solution at 80 cm depth were 10–50 times higher than 0.2 mg l^{-1} , the EU threshold for drinking water quality (Figure 2). This applied for the whole 5 years observation period. At the control plot the Al-concentrations usually remained below this threshold. The Al concentrations at 80 cm depth at the dolomite and phonolite plots scattered around 0.2 mg l^{-1} .

Effects on soil solution pH

With the application of dolomite and phonolite, it was intended on the one hand to introduce buffer substances into the forest soil so that the current acid input from air pollution could be neutralized; on the other hand, step by step the soil pH should gradually increase so that more favorable living conditions would develop for biological soil activity. Figure 3 shows the increase of the pH value in the soil solution below the humus layer, and at 20 cm depth.

Also at the Phonolite plot, a few weeks after fertilization, the pH value began to increase prominently below the humus layer. Within the first year, the difference to the pH at the control plot reached about 1 pH unit. This pH increase remained more or less stable throughout the observation period. This fast and comparatively high increase of the pH value after fertilization with phonolite was unexpected because of the low dissolution rate of silicates. In the depth of 20 cm, the difference in soil solution pH between the control plot and the phonolite plot did not exceed 0.5 pH units.

The pH below the humus layer in the dolomite plot

Table 2. Exchangeable cations (in 1M NH₄Cl extract), pH and base saturation (BS) at the control-, potassium sulfate-, the dolomite- and the phonolite plots 4–5 years after the fertilization. Bold values are in the t-test at p = 5% different from the control, bold and italicized values at p = 1%, * = significant differences between treatments, standard deviations in brackets

plot	depth	pH	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Al ³⁺	Fe ²⁺	H ⁺	CEC	BS
	[cm]	H ₂ O	(μmol _c /g)								%
control	0–5	3.73	0.36	0.90	2.27	1.58	126.67	8.52	9.54	150.63	3.37
		(0.07)	(0.07)	(0.20)	(0.93)	(0.19)	(13.05)	(2.75)	(1.99)	(17.88)	(0.40)
	5–10	4.07	0.29	0.69	0.80	0.71	92.93	1.11	2.56	101.37	2.43
		(0.08)	(0.07)	(0.20)	(0.26)	(0.19)	(14.90)	(0.31)	(0.53)	(16.78)	(0.40)
potassium sulfate	10–30	4.29	0.19	0.54	0.47	0.33	55.67	0.18	0.81	59.70	2.57
		(0.05)	(0.02)	(0.14)	(0.15)	(0.05)	(2.32)	(0.05)	(0.46)	(2.36)	(0.51)
	30–60	4.24	0.27	0.75	0.63	0.43	51.37	0.07	0.89	56.03	3.73
		(0.10)	(0.12)	(0.13)	(0.15)	(0.06)	(7.84)	(0.02)	(0.51)	(8.84)	(0.25)
phonolite	0–5	3.65	0.48	0.97	2.87	1.80	154.37*	13.04	9.93	183.80	3.40
		(0.08)	(0.17)	(0.41)	(1.98)	(0.49)	(16.39)	(2.71)	(1.00)	(17.80)	(1.78)
	5–10	3.90	0.31	0.71	1.03	0.90	126.73*	5.08	4.13	140.17	2.17
		(0.13)	(0.15)	(0.16)	(0.32)	(0.17)	(19.01)	(3.72)	(2.03)	(23.46)	(0.64)
dolomite	10–30	4.25	0.27	0.60	0.87	0.45	77.90	0.41	0.98	83.10	2.63
		(0.05)	(0.01)	(0.13)	(0.38)	(0.20)	(4.62)	(0.06)	(0.63)	(4.65)	(0.84)
	30–60	4.25	0.26	0.74	0.97	0.36	51.67	0.14	0.72	55.93	4.13
		(0.01)	(0.09)	(0.11)	(0.64)	(0.17)	(1.26)	(0.05)	(0.51)	(2.48)	(1.19)
phonolite	0–5	4.04	2.27	0.94	15.30	2.08	129.13	8.90	7.07	166.25	12.23
		(0.09)	(0.64)	(0.33)	(6.03)	(0.65)	(6.67)	(1.77)	(1.92)	(14.62)	(3.70)
	5–10	4.18	1.72	0.74	5.03	1.16	121.18	5.23	3.78	139.55	6.05
		(0.16)	(0.59)	(0.28)	(2.69)	(0.42)	(23.06)	(2.95)	(1.85)	(29.40)	(1.95)
dolomite	10–30	4.50	0.73	0.50	0.98	0.30	58.53	0.23	0.39	62.53	4.05
		(0.09)	(0.14)	(0.28)	(0.48)	(0.04)	(4.69)	(0.05)	(0.23)	(4.92)	(1.06)
	30–60	4.45	0.40	0.43	0.45	0.17	34.33	0.06	0.19	36.68	3.95
		(0.06)	(0.04)	(0.13)	(0.21)	(0.04)	(9.13)	(0.02)	(0.12)	(9.41)	(0.37)
dolomite	0–5	4.27	0.64	1.14	38.78	35.20	78.90*	5.76	6.64	168.10	45.08
		(0.30)	(0.09)	(0.29)	(22.56)	(13.61)	(30.66)	(2.53)	(3.43)	(4.51)	(21.42)
	5–10	4.19	0.55	0.82	13.28	12.16	102.40*	3.53	4.98	139.20	19.50
		(0.11)	(0.17)	(0.10)	(5.03)	(2.76)	(13.56)	(2.17)	(1.52)	(11.99)	(4.99)
dolomite	10–30	4.50	0.38	0.48	4.95	3.22	67.43	0.36	1.24	79.38	11.28
		(0.09)	(0.04)	(0.09)	(2.75)	(1.60)	(9.27)	(0.20)	(0.26)	(10.33)	(4.96)
	30–60	4.47	0.27	0.46	1.68	0.98	40.60	0.15	0.64	45.95	7.33
		(0.06)	(0.04)	(0.08)	(0.50)	(0.40)	(3.29)	(0.06)	(0.19)	(4.00)	(1.61)

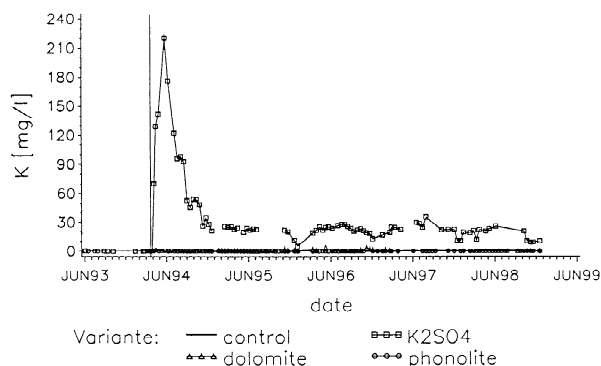


Figure 1. Potassium concentrations in the soil solution at 20 cm depth for phonolite-, dolomite-, potassium sulfate treatment and control. Vertical reference line = time of fertilization.

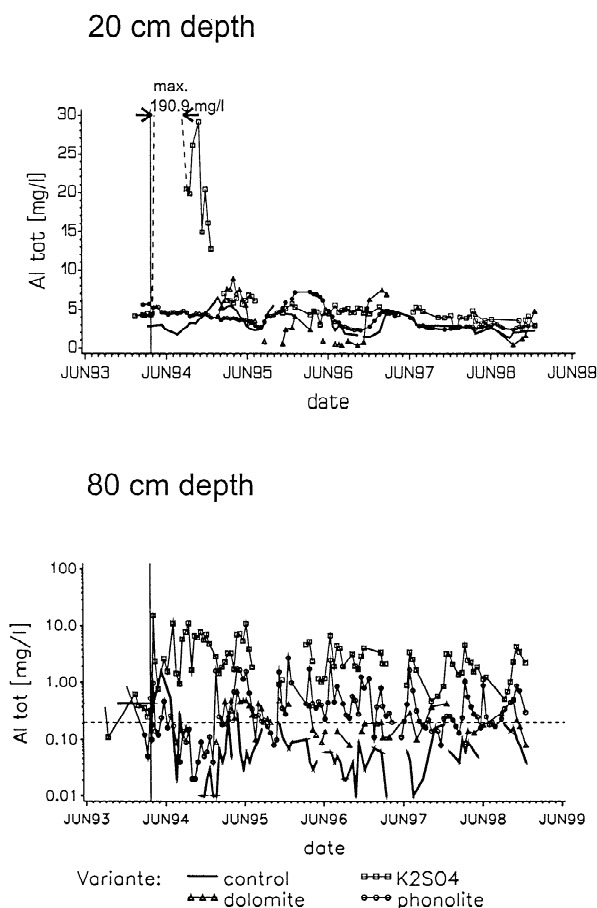


Figure 2. Aluminum concentrations in the soil solution at 20 cm depth (top) and 80 cm depth (below) for phonolite-, dolomite-, potassium sulfate treatment and control. Vertical reference line = time of fertilization. Horizontal reference line = EU threshold of Al concentrations for drinking water (0.2 mg/l).

reached values of up to 7.5, about 2–2.5 pH units higher than in the phonolite plot. Dolomite is the only treatment where the pH at 20 cm depth was also markedly increased. But it was single peaks that reached values up to 2.5 pH units higher than at the other plots rather than a consistently increased level as below the humus layer.

Potassium sulfate caused a sharp pH decrease of about 0.5 pH units that lasted 2–3 months and was correlated with the Al mobilization peak (Figure 2,3). During the following 2 years at the potassium sulfate plot, the pH increased by about 1 pH unit, which can be interpreted as disintegration of the base/acid equilibrium in the soil. In the third year after fertilization below the humus layer, the pH dropped down to the level of the control again.

Release of cations by dolomite and phonolite

The unexpected high and prompt reaction of soil solution pH after phonolite application is correlated with the high release of sodium (Figure 4). The concentration of sodium in the soil solution rose immediately after the application of 10 Mg ha^{-1} phonolite rock powder to ten- to twenty times the values observed at the control and the dolomite plots. This did not provoke such heavy Al exchange as in the case of potassium sulfate fertilization because of the low selectivity of exchanger surfaces in the soil for sodium. The rapid appearance of a Na peak corresponds to the high content of exchangeable sodium in the phonolite. It can be assumed that exchange processes with fast kinetics caused a tem-

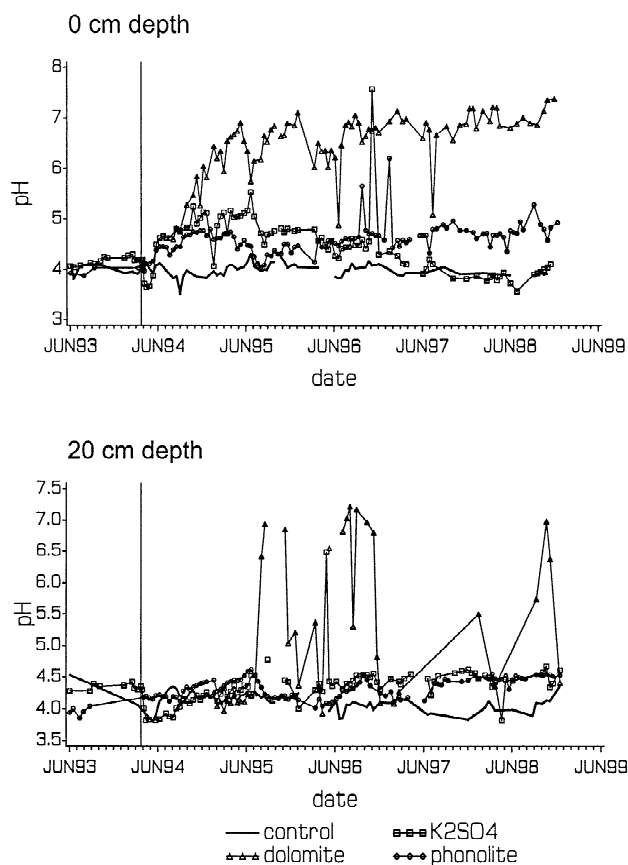


Figure 3. The pH value in the soil solution below the humus layer (top) and at 20 cm depth (below) for phonolite-, dolomite-, potassium sulfate treatment and control. Vertical reference line = time of fertilization.

porary consumption of protons and released sodium from the rock powder. For the first year after the fertilization, we could calibrate a water model and calculate the Na flux. The cumulative sodium flux of 125 kg ha^{-1} was so high that during the first year about 30% of the total sodium content of the rock powder (437 kg ha^{-1}) appeared in the soil solution at the interface between the humus layer and the mineral soil (Figure 4). This is about 40% more than the exchangeable plus water extractable sodium stock in 10 Mg of phonolite rock powder which amounts to 87 kg. Thus, within the first year, the exchangeable sodium content was mobilized and moreover some easily soluble sodium minerals were dissolved. One year after phonolite application, the calcium concentrations below the humus layer began to increase by about $2\text{--}5 \text{ mg l}^{-1}$ in comparison to the control (Figure 5). It is possible that this marks the beginning of the quantitative dissolution of silicates. Because of the

higher solubility of the dolomite, the increase of Ca concentrations was 2 to 5 times higher than in the phonolite treatment. The relation of Ca concentrations between the phonolite, dolomite and the control plots reflects roughly the pH relation between these plots. At the potassium sulfate plot, despite a sharp Ca peak directly appearing after the fertilization, the Ca concentrations lie in the range of the control. The initial Ca peak is accompanied by a wider DOC peak.

For the dolomite plot, the time series of DOC concentrations is in fairly good agreement with the shape of the time series of Ca concentrations. This indicates, that apparently a high share of the Ca which was released by dolomite dissolution was transported in the soil solution as mobile Ca fulvates because of the instability of hydrogen carbonate (Hildebrand and Schack-Kirchner 2000). At the phonolite plot, no evident correlation between Ca concentrations and DOC mobilization was found. At the potassium sul-

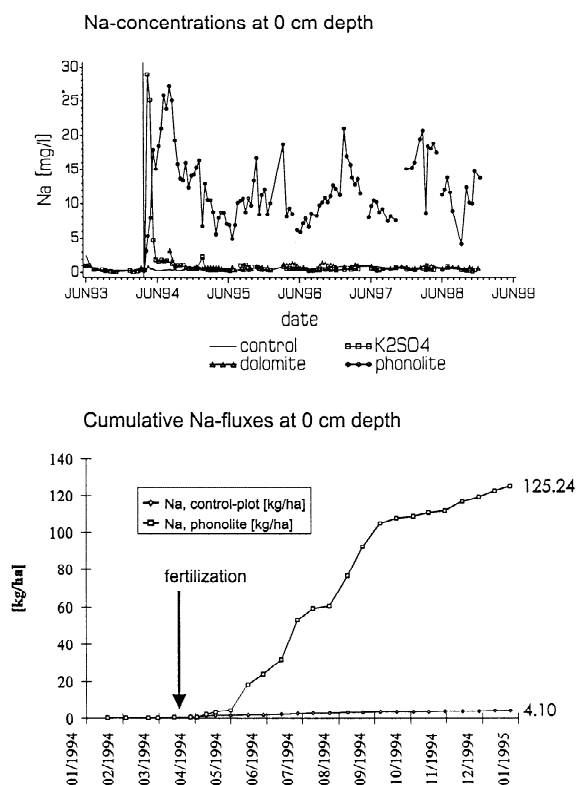


Figure 4. The concentrations of sodium in the soil solution below the humus layer for phonolite-, dolomite-, potassium sulfate treatment and control (top). Vertical reference line = time of fertilization. Cumulative sodium-flux during the first year after the application of phonolite and at the control (below). Arrow = time of fertilization.

fate plot, only the initial dissolution pulse with very high potassium concentrations triggered a broad DOC reaction.

Potassium and magnesium which are essential elements in the forest nutrition were not increased in the soil solution during the first three years after the fertilization with phonolite. Under field conditions it is likely that the Mg and K, which are released in low rates because of the low solubility of Mg²⁺ and K⁺ minerals in the material that we used (Table 1), would have been totally taken up by roots, as the increase of potassium content in the needles at the phonolite plot suggests (Table 3). Liming increased both, magnesium by dissolution of dolomite and potassium which was released by exchange processes from the soil, but there was no K uptake, obviously because of competition for uptake of Ca.

Nitrate mobilization

The fast pH increase in the humus layer and the biologically active Ah-horizon after application of dolomite or phonolite stimulated mineralization of organic N and nitrification. Nitrate pulses occurred periodically which caused an output of nitrate to the groundwater because food chains were not yet adapted to the new "chemical climate" and nutrient cycles were not yet closed. In forest ecosystems, which suffer from nitrogen inputs from air pollution, there is a latent risk of mobilization of the elevated nitrogen pool in the forest soil. The graph (Figure 6) shows the usual seasonal variation of nitrate leaching in forest ecosystems. In the rooting zone, the nitrate concentrations were reduced during the vegetation period by the uptake. Nitrate output occurred mainly in autumn, winter and early spring.

The phonolite rock powder, in spite of the comparatively low solubility of silicates, caused a mobilization of nitrate, which – within the rooting zone (20 cm) – lead to nitrate concentrations above the EU threshold value for drinking water quality with a delay of 1 year, and to concentrations near this threshold in the system output at the depth of 80 cm (Figure 6).

According to the much higher pH increase after liming with dolomite, the nitrate concentrations in the soil solution of the rhizosphere (20 cm depth) showed sharp peaks with values up to twice as high as after the application of phonolite rock powder in equal doses. In the soil solution at 80 cm depth, the nitrate concentrations were usually in the same range as at the phonolite plot, apart from one short-lasting peak which reached 90 mg/l.

After fertilization with potassium sulfate, the nitrate concentrations decreased slightly in comparison to the control and showed a muffled seasonal periodicity. It is not very clear how to interpret this finding. On the one hand it could indicate a decreased biological activity caused by the salt effect of potassium sulfate and high Al activity in the soil solution, on the other hand, enhanced nitrate uptake by the stand could have decreased nitrate concentration in the soil solution.

Effects of dolomite and phonolite application on the exchangeable cation pool

Four to five years after liming as well as after application of phonolite rock powder, we found significant

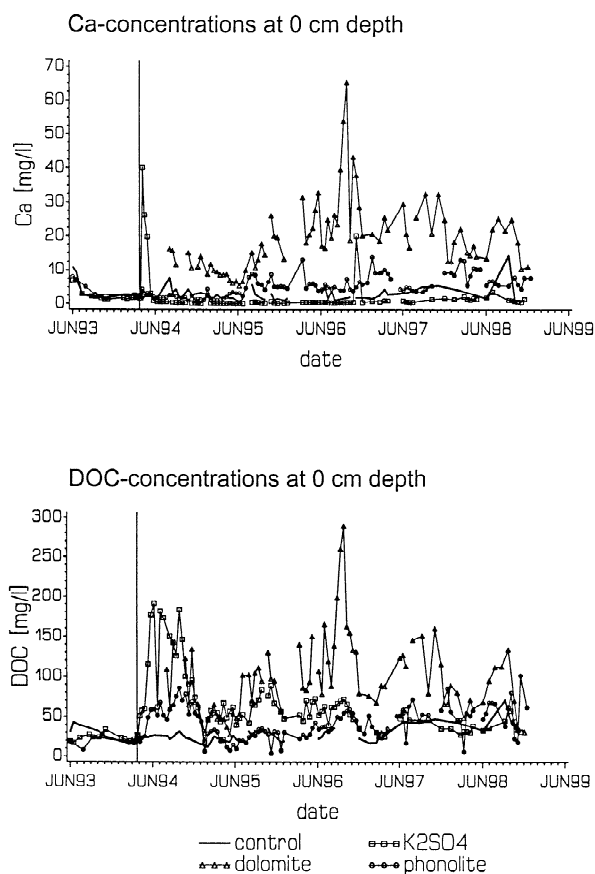


Figure 5. Calcium concentrations in the soil solution below the humus layer (top) and concentrations of dissolved organic carbon (DOC) in the soil solution (below) for phonolite-, dolomite-, potassium sulfate treatment and control. Vertical reference line = time of fertilization.

Table 3. Content of macronutrients in the spruce needles of the upper crown (7th/9th whorl, 1 and 3 years old) four years after the fertilization on the dolomite-, phonolite- and potassium sulfate – plots in comparison to the control plot. Bold values show marked differences relative to the control plot.

Treatment	N	P	K	Ca	Mg
whorl/year	g/kg				
Control					
9/1996	12.5	1.14	2.20	3.96	0.86
9/1994	12.2	0.94	2.26	8.40	0.59
Dolomite					
7/1996	12.4	1.36	2.48	3.69	1.11
7/1994	12.4	0.90	2.23	7.18	0.60
Phonolite					
7/1996	12.8	1.26	3.18	3.53	0.86
7/1994	11.4	0.87	2.57	6.65	0.57
Potassium sulfate					
7/1996	15.6	1.26	4.54	2.97	0.60
7/1994	12.5	0.97	4.65	2.71	0.37
Deficiency thresholds used in Baden-Württemberg					
7/one year old	12.00	1.20	4.75	2.50	0.70
7/three years old	10.80	0.90	3.62	3.15	0.38

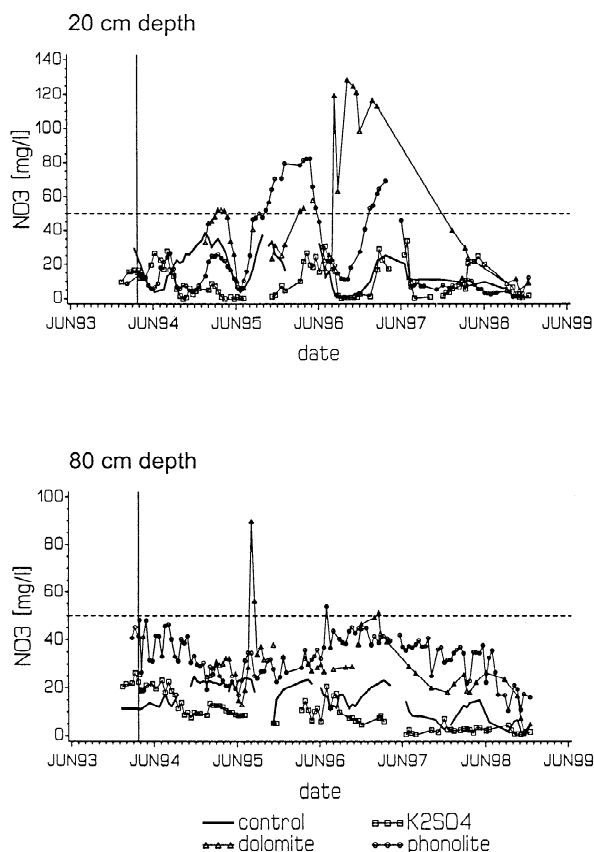


Figure 6. The concentration of nitrate in the soil solution at 20 cm (top) and 80 cm soil depth (below) for phonolite-, dolomite-, potassium sulfate treatment and control. Vertical reference line = time of fertilization, horizontal reference line = EU threshold for drinking water quality (50 mg/l).

changes in the exchangeable ion pool (Table 2). The exchangeable potassium pool was not significantly influenced by any of the treatments, not even by the fertilization with potassium sulfate in spite of the comparatively high dose of 1 Mg ha^{-1} . The lower value at the phonolite plot at 30–60 cm depth corresponds to the lower CEC, which seems to be a slight variability of site characteristics in the subsoil. The exchangeable Ca pool was increased at the dolomite and the phonolite plots. This increase was highly significant ($p = 1\%$) at the dolomite plot through the whole soil profile; at the phonolite plot down to 10 cm depth. The increase of the exchangeable Ca pool in the upper 30 cm of the soil at the dolomite plot amounted to about 70–80% of the Ca content in the dolomite that was applied there. The liming with dolomite also caused a highly significant ($p = 1\%$)

increase in the Mg pool. As a consequence of the Na release of the phonolite rock powder, the Na pool is significantly higher at this plot to the depth of 60 cm. The relatively great depth effect of Na is caused by its mobility.

The exchangeable aluminum pool in the upper 5 cm of the mineral soil was significantly decreased after liming with dolomite. Obviously the aluminum was partly translocated to deeper soil horizons, as Al at 10–30 cm depth was significantly higher than in the control. A similar pattern and translocation tendency was found for Fe and H at the dolomite plot. At the limed soil, these changes can be summarized as a de-acidification of the exchanger surfaces in the 0–5 cm layer. It is remarkable that after the comparatively short time of 4–5 years enough basidity passed through the 4–10 cm thick humus layer and entered the mineral soil and thus caused this de-acidification process in the Ah horizon.

At both the dolomite and phonolite plots, the amelioration of the soil pH reached the mineral soil. In the depth 0–5 cm, the $\text{pH}(\text{H}_2\text{O})$ -value rose after phonolite application by 0.3 and after liming by 0.5–0.6 pH units.

The base saturation (BS), as an integrating parameter that characterizes the acidity/base status of the soil solid phase, was much more influenced by dolomite than by phonolite rock powder amelioration. The increase of base saturation was significant at the 1% level at both the dolomite and the phonolite plots, down to the depth of 30 cm.

Nutritional effects

After nearly 4 years, only little nutritional effect on the potassium content is visible in the needles of the spruce trees after fertilization with phonolite. In both the one and three year-old needles, the potassium content increased by 14–45% ($0.3\text{--}1 \text{ g kg}^{-1}$) but remained below the deficiency threshold. The dolomite caused no change in the potassium supply but an increase in the magnesium content in the 1 year-old needles (Table 3).

The fertilization with potassium sulfate at the experimental dose of 1 Mg ha^{-1} removed the potassium deficiency in both the one and three year-old needles. But simultaneously the concentrations of magnesium and calcium dropped to the deficiency threshold or below. In the young needles, the increase in the

potassium content was accompanied by an increased nitrogen content. Eventually this could be interpreted as recovering of enzyme systems involved in the nitrate uptake (e.g. nitrate reductase) as triggered by increased potassium availability (Mengel 1991). This hypothesis is weakly supported by the lower nitrate concentration that we found in the soil solution at the potassium sulfate plot.

Discussion and conclusions

Fertilization with the soluble salt (potassium sulfate) yielded a fast nutritional effect. Four years after the potassium sulfate application at 1 Mg ha^{-1} , the potassium content of spruce needles was about twice as high as in the control plot. This effect was accompanied by contradictory and antagonistic side effects on the magnesium and calcium supply. The high solubility of potassium sulfate caused a short-term acidification pulse by exchanged acidity – equivalents and at 80 cm depth, an increase of Al concentrations by about 2 orders of magnitude over the whole observation period. The results of soil solid phase analysis showed that potassium sulfate did not ameliorate the acid/base equilibrium and did not increase the exchangeable K-pool. We can therefore state that neutral salt fertilization acts as an effective remedy against acute deficiencies in forest nutrition, but has no potential to ameliorate soil acidification and the export of bases, the most urgent problems in the forest ecosystems of Central Europe, which are afflicted by air pollution. Especially in high doses, it causes severe side effects like the rapid release of exchangeable acidity from exchanger surfaces in the mineral soil, which can cause risks for the groundwater and headwater streams. These side effects might be reduced at lower doses.

Liming, as well as the application of silicate rock powder, represent a different and more sustainable strategy, which attempts to stabilize the ecosystem by balancing the soil chemical status. Subsequently amelioration of forest nutrition should result from stable exchange relations in the soil and higher soil biological activity as a secondary effect.

Within a few years, liming with such an experimental high dose leads to clear de-acidification of exchanger surfaces in the soil with a remarkable depth effect. Until now we have not found any influence on

the potassium supply to the spruce trees. The side effects however, caused by the resulting large increase in soil pH and subsequent nitrate output, were considerable. The forest ecosystems in Oberschwaben are near nitrogen saturation, which could cause risks for groundwater. The risk of a surplus in nitrification can be reduced by using lower doses, e.g. $3\text{--}4 \text{ Mg ha}^{-1}$ which are currently used in soil-recovery liming programs in Germany (Evers 1991; Beese and Meiwes 1995).

Application of phonolite rock powder caused unexpected high initial effects on pH and Na release which must be interpreted as exchange reactions and lasted at least 3–4 years. Schüller (1992) found similar spontaneous release of cations and pH increase after an amelioration with 20 Mg ha^{-1} basalt powder. This corresponds to results from Deutschmann (1996) who found cation exchange capacities between 35 and $180 \mu\text{mol g}^{-1}$ in different silicate bedrocks. Besides these initial processes, the release of Ca from the phonolite was very slow in the first year, which corresponds to the results of the model experiment of (Hildebrand and Schack-Kirchner 2000). During the second and third year however, it reached 20 to 30% of the Ca-amount that was released in the limed plot (Figure 5). This increase of the dissolution rate after a time delay of about one year gives reason for a tendency that under field conditions the dissolution rates of silicates will be higher in the long-run, as short-term laboratory experiments show. One possible reason for this finding in forest soils could be an improvement of neutral cation release by microbial processes like the dissolution of primary silicates by fungi (Jongmans et al. 1997; Eckardt 1979).

The release of sodium by phonolite rock powder is a problematic aspect. In the case of high sodium saturations, a loss of structure stability of the soil is to be feared. However the total amount of sodium imported by the phonolite rock powder is not enough to seriously afflict the aggregate stability. The high initial Na release caused an increase of the Na saturation by a factor 3–5. This can be judged as an initial effect of short duration because Na has a low selectivity and will be replaced by higher charged cations.

The nitrate leaching at 80 cm depth in our study was similar between the phonolite and dolomite treatments. This is a somewhat contradictory finding with respect to the results of the model experiments of (Hildebrand and Schack-Kirchner 2000) who found no nitrate mobilization by silicate rock powder in the

mineral soil. An explanation for this differing result could be the above-average cation exchange capacity of the phonolite that we used in this trial. The proton consumption, as correlated with the Na release, supported nitrification by increasing the pH more than usually expected for silicate rock powders. Because this proton consumption obviously is based upon exchange reactions we expect this effect to be temporary. Long lasting proton buffering occurs with the slower dissolution of silicates.

The potential of soil chemical amelioration is observable in the first 4 to 5 years after liming with dolomite as well as after phonolite rock powder application. Blum et al. (1989b) stated for silicate rock powder of volcanic origin, that their potential for fertilization in agriculture was mainly caused by rapid exchange processes. Sauter and Forest (1987), as well as von Mersi et al. (1992), found an effect on soil pH in forest soils.

Apart from the initial exchange reactions, phonolite rock powder reacted more slowly than dolomite, so we can conclude that the application of silicate rock powder is in principle an operational alternative to conventional liming in regions where the risk of nitrate mobilization is high because of man-made nitrogen saturation in forest ecosystems. The fact of increasing nitrogen saturation in forest soils applies for wide parts of Central Europe. For practical use, high Na contents in silicate rock powders should be avoided to enhance their long-term ameliorative effect. Because of the slower dissolution of silicate rock powders they have to be used at higher doses than dolomite, which is more expensive. Therefore their application must be restricted to areas where special care is recommended, e.g. in preservation areas for drinking water production.

Phonolite caused a visible effect upon the potassium supply of spruce, but could not remove the potassium deficiency within 4 years because of its slow potassium release. If there is an acute potassium deficiency, potassium sulfate should be used at lower doses, e.g. of 500 kg ha^{-1} , as it is the usual measure in the fertilization practice in South Germany (Evers 1991). Because neutral salt fertilization does not ameliorate the long-term soil chemical boundary conditions of the forest nutrition, it should be combined with the "basis therapy" of conventional liming, to achieve both the removal of nutritional deficiencies and the stabilizing of exchange equilibria for neutral cations in the soil.

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