Soil-solution chemistry in a coniferous stand after adding wood ash and nitrogen

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Abstract: Wood-ash applications have been proposed to promote the long-term sustainability of forest production at increased harvest intensities. Effects of wood-ash and nitrogen (N) application on soil-solution chemistry were studied for 9 years following application in a coniferous stand in Sweden. Crushed, self-hardened wood ash was applied at 3, 6, and 9 Mg·ha^{-1} alone, the lowest dosage both with and without 150 kg N·ha^{-1}. Pelleted wood ash (3 Mg·ha^{-1}) and N were also applied alone. The soil solution was sampled by suction cups at 50 cm depth. The crushed, self-hardened ash readily dissolved in water, as reflected in increased soil-solution concentrations of sodium and sulphate. Significant ($p < 0.05$) elevations were also found for potassium, calcium, aluminum, and total organic carbon. Vanadium, chromium, manganese, nickel, copper, zinc, arsenic, and lead were not significantly affected by the ash treatments, but cadmium tended to increase in the treatments with ash alone. From the fourth year onwards, the pH of the soil solution was lowered and the aluminum concentration raised in the plots given 9 Mg crushed ash·ha^{-1}. Fertilization with N alone temporarily increased concentrations of inorganic N, cadmium, aluminum, and zinc and decreased the pH. The crushed ash generally had longer lasting effects than N fertilization.

Résumé : Des applications de cendre de bois ont été proposées afin de promouvoir la durabilité à long terme de la production forestière avec des intensités accrues de récolte. Les effets de l'application de cendre de bois et d'azote (N) sur la chimie de la solution de sol ont été étudiés durant les neuf années suivant l'application dans un peuplement résineux en Suède. La cendre broyée autodurcissante a été appliquée seule aux taux de 3, 6 et 9 Mg·ha^{-1}; le plus faible dosage a été appliqué seul mais aussi avec 150 kg N·ha^{-1}. De la cendre granulée (3 Mg·ha^{-1}) et N ont aussi été appliqués seuls. La solution de sol a été échantillonnée avec des coupes à tension à 50 cm de profondeur. La cendre broyée autodurcissante s'est rapidement dissoute dans l'eau comme l'indiquaient les concentrations accrues de sodium et sulfate dans la solution de sol. Des augmentations significatives ($p < 0,05$) ont aussi été observées pour potassium, calcium, aluminium et carbone organique total. Les concentrations de vanadium, chromium, manganese, nickel, cuivre, zinc, arsenic et plomb n'ont pas été significativement affectées par les applications de cendre mais cadmium avait tendance à augmenter avec les applications de cendre seule. À partir de la quatrième année, le pH de la solution de sol a diminué et la concentration de aluminium a augmenté dans les parcelles traitées avec 9 Mg de cendre broyée·ha^{-1}. La fertilisation avec N seul a temporairement augmenté les concentrations de N inorganique, de cadium, aluminium et zinc et a diminué le pH. La cendre broyée a généralement eu des effets à plus long terme que la fertilisation avec N.

[Traduit par la Rédaction]

Introduction

Biofuels from forest fellings are renewable energy sources, the use of which is consistent with Swedish energy policy and national environmental quality objectives regarding clean air. The extraction of biofuels from forests sometimes implies increasing the harvesting intensity, which may negatively affect the long-term sustainability of forest production and cause unwanted environmental effects. For instance, whole-tree harvesting, that is, the harvesting of all aboveground parts, poses a greater threat to the long-term sustainability of forest production than conventional stem harvesting, which leaves the logging residues on site, because it increases the amounts of nutrients that are removed (Weetman and Webber 1972; Mälkönen 1976).

The burning of forest biofuels produces large amounts of alkaline ash, which contain most of the inorganic nutrients and metals, that have accumulated in the trees. Nitrogen (N), on the other hand, is volatilized in combustion and is not present in the ash. The composition of the ash generated depends on the types of biofuel and boiler involved, the point where the ash is collected within the plant (fly ash or bottom ash), and whether additional fuels, such as petrochemical oil, are used. To date, most of the ashes produced in Sweden have been dumped in landfills, a practice that may cause negative environmental effects on a local scale. It has been suggested that biofuel ash should be recycled instead, that is, returned to forest land, to promote the long-term sustainability of forest production and (or) to counteract anthropogenic acidification. In the short term, however, indications of both increases and decreases in stem growth have been found after wood-ash applications (Jacobson 2003). In a Swedish environmental impact assessment regarding forest biofuels, Egnell

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Table 1. Studied treatments at the 249 Riddarhyttan experiment.

Treatment	Abbreviation	Moisture correction of dosage (%)
Control	Control	—
3 Mg crushed, self-hardened ash·ha^{-1}	3Cr	25
6 Mg crushed, self-hardened ash·ha^{-1}	6Cr	25
9 Mg crushed, self-hardened ash·ha^{-1}	9Cr	25
3 Mg pelleted ash·ha^{-1}	3Pel	10
150 kg N·ha^{-1}	N	—
150 kg N·ha^{-1} + 3 Mg crushed, self-hardened ash·ha^{-1} (simultaneous application)	N + Cr	25 (crushed ash)
150 kg N·ha^{-1} + 3 Mg crushed, self-hardened ash·ha^{-1} (N applied 1 month before ash)	NbeforeCr	25 (crushed ash)

Note: Two treatments with organic pellets were included in the experimental design but excluded from the present paper. The dosages of ash pellets refer to dry masses. Nitrogen (N) was applied as NH_4NO_3 with some dolomite and boron.

et al. (1998) suggested that the effects of increased harvest intensity should be counteracted by recycling wood ash and that the demand for N can be met by conventional forest fertilization with N when necessary. The timing of fertilization is likely to be crucial when applying combinations of N fertilizer and alkaline ash. Simultaneous application of alkaline ash and ammonium (NH_4^+) may increase the formation of ammonia (NH_3) because of the high pH of the ash.

Owing to the potentially adverse effects on both the environment and human health of applying untreated ash to forested sites, it must be "stabilized" before it is applied to forests. The aim of stabilization is to modify the solubility of the ash components and the size of the ash particles, that is, to form dense ash-particle agglomerates (Steenari et al. 1999). Diverse methods for doing this have been tested, for instance pelleting, granulation, and self-hardening and crushing (e.g. Ring et al. 1999). Self-hardening refers to the ability of most ash materials to solidify upon the addition of water (Steenari and Lindqvist 1997). In Sweden, self-hardening followed by crushing has become the most common method for ash stabilization in recent years. However, a laboratory leaching test on self-hardened wood ashes showed that significant proportions of sodium (Na) and potassium (K) were present as salts in these ashes and were rapidly released from them (Steenari et al. 1999). Steenari et al. (1999) found that the simulated short-term release of the Na and K salts was not reduced by any of the stabilization methods applied.

The environmental effects of recycling biofuel ashes need to be fully understood before the practice can be introduced in Swedish silviculture on a large-scale basis. Over the past 15 years, there has been extensive research on recycling biofuel ashes (e.g. Egnell et al. 1998; Nohrstedt 2001; Saarsalmi and Mälkönen 2001; Lundström et al. 2003b; Aronsson and Ekelund 2004). However, the great variations in ash chemistry, stabilization methods used, ash dosage, application dates, and climate complicate the generalization of observed effects (cf. Steenari and Lindqvist 1997; Aronsson and Ekelund 2004). Nevertheless, some general effects on forest soil processes of liming and wood-ash application have been recognized. Lundström et al. (2003b) reviewed a large number of liming and wood-ash experiments performed in European and North American forests. They concluded that liming or wood-ash application generally increased the leaching of dissolved organic carbon (C), decreased the pH in the deep mineral soil solution, and increased the concentrations of

aluminum (Al), sulphate (SO_4^{2-}), and nitrate (NO_3^-), probably as a result of the high ionic strength that they generated and increased microbial activity. In another review, Aronsson and Ekelund (2004) identified issues related to aquatic ecosystems and their responses to terrestrial ash applications as important topics for future research.

The present study was initiated to study the effects on soil-solution chemistry of applying a pelleted wood ash at 3 Mg·ha^{-1} and a crushed, self-hardened wood ash at three different dosages (3, 6, and 9 Mg·ha^{-1}), the lowest dosage both with and without N.

Materials and methods

Site description

The 249 Riddarhyttan experimental site is located on a forested slope (approximately 10%) in south-central Sweden (59°48′N, 15°30′E). The altitude is 180 m a.s.l. A podzolized soil profile has developed on the sandy–silty to silty moraine. The C/N ratio of the mor layer was 31 in the control plots and the pH (H_2O) was 4.0. The uncorrected annual precipitation is on average 728 mm and the annual temperature 4.7 °C (Alexandersson et al. 1991). During most of the study period, the annual precipitation was slightly (3%–10%) lower than the long-term average, while in 1996 and 2000, the precipitation was nearly 20% lower and 40% greater than the long-term average, respectively (data from the Swedish Meteorological and Hydrological Institute). The site was covered by a 60-year-old mixed stand of *Pinus sylvestris* L. and *Picea abies* (L.) Karst. The site quality class was 7.7 m^3·ha^{-1}·year^{-1} and the stand was thinned before the experiment was established.

Experimental design

Ten treatments were tested in a randomized block design with three blocks. The results from eight of these treatments are reported here (Table 1). Study plots sized 22 m × 22 m were laid out with similar tree basal area and number of stems per hectare. The blocking was largely based on a principal components analysis of soil-solution chemistry sampled on two occasions before treatment, but moisture conditions and some site factors were also taken into consideration. The randomization within blocks was not complete, which might have affected the results from the statistical analyses to some extent. Some plots deviated from the general pattern. The

treatment regarded as being of the least potential interest, N applied 1 month before 3 Mg crushed, self-hardened ash·ha^{-1} (NbeforeCr), was therefore applied to the most deviant plots. The ash and N were applied manually between 27 and 30 September 1995. In treatment NbeforeCr, the N fertilizer was applied on 1 September.

Wood-ash characteristics

The crushed, self-hardened ash originated from the combustion of fuel consisting of (on average over the season) 75% biofuels, 23% petrochemical oil, and 2% pine oil at ASSI Kraftliner in Piteå, northern Sweden. Bark accounted for about 50% of the biofuels and logging residues and by-products from sawmills for the remainder. The ash was piled and left to self-harden for about 1 month. It was then crushed and sieved through a 10 mm mesh. A laboratory dry-sieving analysis of the ash showed that the length of over 60% (by mass) of the ash particles exceeded 2.0 mm. Wet sieving and a simple leaching test revealed that a large proportion of the ash was readily soluble in water. According to an X-ray diffraction analysis (Siemens D-5000, PSD-detector, 40 kV, 20 mA), the crushed, self-hardened ash consisted of Na_2SO_4, $K_3Na(SO_4)_2$, $Na_2SO_4\cdot10H_2O$, $CaCO_3$, and traces of SiO_2, among which the sulphates dissolve readily in water.

The pelleted ash originated from combustion at the Ortviken pulp plant. It was pelleted by IKAB AB, Iggesund, including 8%–10% pine oil as a binding agent. The pellets dissolved quite readily in water according to the leaching test already mentioned but less readily than the crushed, self-hardened ash. The pellets consisted mainly of SiO_2, $CaCO_3$, and MgO, but $Ca_2Al_2SiO_7$, $NaAlSi_3O_8$, $KAlSi_3O_8$, and probably KCl and Fe_2O_3 were also present.

Generally, the contents of major elements in the two ashes applied at experiment 249 were comparable with those of other wood fuel ashes ($n = 121–156$) as compiled by Steenari and Lindqvist (1997). Compared with these ashes, the crushed ash was high in sodium (Na) and sulphur (S), whereas the pelleted ash was rather high in Al (Table 2). Compared with the ash pellets, the crushed ash had higher concentrations of Na, potassium (K), S, boron (B), barium (Ba), nickel (Ni), lead (Pb), and vanadium (V) and lower concentrations of Al, iron (Fe), silicon (Si), C, arsenic (As), and mercury (Hg). The high concentrations of Ni and V in the crushed ash were probably due to the cocombustion of petrochemical oil. The N fertilizer was NH_4NO_3 (27.2% N) with some dolomite and B supplied as colemanite (Table 2).

Soil-solution sampling

Six suction cups were installed in each study plot: three Teflon® cups (type PRENART Super Quartz supplied by PRENART Equipment ApS, http://www.prenart.dk) and three ceramic cups as backups. Since the Teflon cups worked adequately, the results presented refer solely to the soil solutions that they retrieved. The Teflon and ceramic cups in each plot were installed alternately at fixed cardinal points in a circle with a diameter of about 6 m at approximately 0.5 m depth in the mineral soil and at an angle of 60°–70° to the soil surface. The sampling depth corresponded to the lower B or upper C horizon. The Teflon cups were installed in a slurry of water and quartz flour that consisted of 99.5% SiO_2, 0.15% Al_2O_3, 0.035% Fe_2O_3, and 0.05% TiO_2 according to the

manufacturer. The sampled soil solutions were collected in 1 L glass flasks, which were buried at 0.5 m depth up to 1 m away from the suction cups. To speed up equilibration with the soil, the cups were sampled and the collected soil solutions were discarded twice. All but one of the Teflon cups were installed 2–7 weeks before the sampling commenced, corresponding to 3.5 months prior to the treatments.

During sampling, a suction of 70–80 kPa was applied by manual pumping and the soil-solution samplers were left to fill for 3–5 days. The soil-solution samples were collected in acid-washed plastic flasks in the early part of the study period and thereafter in unwashed polyethylene flasks, which had been tested and approved by the accredited laboratory used, and frozen as soon as possible after sampling. The soil solutions retrieved from the three cups on each plot were mixed in equal proportions to create a composite sample representing the plot. In total, 97% of all potential samples in the studied treatments were obtained. However, some missing or incomplete samples, that is, samples retrieved from less than three Teflon cups, were obtained from nearly all study plots: in all, 23% of the collected samples were retrieved from only two cups per plot and 3.5% from only one cup. Most of the failures were due to some cups repeatedly failing to retrieve water. Three samplings were performed before and 22 after the treatments.

Each soil-solution sample was analysed unfiltered with respect to electrical conductivity (κ), pH, and concentrations of K, Ca, Al, Cu, Cd, Pb, NH_4^+-N, NO_3^--N, phosphate-P (PO_4^{3-}-P), and SO_4^{2-}-S. The sampling period after application covered 6 years for most variables, but for pH and K, Al, Cd, Pb, NO_3^--N, and SO_4^{2-}-S contents it was 9 years. The following constituents were only determined in a subset of the samplings: Na, magnesium (Mg), V, chromium (Cr), manganese (Mn), Ni, zinc (Zn), As, chloride (Cl^-), and total organic C (TOC). B was determined only in the control and N treatments. The chemical analyses were performed by an accredited laboratory (KM Laboratorierna AB, currently ALcontrol AB in Linköping). The electrical conductivity was determined according to Swedish standard SS-EN 27888. The pH value was determined with a pH meter equipped with a glass electrode (combined electrode) according to Swedish standard SS 028122-2. Na, K, Mg, and Ca were measured by optical plasma emission spectrometry, ICP-AES (SS-EN ISO 11885-1). Al and Mn were measured by either ICP-AES or by mass spectrometry (MS), ICP-MS (EPA 200.8). Cu, Pb, and Zn were analysed with an atomic absorption spectrometer equipped with a graphite furnace device. However, from 1999 onwards, the ICP-MS technique was used. V, Cr, and As were analysed by ICP-MS (initially also with an AAS graphite furnace). For As and Cr, the dynamic reaction cell technique was employed using ammonia as collision gas. Total N was converted to NO_3^--N after digestion with peroxodisulphate and determined photometrically by the autoanalyser technique. NO_3^--N was reduced to NO_2^--N and the reagents sulfanile amide and *N*-(1-naphtyle) ethylene diamide gave a coloured complex measured at 545 nm. NO_3^--N was measured by the same principle. First, the sum of NO_3^--N and NO_2^--N was determined followed by the separate analysis and subtraction of NO_2^--N. NH_4^+-N was analysed with an autoanalyser. NH_4^+-N was reacted with sodium salicylate and dichloroisocyanuric acid forming a blue complex measured at 660 nm. PO_4^{3-}-P was

Table 2. Chemical contents of the studied products.

	Crushed ash (n = 4)	Pelleted ash (n = 2)	Nitrogen (Skog-CAN)[a] (n = 1)
Moisture content (%)	26	14	na
LOI (%)	8.7	34	na
Total concentration (% of dry mass)			
Na	11	1.1	na
K	6.4	3.5	na
Mg	1.4	1.4	2.2[b]
Ca	14	15.2	4.7[b]
Al	1.9	3.1	na
Mn	0.8	1.0	na
Fe	1.1	2.1	na
Si	5.6	9.4	na
Ti	0.13	0.14	na
P	0.80	0.80	na
S	11	1.6	na
C	2.0	22	na
Total concentration (ppm of dry mass)			
As	9.3	15	7.2
B	300	140	2[b]
Ba	1300	760	na
Be	<1.2	<1.2	na
Cd	12	9.4	<0.1
Co	15	21	na
Cr	56	54	1.4
Cu	110	100	1.4
Hg	0.28	0.87	na
La	14	17	na
Mo	7.7	<5.9	na
Nb	<12	<12	na
Ni	110	39	<0.5
Pb	110	70	<1
Sc	<2.4	3.1	na
Sn	<24	<24	na
Sr	440	530	na
V	77	37	<2
W	<24	<24	na
Y	5.5	8.2	na
Yb	1.4	1.7	na
Zn	3400	4000	4
Zr	58	72	na

Note: The ash analyses were performed by Svensk Grundämnesanalys AB in Luleå, Sweden, and the analysis of the N fertilizer (Skog-CAN) by KM Laboratorierna AB (currently ALcontrol) in Uppsala, Sweden. The ash analyses were conducted as follows: the samples were dried at 105 °C. As, Cd, Co, Cu, Hg, Ni, Pb, and Zn were measured after dissolving dried samples in HNO_3–H_2O (1:1) in closed Teflon® vessels in a microwave oven. The other elements were measured after melting 0.125 g samples with 0.375 g of $LiBO_2$ and dissolving the resulting mixture in HNO_3. Concentrations were measured by ICP-AES and ICP-MS. S was determined using a Carlo-Erba analyser and by ICP-AES after digestion in HF and HNO_3. ICP-AES probably gave the best estimates of the S contents of the ash products, since S appears to have been present in the ash products mainly as SO_4^{2-}. n, number of samples; na, not analysed.
[a]Concentrations in ppm of fresh sample.
[b]According to the manufacturer.

analysed spectrophotometrically with an autoanalyser. In a solution acidified with sulphuric acid, orthophosphate formed a blue-coloured complex together with molybdate, trivalent antimony, and ascorbic acid (measured at 880 nm). SO_4^{2-}-S and Cl^- were analysed by ionic chromatography according to Swedish (and international) standard SS-EN ISO 10304-1. Finally, TOC was determined by catalytic combustion of the sample followed by spectrometric measurement (IR) of formed

CO_2. Prior to the combustion, the sample was acidified and aerated to remove inorganic C (SS-EN 1484). The concentrations of Cu, Cd, Pb, NH_4^+-N, NO_3^--N, and PO_4^{3-}-P were often below the limits of detection. For V, all concentrations were below the limit of detection. All values below the detection limit for any variable were set equal to it. The valence of Cu, Cd, and Pb was assumed to be 2+ and that of Al 3+. Whitish flakes (of uncertain composition and origin) were oc-

casionally observed in the early samples. The results from the samples with flakes are included in the data presented here.

Leaching

The total amount of K, NO_3^--N, and SO_4^{2-}-S leached annually from some of the treatments was calculated by multiplying the annual mean concentration of the elements in the soil solution at 50 cm depth by the estimated annual percolation in the area. The annual percolation was estimated as the annual precipitation measured at Swedish Meteorological and Hydrological Institute station 9549 Riddarhyttan corrected by +10% minus the annual mean evapotranspiration (500 mm) for the area (Brandt et al. 1994).

Statistical analysis

The data were analysed according to the following mixed linear model (model 1) by means of SAS® Proc MIXED ver. 8.02 (SAS Institute Inc. 1999):

$$[1] \qquad y_{ijk} = \mu + \alpha_i + b_j + d_{ij} + \tau_k + (\alpha\tau)_{ik} + e_{ijk}$$

where y_{ijk} is the concentration of the variable under consideration in the soil solution, μ is the overall mean, α_i is the fixed effect of treatment, $i = 1,..., 10$, b_j is the random effect of block, $j = 1, 2, 3$, d_{ij} is the random effect of interaction between treatment and block, τ_k is the fixed effect of time, $k = 1,..., 22$ (maximum), $(\alpha\tau)_{ik}$ is the fixed effect of interaction between treatment and time, and e_{ijk} is random error.

The data related to all 10 treatments in Table 1 were analysed using model 1. To account for the dependence between repeated measurements, a spatial covariance structure on residuals was used ($\sigma^2\rho^{t_{ij}}$) in which the dependence between samplings (ρ) declines with increasing time intervals (t_{ij}) (SAS Institute Inc. 1999). The denominator degrees of freedom for the tests of fixed effects were estimated according to a general Satterthwaite approximation (SAS Institute Inc. 1999). The need for transformation was judged by considering the skewness and kurtosis of the residuals and by visual interpretation of their distribution. The normality of the distributions of residuals improved after logarithmic transformation for all variables except PO_4^{3-}-P and B. Cu also showed a better distribution of residuals after logarithmic transformation, but then the iteration did not converge. The analysis was therefore performed on untransformed Cu concentrations. The pH values were converted to H^+ concentrations, which gave a closer to normal distribution of the residuals. Treatment means over blocks were calculated by the least-square means method and included an adjustment for missing values. The nonlogarithmic least-square means that are presented in the figures were calculated by running model 1 on untransformed concentrations. Model 1 was modified for application to single samplings by excluding the factors τ_k and $(\alpha\tau)_{ik}$, resulting in model 2. The effects of different treatments were compared by calculating differences of least-square means adjusted for multiple comparisons according to Tukey–Kramer (SAS Institute Inc. 1999). Pearson's correlation coefficients were calculated based on all postapplication observations within single treatments ($n = 1$ treatment × 3 blocks × number of samplings). Effects were considered statistically significant if $p < 0.05$.

Results

The concentrations of the measured elements in the soil solution of the control plots during the study period were as follows (mean concentrations in $\mu mol_c \cdot L^{-1}$ for all samplings, $10 \leq n \leq 22$, with standard deviations in parentheses): K, 7.8 (2.6); Ca, 53 (11); Al, 51 (11); Cd, 0.0012 (0.00086); Pb, 0.0044 (0.0041); Cu, 0.039 (0.036); NH_4^+-N, 0.62 (0.81); NO_3^--N, 0.44 (0.24); PO_4^{3-}-P, 0.46 (0.12); SO_4^{2-}-S, 140 (56); and TOC, 2.8 (0.71) mg·L^{-1}. The median pH was 4.6 (minimum 4.5, maximum 4.8) and mean κ was 3.8 (0.57) mS·m^{-1}.

According to model 1, there was a significant effect of either treatment (α_i) or interaction between treatment and time $(\alpha\tau)_{ik}$ for all of the studied variables except the Mn, Cr, Pb, and As concentrations. Significant effects of treatment were found for κ, K, Ca, Al, Cd, NH_4^+-N, NO_3^--N, and SO_4^{2-}-S, all of which were measured on 18–22 occasions after application, and for Na, Cl$^-$, and TOC, which were measured on 5–10 occasions after application. An effect of treatment was indicated for H^+, Mg, Cu, and Cr ($0.087 < p < 0.13$). Mn, Ni, Zn, As, and PO_4^{3-}-P were not significantly affected by treatment, but significant interactions between treatment and time were found for Ni, Zn, and PO_4^{3-}-P contents. Such interactions were also present for κ, H^+, Na, K, Mg, Ca, Al, Cu, Cd, NH_4^+-N, NO_3^--N, SO_4^{2-}-S, and TOC.

Most of the studied variables showed a distinct temporal pattern, manifested in a significant effect of time for all variables. Soon after application, κ, Na, K, Mg, Ca, Mn, Cd, Cl$^-$, inorganic N, SO_4^{2-}-S, and TOC increased (Figs. 1 and 2). These increases were often followed by gradual declines in the ash treatments. In the pure N treatment, on the other hand, the concentrations shortly returned to pretreatment levels. Most of the effects of the N fertilization lasted for 1–2 years.

3, 6, and 9 Mg crushed ash (3Cr, 6Cr, and 9Cr)

During the first year after application, a pronounced increase in soil-solution κ was observed in the 3Cr, 6Cr, and 9Cr treatments (Fig. 1). The electrical conductivity was significantly elevated for about 1 year in the 3Cr treatment, 3 years in the 6Cr treatment, and at least 6 years in the 9Cr treatment (model 2). The soil-solution pH was only significantly affected in the 9Cr treatment. Starting about 4 years after the application, the pH in the 9Cr treatment was lower than in the control and remained lower for several years (Fig. 1). The pH in the 9Cr treatment was positively correlated with K and SO_4^{2-}-S (Pearson's correlation coefficients 0.26 and 0.74, respectively) and negatively correlated with Al (–0.39). The Al concentration was elevated in the 9Cr treatment compared with the control (models 1 and 2) (Fig. 1).

The K and Ca concentrations showed a large rise initially followed by a gradual decline (Fig. 1). K was elevated in all treatments with crushed ash, whereas Ca was significantly elevated only in the 9Cr treatment (model 1). The increase in K persisted for about 4 years in the 3Cr treatment, 7 years in the 6Cr treatment, and at least 9 years in the 9Cr treatment (model 2). The effect on K appeared at lower ash dosages and was more long-lasting than the effect on Ca. The effects on Na and Mg seemed to follow the same temporal patterns as for K and Ca, respectively.

The Cd concentration was significantly elevated in the 9Cr treatment compared with the control (model 1), and in the 6Cr treatment, a rise in Cd concentration was indicated

Fig. 1. Changes in soil solution chemical variables at 50 cm depth in the pure ash treatments at experiment 249 over time (least-square means over block after application): control (●), 3Cr (▲), 6Cr (−), 9Cr (■), and 3Pel (×). Note that the units and scales differ for the different elements.
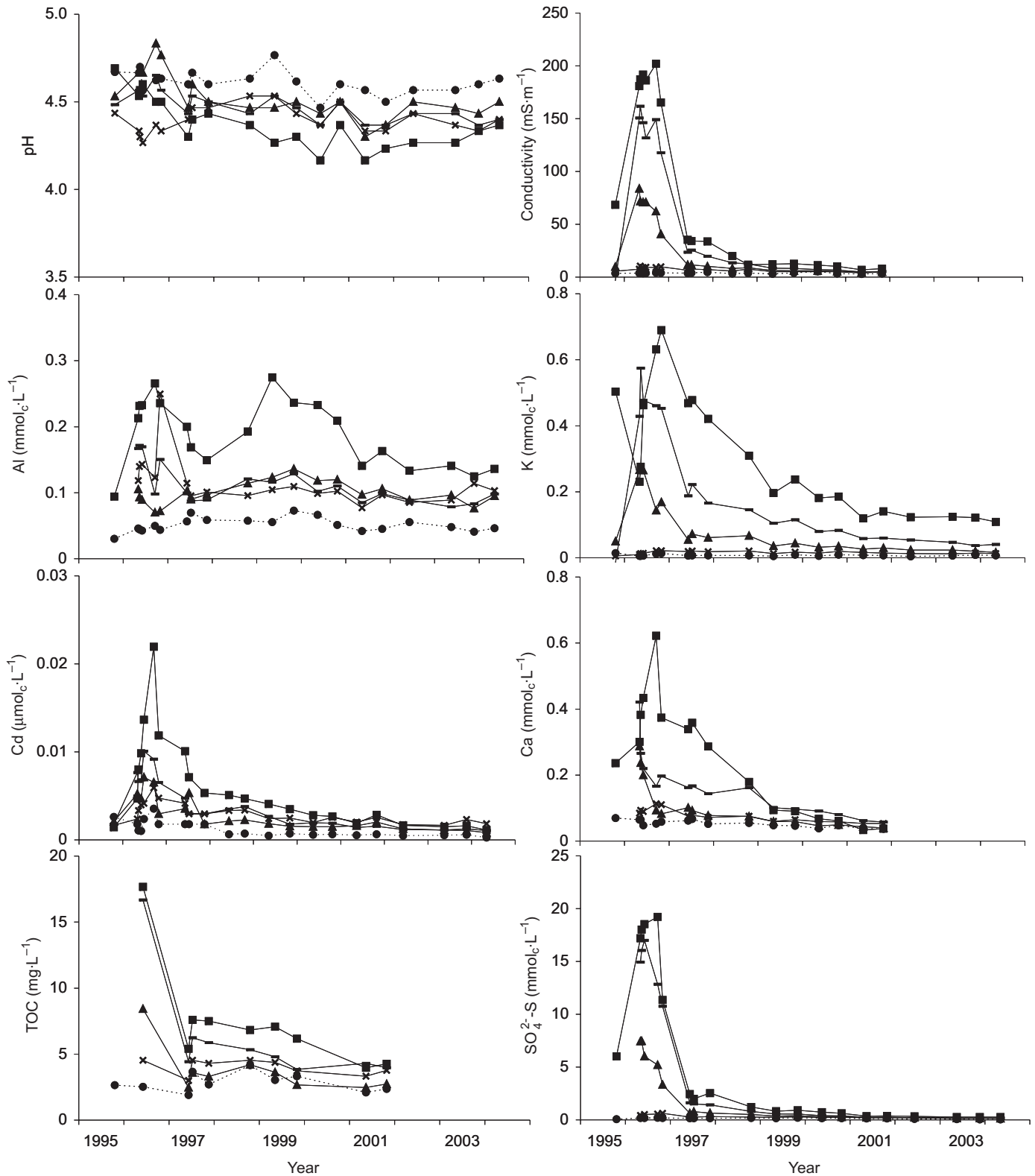
($p = 0.10$). According to model 2, the elevation in the 9Cr treatment was present from the second to the sixth year after application. Zn showed an initial increase followed by a de-cline, similar to the patterns for Na and Mg, all of which were measured on five occasions after the application. The highest Zn concentration (least-square mean) in the treat-

Fig. 2. Changes in soil solution chemical variables at 50 cm depth in the N and low ash treatments at experiment 249 over time (least-square means over block after application): control (●), N (◆), N + Cr (×), NbeforeCr (+), and 3Cr (▲). Note that the units and scales differ for the different elements.
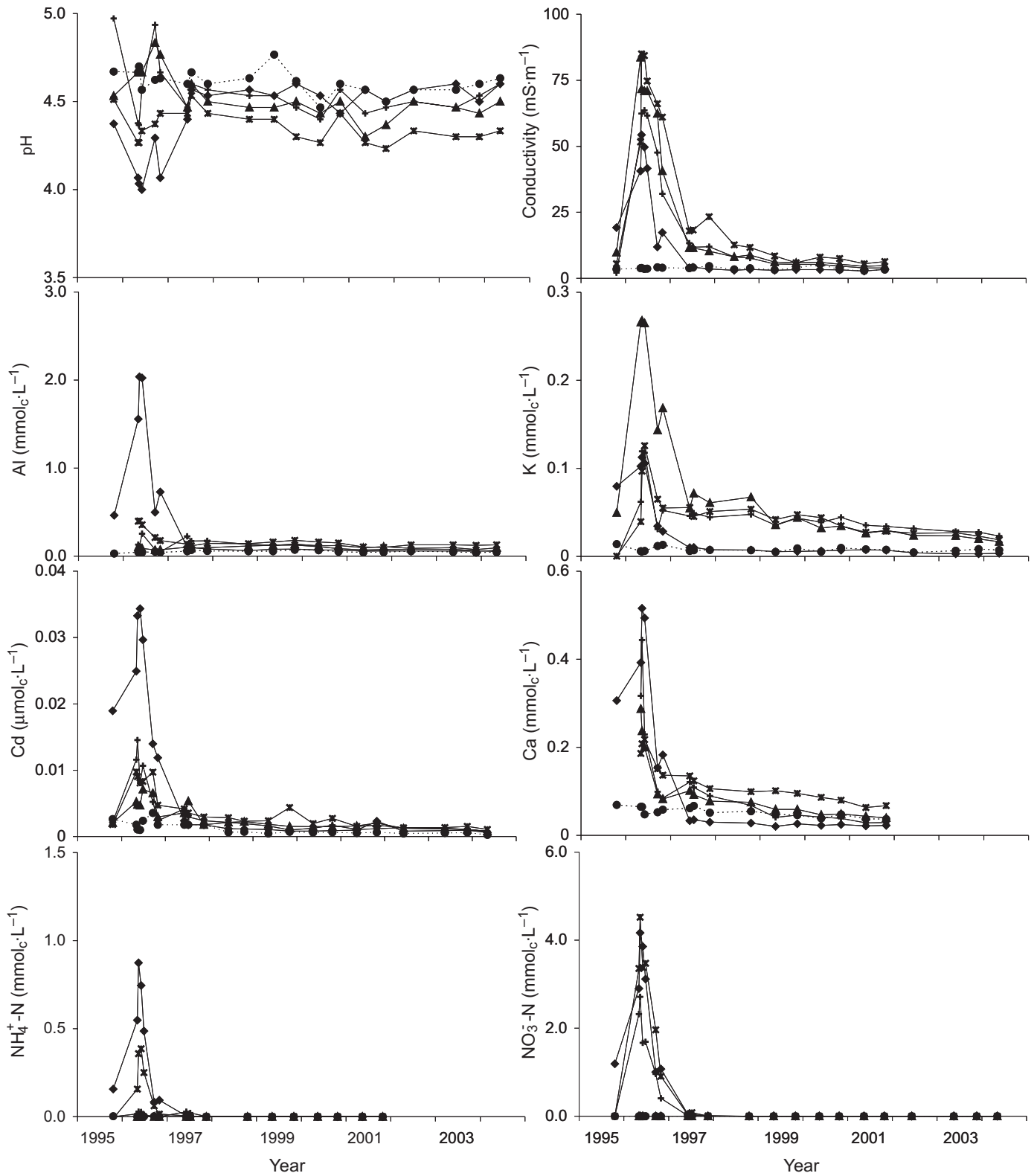
ments with crushed ash was 2.1 µmol$_c$·L^{-1} (in 3Cr). Significant effects were detected on zero, two, and one occasions for Cu, Pb, and PO$_4^{3-}$-P, respectively (model 2), but a large proportion of the Cu, Pb, and PO$_4^{3-}$-P concentrations were below the detection limits, thus adversely affecting the results of the statistical analyses. The highest concentrations (least-square mean) of these elements among all treatments were 0.47 µmol$_c$ Cu·L^{-1} (in 6Cr), 0.026 µmol$_c$ Pb·L^{-1} (in 3Pel (3 Mg ash pellets)), and 1.1 µmol$_c$ PO$_4^{3-}$-P·L^{-1} (in 9Cr).

Inorganic N contents were not significantly affected by the 3Cr, 6Cr, or 9Cr treatments. All measured concentrations of NH$_4^+$-N and NO$_3^-$-N were below 1.2 and 21 µmol$_c$·L^{-1}, respectively. The SO$_4^{2-}$-S concentrations, on the other hand, were considerably increased by these treatments compared with the control (Fig. 1). Although measured less frequently, Cl$^-$ appeared to follow the same temporal pattern as SO$_4^{2-}$-S, although no significant changes in Cl$^-$ were detected with model 2.

Soil-solution TOC was increased by the application of crushed ash. All the treatments with crushed ash, including N + Cr and NbeforeCr, resulted in elevated TOC concentrations a year after application (Fig. 1). In 9Cr plots, the TOC remained elevated for 2 years following the application.

The data shown in Fig. 1 suggest that the effects of the crushed ash on several chemical variables were related to its dosage. However, models 1 and 2 revealed few such differences. According to model 1, κ and K were significantly elevated in 9Cr compared with 3Cr, but no significant differences in the Cd concentrations were found. According to model 2, κ, K, Cd, Pb, PO$_4^{3-}$-P, and SO$_4^{2-}$-S differed occasionally between two ash dosages. A prerequisite for such comparisons was that least-square means could be calculated for all treatments. With model 1, this could only be done for κ, H$^+$, K, Cu, Cd, Pb, and PO$_4^{3-}$-P. For Ca, Al, inorganic N, SO$_4^{2-}$-S, and TOC, least-square means could not be calculated for some or all treatments, probably because of missing data. However, some effects could be related to the ash dosage by linear regression. When regressing the treatment means (µ + α$_i$ according to model 1) of κ, H$^+$, K, Cd, Pb, and PO$_4^{3-}$-P against the ash dosage, that is, 0, 3, 6, and 9 Mg·ha^{-1}, positive linear relationships ($p < 0.05$) were obtained with R^2 values ranging between 0.92 and 0.97. For Cu, no such relationship was detected.

3 Mg ash pellets (3Pel)

The effects of the 3Pel treatment were not significantly different from the control for any of the studied variables apart from SO$_4^{2-}$-S on one occasion and Al on the last two occasions (model 2) (Fig. 1). The data indicate that there were small increases in some variables, for example, κ, K, Ca, Cd, and Zn. A comparison between the 3Pel and 3Cr treatments revealed few significant differences. Only the effects on κ, Na, and SO$_4^{2-}$-S differed occasionally between the two ash products, with 3Cr giving the highest values (model 2).

N and N + 3 Mg crushed ash

Following the N treatment, the NH$_4^+$-N and NO$_3^-$-N concentrations were elevated for 1 and nearly 2 years, respectively (Fig. 2). Soon after fertilization, the pH fell by approxi-

Fig. 3. Average Al concentration from June 1997 onwards, that is, after the initial peak in the N treatment. The average values were calculated on the least-square means presented in Fig. 2. The bars show the standard deviation, which in this case reflects the temporal variation.
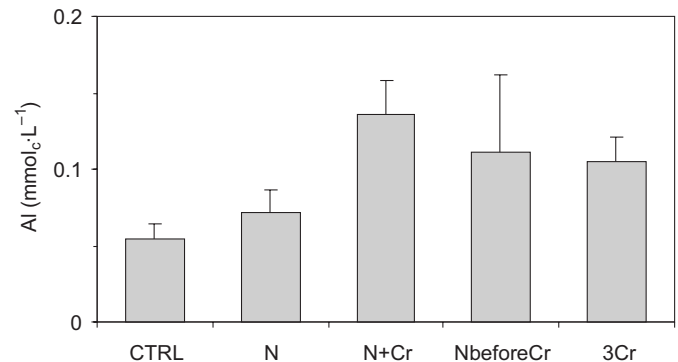
mately 0.6 unit in the N treatment compared with the control. This drop was accompanied by increases in Al, Cd, and Zn. The maximum concentrations of these elements were 2.0 mmol$_c$ Al·L^{-1}, 0.034 µmol$_c$ Cd·L^{-1}, and 11 µmol$_c$ Zn·L^{-1}. A significant increase in B was detected in the N treatment 6 years after fertilization. On this occasion, the B concentration was 20 µg·L^{-1} in the control and 42 µg·L^{-1} in the N treatment. All of these concentrations were above the detection limit.

Despite the simultaneous application of crushed ash, the pH in N + Cr plots initially dropped by 0.4 unit compared with the control (Fig. 2). The pH in N + Cr plots also tended to fall below the control values in 1999 ($p = 0.053$ and 0.054) (Fig. 2). On these occasions, there was no significant difference in the pH values between the N and the N + Cr treatments. As in the N treatment, the Al concentration increased initially in N + Cr plots, and additional increases were recorded at the end of the study period (Figs. 2 and 3). In contrast with the effects of the N treatment, the Cd and Zn concentrations were not significantly increased in N + Cr plots. Compared with the N treatment, the NH$_4^+$-N concentration was lower in NbeforeCr plots, but no significant difference was found for NO$_3^-$-N. As shown in Fig. 2, the N + Cr treatment seemed to produce a smaller peak in NH$_4^+$-N than the N treatment, whereas the peaks in NO$_3^-$-N were similar.

Leaching

The calculated annual percolation in 1996–2003 varied between 165 and 628 mm, with an average of 303 mm, which is of the same order as the long-term average in the area (Brandt et al. 1994). Leaching of K, Ca, Cd, and SO$_4^{2-}$-S was higher in the crushed ash-treated plots than in the control plots (Table 3). The Cd leaching in the N-treated plots was also higher than in the control plots. However, 64% of the Cd leaching in the N-treated plots occurred in the 1st year after fertilization, whereas the Cd leaching in the treatments with crushed ash occurred more evenly during the study period. In general, the leaching increased with increasing ash dosage. The calculations suggest that Ca was retained in the soil to a greater extent than K (Table 3).

Table 3. Estimated amounts of potassium (K), cadmium (Cd), and SO_4^{2-}-S leached in 1996–2003 and of calcium (Ca) leached in 1996–2001.

Treatment	K (kg·ha^{-1})[a]	Ca (kg·ha^{-1})	Cd (g·ha^{-1})	SO_4^{2-}-S (kg·ha^{-1})
Control	6.7	18	1.1	55
3Cr	49 (22%)	27 (2%)	2.7 (5%)	280 (69%)
6Cr	120 (28%)	46 (3%)	3.5 (3%)	570 (79%)
9Cr	220 (37%)	56 (3%)	5.4 (4%)	750 (71%)
N	ne	ne	3.6	ne

Note: The additional leaching (X) compared with the added amount is given in parentheses; X = (leaching$_{treatment}$ − leaching$_{control}$)/added amount; ne, not estimated.

[a]The leaching of K in 1996–2001 was 5.5, 44, 110, and 190 kg from the control, 3Cr, 6Cr, and 9Cr plots, respectively.

Discussion

A Swedish environmental impact assessment of forest biofuels and ash recycling to forests recommended that the maximum dosage of ash should be 3 Mg·ha^{-1} per rotation period (Egnell et al. 1998). The study presented here covered both this and substantially higher ash dosages (up to 9 Mg·ha^{-1}). However, in practical applications of crushed ash, there is likely to be great spatial variability in dosages. Although a dosage of 3 Mg·ha^{-1} might be obtained on an average over a large area, spots with dosages up to 9 Mg·ha^{-1} do not seem unlikely. Effects related to the ash dosage were anticipated in the present study, since the crushed ash was readily soluble and the experimental design encompassed a wide range in the dosages. Such effects were revealed when treatment mean concentrations of H$^+$, K, Cd, Pb, and PO$_4^{3-}$-P and the electrical conductivity were regressed against the ash dosage (0–9 Mg·ha^{-1}). The average concentrations of these elements (and κ) after application increased linearly with increasing ash dosage. A study on the ammonium lactate extractable nutrients in the soil at experiment 249 showed that the K store in the upper mineral soil 5 years after the application increased with increasing ash dosage (Jacobson et al. 2004). The stores of Mg, Ca, and P in the mor layer and (or) the upper mineral soil were significantly increased in the 6Cr and 9Cr treatments compared with the control but did not significantly differ from each other.

The high solubility and high contents of Na and S in the crushed, self-hardened ash were reflected in the results. The ash applied at experiment 249 included readily soluble salts such as Na$_2$SO$_4$, K$_3$Na(SO$_4$)$_2$, and Na$_2$SO$_4$·10H$_2$O, thus generating high concentrations of Na and SO$_4^{2-}$ in the soil solution. In May 1996, for instance, Na accounted for about 90% of the positive charge in the soil solution in the 3Cr, 6Cr, and 9Cr treatments. SO$_4^{2-}$ accounted for an even higher percentage of the negative charge. Given the very high SO$_4^{2-}$ concentrations found and their temporal pattern, it seems likely that the SO$_4^{2-}$ found in the soil solution of the treated plots largely originated from salts in the ash. Four years after the addition of 4.28 Mg wood ash·ha^{-1}, Lundström et al. (2003a) measured elevated concentrations of SO$_4^{2-}$ in the soil solution at 25–30 cm depth at a site in southern Sweden. They suggested that the observed increase in SO$_4^{2-}$ concentration was caused by desorption. In a laboratory leaching test of self-hardened wood ashes, high concentrations of Na, K, Ca, Cl$^-$, and SO$_4^{2-}$ were detected in the initial leachates (Steenari

et al. 1999). Our results demonstrate that similar effects may occur initially in the deep soil solution.

The treatments with crushed ash also increased the concentrations of K, Mg, Ca, Al, and TOC. Despite the high solubility of the crushed ash, the effects on K (and SO$_4^{2-}$) of the 9Cr treatment persisted throughout the 9 years of the study. Lundström et al. (2003a) measured increased concentrations of dissolved organic C in the upper soil 4 years after the application of 4.28 Mg wood ash·ha^{-1} at a site in southern Sweden. At experiment 249, the effect on TOC disappeared after about 2 years. Leaching from damaged bryophytes in the treatments with crushed ash might have contributed to the increases in TOC at experiment 249, since severe damage on some bryophytes was reported from the treatments with crushed ash in a nearby experiment comprising the same treatments and ashes (Jacobson and Gustafsson 2001). In contrast with two other studies on wood-ash application (Högbom et al. 2001b; Ludwig et al. 2002), the ash treatments at experiment 249 did not significantly affect the concentration of inorganic N in the soil solution. The low background leaching of inorganic N, <0.1 kg N·ha^{-1}·year^{-1}, and the C/N ratio in the mor layer (31) suggest that the N limitation of the forest at experiment 249 is more pronounced, which might explain why the ash treatments did not induce an excess leaching of N.

One of the major environmental concerns regarding wood-ash application is the risk of the availability of heavy metals like Cd increasing (e.g., Zhan et al. 1996). Few studies have considered the leaching of Cd in water after wood-ash applications (cf. Aronsson and Ekelund 2004). However, no effects of wood-ash application on the Cd concentration in the soil solution were detected at a Swedish site (Ring et al. 1999) and a Finnish site (Perkiömäki et al. 2003). The present study showed that wood-ash application at high dosages might increase the Cd concentration in the soil solution for several years. According to the leaching calculations, the accumulated leaching of Cd corresponded to about 5% of the amount added in the treatments with crushed ash. Note, however, that the leached Cd might have originated from the soil as well as from the ash. In a nearby experiment, where the same treatments and ashes were tested, elevated concentrations of Cd (and Zn) were measured in the current-year pine needles 2 years after the ash applications (data not shown). Perkiömäki et al. (2003), on the other hand, found no significant elevation in the Cd concentration in pine needles or in the soil solution during 2 and 4 years, respectively, follow-

ing ash addition, even after the addition of Cd-enriched loose wood ash.

The pelleted ash did not have statistically significant effects on the measured soil-solution chemistry parameters, but increases in some variables are indicated in Fig. 1. Since many of the monitored variables spanned a wide range in concentrations (Figs. 1 and 2), the variation of the residuals was probably quite large, thus reducing the likelihood of detecting weak effects such as those indicated for the 3Pel treatment. We applied model 1 to the control and the 3Pel treatment alone and found that the pH was significantly lower and both κ and K were significantly greater in 3Pel than in the control. In addition, tendencies (p = 0.05–0.07) for the treatment to increase Ca, Al, Cd, SO_4^{2-}, and TOC were found.

The effects of pelleted ash were compared with those of the same dosage of crushed, self-hardened ash. The effects on the soil and soil-solution chemical variables of the two ash products could seldom be statistically separated from each other. Jacobson et al. (2004) found no significant differences in pH, K, Mg, Ca, P, N, and C in the mor layer down to 15 cm in the mineral soil 5 years after the ash application. The leaching test suggested that the solubility of the crushed ash was higher than that of the pelleted ash. The higher solubility of the crushed ash was further demonstrated by the fact that three frequently occurring bryophytes were severely damaged initially in all treatments with crushed ash at a nearby experiment with an identical experimental design (both regarding treatments and ashes) as at experiment 249, whereas no damage to them was observed in the treatment with pelleted ash (Jacobson and Gustafsson 2001).

In experiment 249, significant decreases in the pH of the soil solution, accompanied by increases in Al, were found in 9Cr during the last 5 years of the study. Decreases in the soil-solution pH and increased Al concentrations have also been observed in other studies following wood-ash application or liming (Lundström et al. 2003a, 2003b; Aronsson and Ekelund 2004). Lundström et al. (2003a) hypothesized that lowered pH values measured 4 years after the application of 4.28 Mg wood ash·ha^{-1} in southern Sweden were due to an increased flow of H$^+$ from the upper soil as a result of displacement by Ca and Mg in the enlarged exchangeable pool. We do not know how the exchangeable pool at experiment 249 was affected by the treatments. However, the stores of Ca and Mg were significantly elevated in the mor layer in the 6Cr and 9Cr treatments 5 years after the application (Jacobson et al. 2004). The pH values of the mor layer and the upper 7.5 cm of the mineral soil were significantly increased only in the 6Cr treatment.

The N treatment was included mainly as a reference for the combined treatments with N and crushed ash, but the N treatment per se was also of interest. Effects on soil-solution chemistry of this type of N fertilizer (NH_4NO_3 with dolomite), which is the only N fertilizer used on a broad scale in Swedish forestry today, had not been tested, to our knowledge, in detail in the field at that point. Some unexpected effects of the N treatment were observed, of which the increases in Al, Zn, and Cd were the most striking. Similar results were obtained in a followup study by Högbom et al. (2001a) and were attributed to a temporal decrease in the pH. Högbom et al. (2001a) suggested that the mobilized Al, Zn, and Cd

were insolubilized further down in the soil profile, since no effects on the concentrations of these elements in the streams draining the fertilized areas were observed. The elevated Al, Zn, and Cd concentrations in experiment 249 originated from exchange reactions in the soil rather than from the N fertilizer. A simple calculation showed that the Cd and Zn contents of the fertilizer had a negligible impact on the soil-solution concentrations of these elements. The probable mechanisms causing the increases in Cd, Al, and Zn were ion exchange with NH_4^+ from the fertilizer and (or) ion release from the soil matrix because of the lowered soil-solution pH. The negative correlation (–0.8, p < 0.001) between the pH in the N-treated plots and the soil-solution concentrations of both Cd and Al suggest that the decrease in pH contributed to the reported increases in Al, Zn, and Cd. Thus, the present study supports the conclusions drawn by Högbom et al. (2001a), including the finding that the dolomite supplied with the NH_4NO_3 does not counteract the reductions in pH in the soil solution, as found in an earlier study with pure NH_4NO_3 (Nohrstedt 1992). Based on results from liming experiments (Lundström et al. 2003b), the dolomite is probably largely retained in the mor layer, whereas NH_4^+ and NO_3^- move much faster through the soil profile. All effects in the N treatment, apart from the effects on B, were confined to the first 1–2 years with high concentrations of inorganic N.

Unfortunately, the effects of the N + Cr and NbeforeCr treatments could not be validly compared. Uptake and leaching of fertilizer N may have differed between the treatments, since the applications were made late in the growing season and 24 mm of rain fell between the first and second applications of N. Simultaneous application of NH_4NO_3 and ash risks the formation of NH_3. Indeed, the NH_4^+-N concentration shortly after the applications appeared to be lower in the N + Cr treated plots than in the N-treated plots, while the NO_3^--N concentrations were similar (Fig. 2). This implies that the simultaneous application of NH_4NO_3 and ash in experiment 249 resulted in ammonia volatilization.

Plotwise charge balances for the soil-solution chemistry revealed a large surplus in negative charge in about half of the plots in May 1996 during the period of rapid increase in ionic contents. In a few plots, a large surplus in positive charge was found. Since the soil was podzolized, a surplus in positive charge was expected, since organic anions were not monitored (Cronan and Aiken 1985; Lundström 1993). When the soil solution was unaffected, or only slightly affected, by the treatments, for instance before application of ashes and N and in November 1999, a surplus in positive charge (62 and 48 μmol$_c$·L^{-1}) was found at experiment 249. We believe that the uncertainties in the chemical analyses at high concentrations contributed to the large surplus charges. For instance, the maximum uncertainty in the SO_4^{2-} analysis (+15%) was often of the same magnitude as the surplus negative charge in the plots with crushed ash in May 1996.

In principle, the soil-solution concentrations of the various elements reflect their respective leaching rates, since most of the ash treatments probably had a negligible impact on tree growth and thus the water balance (Jacobson 2003). However, since the forest growth at experiment 249 is N limited, the treatments with N might have decreased the percolation, since N fertilization at N-limited sites increases the leaf area

index and hence evapotranspiration (Berdén et al. 1997; Alavi 2002). No corresponding correction for the potential decrease in percolation was made for the N treatment. Only a few observations per year were available for calculating the annual mean concentrations. Although the calculations are rough, they suggest that Ca was retained in the soil to a greater extent than K, as expected, and that the elevated leaching of K, Ca, Cd, and SO_4^{2-} in the treatments with ash might continue for several years to come.

The soil-solution chemistry at the study site did not display any obvious signs of severe acidification prior to treatment, but we found the studied forest realistic for practical biofuel extractions and hence wood-ash application. Our overall conclusions of the rather short-term effects of the studied wood-ash applications are that improvements of the soil-solution chemistry were lacking and, at high dosages, adverse effects were obtained.

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