Negative impact of nitrogen deposition on soil buffering capacity

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Anthropogenic nitrogen deposition over the past half century has had a detrimental impact on temperate ecosystems in Europe and North America, resulting in soil acidification and a reduction in plant biodiversity[1,2]. During the acidification process, soils release base cations, such as calcium and magnesium, neutralizing the increase in acidity. Once these base cations have been depleted, aluminium is released from the soils, often reaching toxic levels. Here, we present results from a nitrogen deposition experiment that suggests that a long legacy of acid deposition in the Western Tatra Mountains of Slovakia has pushed soils to a new threshold of acidification usually associated with acid mine drainage soils. We show that increases in nitrogen deposition in the region result in a depletion of both base cations and soluble aluminium, and an increase in extractable iron concentrations. In conjunction with this, we observe a nitrogen-deposition-induced reduction in the biomass of vascular plants, associated with a decrease in shoot calcium and magnesium concentrations. We suggest that this site, and potentially others in central Europe, have reached a new and potentially more toxic level of soil acidification in which aluminium release is superseded by iron release into soil water.

Acid precipitation has resulted in environmental degradation of surface waters, forests and grasslands in central and northern Europe and eastern North America during the past five decades[1,2]. Legislation regulating the emissions of sulphur oxides in Europe and eastern North America in the 1990s lowered rates of sulphuric acid deposition in these regions[3]. However, the contribution of anthropogenic nitrogen (N) deposition to acid precipitation and environmental degradation continues to be a concern. N deposition rates are above critical loads in many industrially developed countries[4]. The potential for detrimental impacts of N deposition is particularly high in cold mountainous regions, as ecosystems with short growing seasons, shallow soils and steep terrain have lower capacities to sequester N (refs 5,6).

During acidification, soils undergo a transition through different ranges of buffering associated with the weathering and liberation of different elements[7] (Fig. 1). Most temperate-zone soils are buffered by base cations, which are replaced by Al^{3+} at pH ranges below pH 4.5. Acid deposition has shifted forest and grassland soils in parts of Europe and North America into the Al^{3+} buffering range[8–10]. Associated changes in forest health due to loss of nutrient cations and increases in soluble Al^{3+} include foliar injury and increased susceptibility to temperature stress[11,12]. Although hypothesized by Ulrich[13], the stage beyond Al, towards Fe buffering of soils, has not been described in association with atmospheric deposition, and is known primarily from acid mine drainage soils[14].

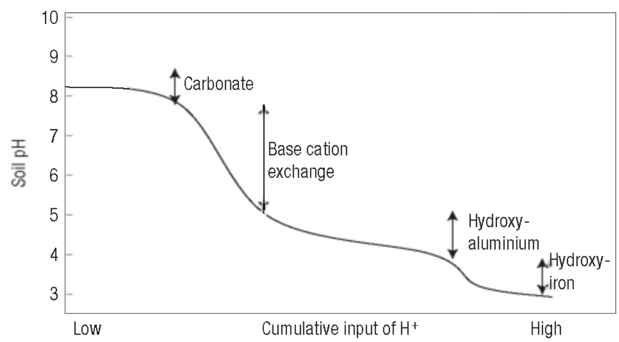

Figure 1 Hypothetical changes in soil buffering systems associated with increasing inputs of protons and associated changes in soil pH. Modified from refs 7 and 30.

To evaluate the effect of elevated anthropogenic N deposition at a site with a long legacy of high acid deposition, we carried out a N deposition simulation experiment in an alpine ecosystem near Mount Salatín, in the Tatra National Park of Slovakia. Atmospheric deposition in the Tatra Mountains increased substantially during rapid industrialization in Poland, East Germany and Czechoslovakia in the middle of the twentieth century[15]. Maximum rates of wet deposition in the neighbouring High Tatra Mountains were at least 15–20 kg N ha^{-1} yr^{-1} and 20–25 kg S ha^{-1} yr^{-1}, with estimated total N inputs of 960 kg ha^{-1} and total S inputs of 1,100 kg ha^{-1} between 1850 and 2000 (ref. 15). Deposition rates decreased regionally by about 30–40% after 1990. Deposition rates at our study site in the Western Tatra Mountains are higher than at the High Tatra Mountains, and are now estimated at 12 kg N ha^{-1} yr^{-1} and 11 kg S ha^{-1} yr^{-1}, based on periodic bulk deposition measurements made at the research site and comparison with long-term measurements in the High and Low Tatra mountains (unpublished data of Tatra National Park).

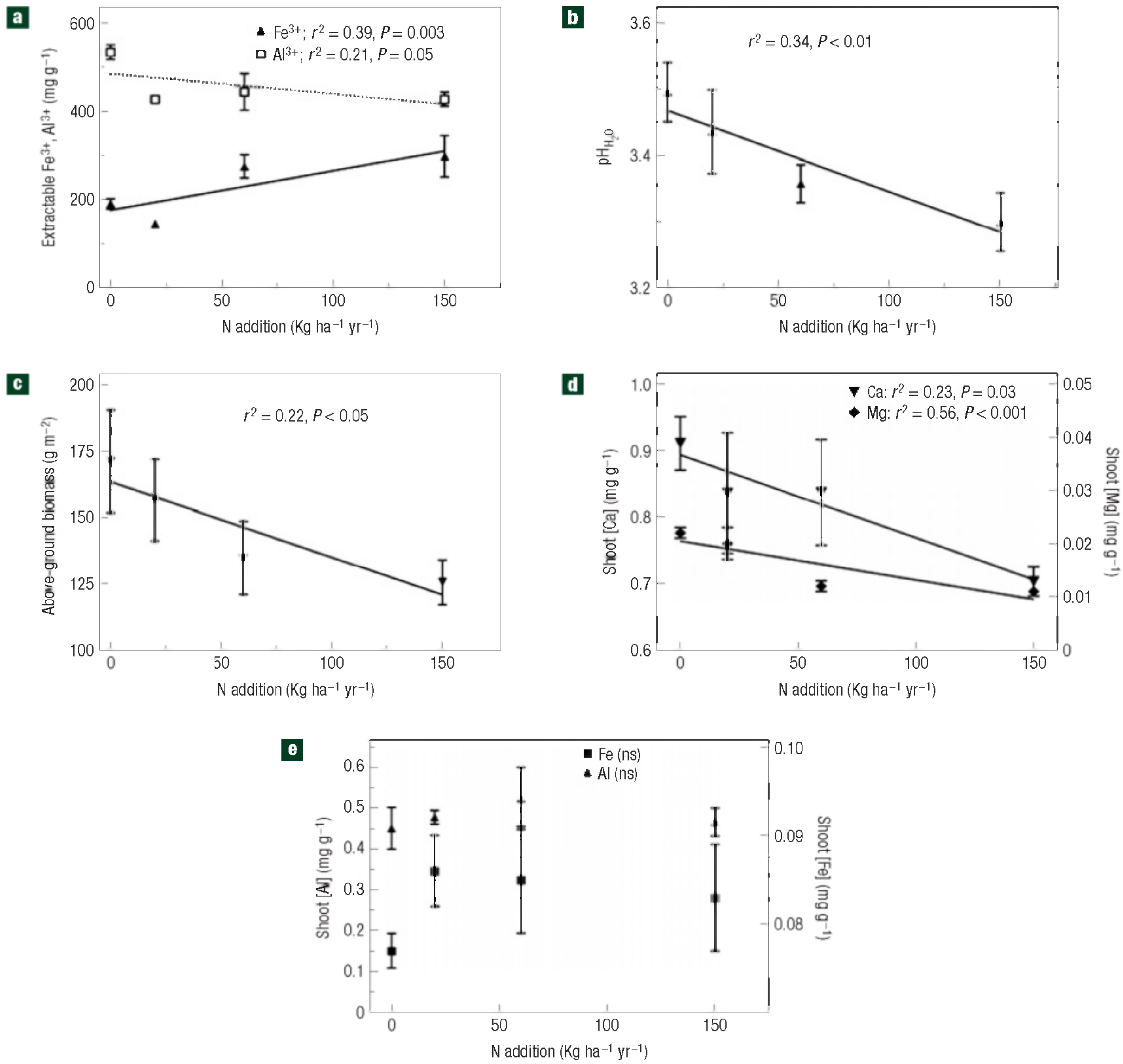

Figure 2 Soil and plant responses to simulated N deposition in the Western Tatra Mountains. **a**, Soil-extractable Al^{3+} (open squares) and Fe^{3+} (triangles). **b**, Soil pH. **c**, Above-ground biomass of vascular plants. **d**, Shoot Ca (triangles) and Mg (diamonds) concentrations. **e**, Shoot Al (triangles) and Fe (squares) concentrations. Lines represent significant least-squares linear regression fits, with goodness of fit and *P* values reported above the lines. Error bars indicate ±1 s.e.m., with $n = 5$ plots per treatment.

Three levels of N input (20, 60 and 150 kg N ha^{-1} yr^{-1}), one phosphorus (P) treatment (50 kg P ha^{-1} yr^{-1}) and a control treatment (ambient deposition, about 12 kg N ha^{-1} yr^{-1}) were applied to experimental plots. The levels of N input were selected to obtain a response function of soils and vegetation to increasing N deposition rates, rather than to represent future deposition scenarios *per se*. However, the rates of N fertilization we used (20 and 60 kg ha^{-1} yr^{-1} treatments) are within the range of projections for N deposition into 2030 for this region[16]. The P treatment was included to evaluate whether primary production was P limited at the site. After three years of treatment application, N-treated and control soils were collected and analysed for water-extractable pH (pH_{H_2O}) and $BaCl_2$-extractable cation concentrations. Above-ground plant production was estimated in all treatments by clipping the current year's biomass in subplots within each experimental plot (see the Methods section for further details).

Soil pH values measured in the study plots at the initiation of the experiment (3.55 ± 0.05 s.e.m.) were in the range of the most acidified soils reported for Europe[17]. Consistent with the low pH values of these soils, extractable cation pools were dominated by Al^{3+} in all treatment plots, with Fe^{3+}, Ca^{2+} and K^+ contributing lesser amounts to the total pool of cations (Fig. 2a, Table 1). However, extractable Al^{3+} decreased with increasing inputs of inorganic N (Fig. 2a). This result differs from most experimental studies of N deposition, which show that soil-extractable Al^{3+} increases with increasing soil acidification or inorganic N inputs[8–10,18]. Decreases in organic Al compounds, important components of the buffering system, have also been noted in forest soils in response to acid deposition[18]. The decrease in Al^{3+} we observed indicates leaching losses exceeded Al^{3+} inputs from rock weathering with simulated increases in N deposition. In contrast to the response of Al^{3+}, extractable Fe^{3+} increased

Table 1 Concentrations of extractable cations from soils in experimental plots at Mount Salatín (Western Tatra Mountains, Slovakia). The plots were subjected to simulated N deposition (20, 60, and 150 kg^{-1} ha^{-1} yr^{-1}) and a control (ambient) treatment. Values are means ± s.e.m., $n = 5$ plots per treatment. All cations declined significantly with increasing N input (Ca: $r^2 = 0.33$, $P < 0.01$; K: $r^2 = 0.31$, $P = 0.01$; Mg: $r^2 = 0.22$, $P < 0.05$; Mn: $r^2 = 0.24$, $P < 0.05$), as determined using least-squares linear regression.

Cation	Treatment (Kg N ha^{-1} yr^{-1})			
	Control	20	60	150
	(Concentration (mg kg^{-1}))			
Ca^{2+}	158.7 ± 14.0	109.6 ± 13.3	99.6 ± 12.0	86.1 ± 13.2
K^{+}	164.1 ± 10.8	117.9 ± 10.0	99.8 ± 4.7	102.3 ± 11.9
Mg^{2+}	56.6 ± 4.6	40.9 ± 5.0	41.9 ± 4.0	36.4 ± 5.1
Mn^{2+}	7.3 ± 0.9	5.1 ± 0.5	5.4 ± 0.6	4.4 ± 0.6

with increasing N inputs (Fig. 2a). At soil pH values less than 3.2, soluble Fe^{3+} is liberated from granitic parent material faster than Al^{3+}(ref. 19). Taken together, the responses of extractable Al^{3+} and Fe^{3+} to simulated N deposition indicate soils at our study site are at a threshold between Al^{3+} and Fe^{3+} dominated buffering of the soil. This previously hypothesized threshold[13] has not been observed experimentally in a field setting.

Base cation concentrations and pH_{H2O} of the study soils decreased with increasing inputs of inorganic N (Table 1, Fig. 2b). Extractable Mg^{2+}, Ca^{2+}, K^+ and Mn^{2+} decreased significantly with increasing N inputs, lowering their availability as nutrients and decreasing their potential contribution to soil buffering capacity.

Above-ground plant biomass decreased with increasing inputs of inorganic N in the study plots (Fig. 2c), a marked contrast from most temperate and Arctic ecosystems, where N limits primary production[20]. This result is consistent with a decrease in primary production associated with chronic N deposition, which was hypothesized for forest ecosystems by Aber *et al.*[21]. Multiple decades of elevated anthropogenic N deposition may have alleviated any pre-existing N limitation of production, and simultaneously exacerbated plant P limitation through higher P occlusion with increasing soil acidification. Indeed, plant biomass increased at our study site in response to the P additions (155 ± 15 (s.e.m.) g) relative to the control treatments (110 + 9 (s.e.m.) g, $P < 0.05$), indicating a P limitation of primary production.

Although acidification of soils and related increases in soluble Al^{3+} and Fe^{3+} result in loss of plant-available P, due to occlusion in insoluble minerals, decreasing P availability in the N addition plots did not contribute to the decrease in biomass production at our study site. The estimated pool of plant-available P did not change in the N addition treatments (data not shown), and the combined pool of extractable Al^{3+} and Fe^{3+} which could complex with available P did not change with the N addition treatments, as increases in Fe^{3+} offset decreases in Al^{3+}.

We believe the loss of base cations essential to plant growth, in combination with toxicity of Al^{3+} and Fe^{3+}, contributed to the decrease in plant biomass we observed with increasing N inputs. Although other studies using similar treatment application procedures, but lower concentrations of N, have shown a stimulation of plant growth, it is possible that the concentrations of N we applied to the plants may also have contributed to the inhibition of growth on the short-term before dilution by precipitation.

Soil-extractable base cations decreased by 46% for Ca^{2+}, 37% for Mg^{2+} and 38% for K^+ at the highest input of inorganic N. Shoot concentrations of Mg and Ca decreased in association with the changes in soil pools of these nutrients (Fig. 2d). Loss of cations, in particular Ca^{2+}, has been implicated in the declining health of forests with acid deposition[22], and has been linked to increased susceptibility to other stresses (for example, low temperature, drought and herbivory).

Soluble Al^{3+} and Fe^{3+} are both toxic to plants in the concentrations found in the soils at our study site[23], and increases in soil pools of soluble Fe^{3+} may have contributed to the lower plant growth. Aluminium inhibits root growth in plants, and may interfere with uptake of Ca^{2+} (ref. 24). Although the combined pool of Fe^{3+} and Al^{3+} did not increase with increasing N inputs, the presence of Al^{3+} has been shown to enhance the detrimental effects of Fe^{3+} on plant growth[25]. Shoot Fe concentrations did not increase with increasing N (Fig. 2e), although tissue concentrations of both Fe and Al were in the range considered to be toxic to plant function[23]. The occurrence of Fe toxicity in plants is relatively rare, occurring primarily in association with the microbial generation of Fe^{2+} in waterlogged soils[23] and in acid mine drainage sites. To the best of our knowledge, the potential for Fe^{3+}-related inhibition of plant growth in soils affected by anthropogenic acid deposition has not been previously described.

Although rates of acid deposition have decreased throughout Europe owing to stricter regulations[26], the multi-decadal legacy of elevated N inputs continues to have a negative environmental impact. Some soils remain sensitive to inputs of acidic elements because of the leaching losses of base cations and slow rates of replacement from weathering[3,27]. In particular, high-elevation sites with acidic granitic parent material are highly sensitive to continued inputs of N deposition[6]. Recovery from N saturation and acidification of soils in these sensitive sites may require decades[4]. Rates of N deposition still exceed critical loads in parts of Europe[28].

Mountain ecosystems provide clean water, forage for livestock, wildlife habitat, timber and recreation[29]. Maintaining the integrity of these ecosystem services depends on soil functions that are sensitive to chronic acid deposition. Our findings strongly suggest that N deposition at current levels in parts of central Europe will compromise the capacity of some mountain ecosystems to provide these services, particularly where soils are at or beyond the transition of stages of soil buffering states. Mobilization of Fe^{3+} in soils already characterized by high concentrations of soluble Al^{3+}, along with continued losses of base cations, will lead to lower plant production and continued acidification of already heavily impacted soils. Rates of N deposition in regions such as the Tatra Mountains have declined over the past few decades, but are expected to increase over the next four decades[16]. Our results suggest that the cumulative effects of recent high N deposition inputs has enhanced their sensitivity to continued inputs of N and brought regions such as the Western Tatra Mountains dangerously close to toxic conditions.

METHODS

SITE DESCRIPTION

The experiment was carried out in an alpine grassland on a ridge extending westward from the summit of Mount Salatín in the western edge of the Western Tatra Mountains, Tatra National Park, Slovakia. Vegetation at the site is dominated by graminoid species, including *Oreochloa disticha*, *Festuca supina* and *Agrostis rupestris*, with lower cover of forb and shrub species. Soils at the site are humic ferruginous podzols, derived from biotite granodiorite parent material. The soil organic matter content in the top 15 cm is 12.5 ± 1.5% (s.e.m., $n = 10$) and the soil C:N ratio is 17.1 ± 0.25 (s.e.m., $n = 10$). Average annual precipitation at the site is approximately 1,500 mm, and annual average temperature is −1.3°, based on four years of microclimate measurements at the site and comparisons with long-term climate records in the High Tatras.

METHOD DETAILS

Five replicate 2 × 2 m plots per treatment were arrayed in a blocked design, with one plot of each treatment in five blocks. Treatments of 20, 60 and

150 kg N ha^{-1} yr^{-1} and 50 kg P ha^{-1} yr^{-1} were applied by spraying solutions of NH_4NO_3 or KH_2PO_4 onto the plots in three equal applications during the growing season (late May, late June and late July or early August), starting in May 2002. Control treatments consisted only of water. Each plot received 3 l of water with each application. The treatment solution was further diluted by the soil solution; measurements of soil solution inorganic N concentrations were two or more orders of magnitude lower than the treatment solution applied to the plots. After three years of treatment, above-ground biomass was clipped in three 0.04 m^2 subplots within each larger experimental plot, to estimate above-ground primary production responses to the treatments. The biomass was oven dried to constant mass at 70 °C for 48 h, and then weighed to the nearest 0.01 g. The tissue was then ground in a Tecator mill, acid-digested and analysed for cation concentrations using an ARL 3410 inductively coupled plasma emission spectrophotometer (Thermo Electron).

Soils were collected after three years of treatment for pH and cation measurements. Two 2-cm-diameter by 15-cm-depth cores were collected from each plot and composited into a single sample. The soils were passed through a 2 mm sieve to remove rocks and coarse plant material. Soil pH values were measured on a soil/deionized water paste (1:1) using a Thermo Orion Model 620 pH meter (Thermo Electron). The soils were extracted in 0.1 mol l^{-1} $BaCl_2$, and exchangeable cations analysed using an ARL 3410 inductively coupled plasma emission spectrophotometer (Thermo Electron).

The effects of the N treatments on the response variables (soil cations and pH, foliar biomass and Ca, Mg, Al and Fe concentrations) were evaluated using least-squares linear regression. The difference in above-ground biomass production between control and P treatments was analysed using analysis of variance. All data met the assumptions of the tests.

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Author contributions

W.D.B. determined the research plan, obtained financial support, participated in the field work, analysed the plant samples and wrote the paper. C.C.C. participated in field work, analysed the soil samples and contributed to the writing of the paper. L.H. obtained financial support and along with J.H. supervised the field crews maintaining the experiment and assisted with collection of plant and soil samples. J.S.B. assisted with interpretation of the results and contributed to the writing of the paper.

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