POLISH JOURNAL OF ECOLOGY (Pol. J. Ecol.)	48	1	63–75	2000

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THE INFLUENCE OF EXPERIMENTAL SOIL ACIDIFICATION AND LIMING ON CONCENTRATIONS OF SOME BASIC AND TRACE METALS IN SCOTS PINE (*PINUS SYLVESTRIS* L.) NEEDLES

ABSTRACT: Two years after last application of sulphuric acid and magnesium lime to the soil of a Scots pine thicket growing in an unpolluted area (NW Poland), concentrations of Ca, Mg, Mn, Cu, Zn, Fe, Cd, Pb and Al in the pine needles of different ages were examined. Soil acidification significantly reduced Ca and Mg concentrations, and raised Al level. In contrast, soil liming increased Ca and Mg, and lowered Al and Mn concentrations. Unexpectedly, lime application led to a significant increase in foliar Zn, Cu, Cd and particularly Pb levels, presumably as an effect of the lime fertiliser contamination. Except Cu and Mg, the concentrations of which significantly decreased with needle age, the examined metals increased or did not change their levels. The tendencies were rather consistent across the treatments, although some site-to-site differences occurred, consisting in variable rates of the changes with time. Although different accumulation rates (mainly Al and Mn) in ageing needles cannot be excluded, the variability seems to have resulted from differences in the treatment effect duration. Thus, Al and Mn were affected for a relatively short time, whereas Cu, Ca, Mg, Zn and Cd (limed site) – for a longer period. Moreover, the effect of soil acidification on Ca and Mg seems to have been slightly intensified with time.

KEY WORDS: acidification, liming, Scots pine, needles, trace metals, calcium, magnesium, treatment effect duration

1. INTRODUCTION

It is generally accepted that soil acidification enhances mobility of ionic Al and other trace metals (Bergkvist 1986, Nouri and Reddy 1995, Reddy *et al.* 1995), leading eventually to disturbances in mineral nutrition of plants. These may include Ca and Mg deficiencies due to antagonistic effect of Al (Shortle and Smith 1988, Rengel and Robinson 1989, Gransson and Eldhuset 1991) or/and leaching from the soil profile (e.g. Ulrich *et al.* 1980, Johnson and Lindberg 1992), and even direct toxicity of Al and other trace metals to plants (Cronan *et al.* 1989, Lamersdorf *et al.* 1991). To mitigate the adverse effects of acidification, soil liming has widely been used in European forests, sometimes combined with correction fertilisation with Mg and other elements (Hüettl 1989, Hüttl and Zöttl 1993, Meiwes 1995). There are many reports of improving growth, vitality and mineral nutrition of the fertilised stands (e.g. Katzensteiner *et al.* 1992, Dreyer *et al.* 1994, Katzensteiner *et al.* 1995). However, soil liming may have undesirable side effects including deficiencies of micronutrients, such as Mn, Zn, Cu, Fe, B (Andersson and Persson 1988, Kabata-Pendias and Pendias 1993, Kreuzer 1995). Moreover, remobilisation of heavy metals from the organic soil layers may occur due to enhanced release of organic complexing agents (Kreuzer 1995).

This work aimed at determining the influence of experimental acidification and liming of the soil in a Scots pine thicket on foliar levels of Ca, Mg and some trace metals. Because elemental concentrations vary during leaf lives, tendencies in concentrations of the metals with needle age were also analysed.

2. STUDY AREA, MATERIAL AND METHODS

The studies were carried out in an experimentally treated Scots pine (*Pinus sylvestris* L.) thicket in a relatively unpolluted region of the country (Człuchów Forest, NW Poland, 53°55' N, 17°10'E) (Tarabuła 1996). The soil was brown podzolic derived from weakly loamy sand on loose sands of fluvioglacial origin. It was characterised by high acidity (pH_{H2O} = 4.4–4.6) and very low effective cation exchange capacity (CEC_E = 19–32 meq kg^{-1}) and base saturation (BS = 7–12%) (Czerwiński *et al.*, unpublished). The examined stand was subdivided into several plots, and the soil was treated with various chemical substances. Three plots were selected to this study, each one of 25 x 25 m in size. These included:

1. "Acid" – soil acidification with diluted H_2SO_4 – 300 and 1200 kg ha^{-1} yr^{-1} in 1986–88 and 1991, respectively,

2. "Lime" – soil liming with burned magnesium lime – 1500 and 18000 kg ha^{-1} yr^{-1} in 1986 and 1991, respectively,

3. "Control" – no treatment.

The untreated (control) plot served as a reference area.

Because the experiment was primarily designed for investigations of entomofauna (Szujecki 1990), limited soil studies were only performed, which did not included trace element analyses. The soil was examined in 1991 after last application of the chemical agents and additionally in 1995 (soil water only).

Samples of live pine needles of different age-classes (current ≥C, C+1, and C+2) were taken from ten to twenty trees per plot on 8 sampling occasions from 8.Jun–31.Oct, 1993, i.e. 2 years after last application of the chemical agents. In the sampling year, the stand was 16-year-old. The needle samples were mineralised at 450° C and dissolved in ultrapure 3N HNO_3. Concentrations of Ca, Mg and Fe were assessed by ASA (Varian Techtron), Zn, Cu, Pb and Cd – by the inverse voltamperometry with standard addition (DPASV, Methrom), and that of Al – colorimetrically with chromasurol S and ascorbic acid addition (spectrophotometer Shimadzu). Mn concentration was determined by ionic chromatography (Methrom) in homogenised samples after extraction with deionised water. The needles were not washed prior to the analyses.

Mean metal concentrations in foliage for each date (in mg g^{-1} or µg g^{-1} dw) were calculated as means weighed by percentage contribution of needles of different age-classes to total foliage biomass estimated previously (Tarabuła and Żero 1997). Comparisons between the treatments and the control plot were made using paired t-test for successive sampling dates. The same procedure was applied to assess significance of differences across various needle cohorts.

3. RESULTS

After application of sulphuric acid, soil pH did not change significantly and approximated the control level in both 1991 and 1995. However, base saturation, was as low as 5.9% at the Acid plot, whereas at the Control it amounted to 10.4%. Moreover, acid addition resulted in a slightly, yet significantly raised saturation with Al ions (90.5% *vs* 86.0% at the Control) (Table 1). These were most likely reasons of significantly increased concentration of Al in the pine needles and substantially reduced concentrations of Ca and Mg. Mean foliar levels of the two latter elements amounted to 1.5 and 0.4 mg g^{-1}, whereas at the control plot the respective values were 2.1 and 0.6 mg g^{-1} (Table 2). Acidification had little effect on concentrations of other metals examined. A 3-fold increase in foliar level of Pb, when compare with the control plot, appeared to be statistically insignificant (Table 2).

Although soil pH at the limed plot did not increase significantly in 1991, it was much higher after several years since the treatment and amounted to 6.03, whereas at the control plot it was only 4.74. In contrast to soil acidification, application of magnesium lime increased saturation with basic cations by several times (to 57.1%) (Table 1). As a consequence, mean foliar Mg concentration

Table 1. Some properties of the upper 15 cm soil layer. The data are means of 3 samplings made in 1991 after last application of the chemical substances. Additionally, pH in H_2O values for 1995 are given (n=8). Significance of the differences between the treatments and the control were assessed using Student t-test for independent samples
(*ns* – not significant, * – $P < 0.05$, ** – $P < 0.01$, *** – $P <$ 001)

Treatment	pH (H_2O)	pH (KCl)	pH (H_2O)	CEC_E	BS	HS	AlS
	1991		1995	meq kg^{-1}		$\%CEC_E$	
Control	4.23	3.61	4.74	33.4	10.4	3.6	86.0
Acid	3.81 *ns*	3.61 *ns*	4.61 *ns*	34.4 *ns*	5.9^{**}	3.6 *ns*	90.5^{*}
Lime	4.88 *ns*	4.23 *ns*	6.02^{***}	29.9 *ns*	57.1^{*}	2.4 *ns*	40.5^{*}

CEC_E – effective cation exchange capacity = meq$\Sigma(Ca^{2+}, Mg^{2+}, K^+, Na^+, H^+, Al^{3+})$
BS – base saturation = meq$\Sigma(Ca^{2+}, Mg^{2+}, K^+, Na^+)$
HS – hydrogen saturation = meq $H^+\times100/CEC_E$
AlS – aluminium saturation = meq $Al^{3+}\times100/CEC_E$

Table 2. Mean metal concentrations (and standard deviations) in Scots pine needles. Significant differences between the treatments and the control according to paired t-test for successive sampling date (n = 8) are marked with stars
* – P<0.05, ** – P<0.01, *** – P<0.001

Treatment	Ca	Mg	Mn	Fe	Zn	Cu	Cd	Pb	Al
		mg g^{-1}				μg g^{-1}			
Control	2.08 (0.29)	0.57 (0.08)	0.66 (0.08)	43.9 (19.8)	23.1 (5.0)	1.85 (0.15)	0.06 (0.01)	0.07 (0.06)	27.5 (8.6)
Acid	1.53*** (0.25)	0.43*** (0.06)	0.67 (0.12)	43.2 (7.6)	19.1 (1.5)	1.92 (0.30)	0.06 (0.01)	0.23 (0.30)	36.8** (9.2)
Lime	2.77*** (0.27)	1.79*** (0.16)	0.44*** (0.05)	43.4 (7.0)	35.2*** (4.4)	2.49*** (0.17)	0.09* (0.02)	0.37** (0.22)	21.8* (5.2)

was more than 3 times higher when compare with the control plot and approximated 1.8 mg g^{-1}. Foliar concentration of Ca was also significantly raised (to 2.8 mg g^{-1}) though the relative increase (in per cent relative to the control level) was much less pronounced than that for Mg (Table 2). Additionally, soil liming resulted in significantly reduced foliar levels of Mn and Al (Table 2). However, the Al concentration did not fall much (from 27. 5 µg g^{-1} at the Control to 21.8 µg g^{-1} at the limed plot) when one would take into account more than twofold reduction of Al saturation in the limed soil (86.0% to 40.5%) (Table 1). Unexpectedly, concentrations of Zn, Cu, Cd and particularly Pb were statistically higher at the limed than the control plot, with the foliar level of lead having been about 5 times higher than that found at the Control (Table 2). Nevertheless, concentrations of the trace metals remained at fairly low levels.

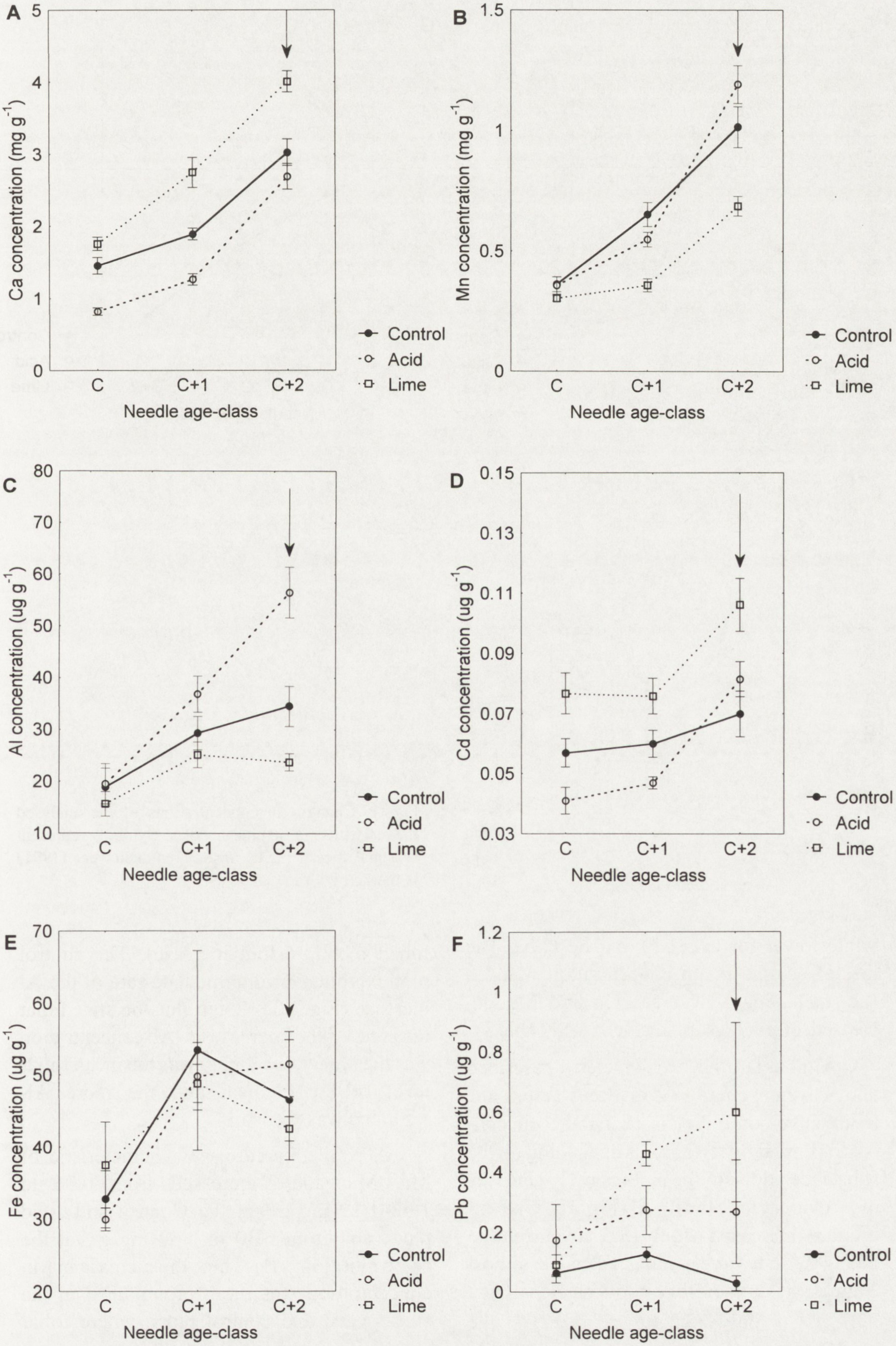
Because elemental concentrations in needles change naturally with the needle age-class, the treatments' effects should be analysed in a more detailed way. First of all, it is to find what is a general pattern of changes in the metal concentrations with the needle age. Secondly, it is to recognise how the pattern has been modified by particular soil treatments.

On the basis of general tendencies in concentrations with needle age (means for the three plots), several groups were distinguished among the examined metals. The first group included metals, the concentrations of which grew significantly from year to year during entire period of the needle lives (Ca, Mn, Al) (Table 3, Fig. 1A, B, C). Cadmium, Fe and Pb could also be qualified to the group, as their concentrations significantly increased, though during one year only, while remained unchanged during the other year (Table 3, Fig. 1 D, E, F). There is some statistical uncertainty about Pb behaviour, as variability in this metal concentration was very high, especially in the oldest needles (Table 3, Fig. 1F). Next group consisted of Cu and Mg, both metals displaying a tendency to decline their concentrations with needle age (Table 3, Fig. 1G, H). Finally, Zn represented a separate category, as its concentration decreased and then increased reaching the same level as in current needles (Table 3, Fig. 1I).

The overall rate of increase in concentration of a given metal (from age C to C+2) can be expressed as the concentration ratio between two-year-old and current needles, whereas the decrease – as its reverse (Table 3). Thus, the factor would inform by how many times concentration of a given element increases or decreases during the needle lives. It appeared that the highest rate of increase was characteristic of Mn (2.9). The index was also high for Pb, Ca and Al (>2),

Table 3. Changes in mean concentrations of metals with age of pine needles. The data are means of 8 sampling occasions and three plots. Different letters denote significant differences between needle classes according to paired t-test for consecutive sampling dates. The factors of increase/decrease were calculated as concentration ratios of C+2 to C needles (increase – positive values) or c to C+2 (decrease – negative values).

Needle age class	Ca	Mg	Mn	Fe	Zn	Cu	Cd	Pb	Al
		mg g^{-1}					µg g^{-1}		
C	1.34**a**	1.15**a**	0.34**a**	37.2**a**	27.6**a**	2.52**a**	0.058**a**	0.11**a**	18.0**a**
C+1	1.97**b**	0.84**b**	0.52**b**	48.6**b**	21.7**b**	2.05**b**	0.061**a**	0.29**b**	30.5**b**
C+2	3.24**c**	0.78**b**	0.97**c**	46.8**b**	28.4**a**	1.66**c**	0.086**b**	0.30**ab**	38.3**c**
Factor of increase/decrease	2.4	–1.5	2.9	1.3	1.0	–1.5	1.5	2.7	2.1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3
4
5
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C+1
C+2
Needle age-class
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Lime
B
Mn concentration (mg g-1)
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0.5
1
1.5
C
C+1
C+2
Needle age-class
Control
Acid
Lime
C
Al concentration (ug g-1)
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20
30
40
50
60
70
80
C
C+1
C+2
Needle age-class
Control
Acid
Lime
D
Cd concentration (ug g-1)
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0.05
0.07
0.09
0.11
0.13
0.15
C
C+1
C+2
Needle age-class
Control
Acid
Lime
E
Fe concentration (ug g-1)
20
30
40
50
60
70
C
C+1
C+2
Needle age-class
Control
Acid
Lime
F
Pb concentration (ug g-1)
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0.2
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C+2
Needle age-class
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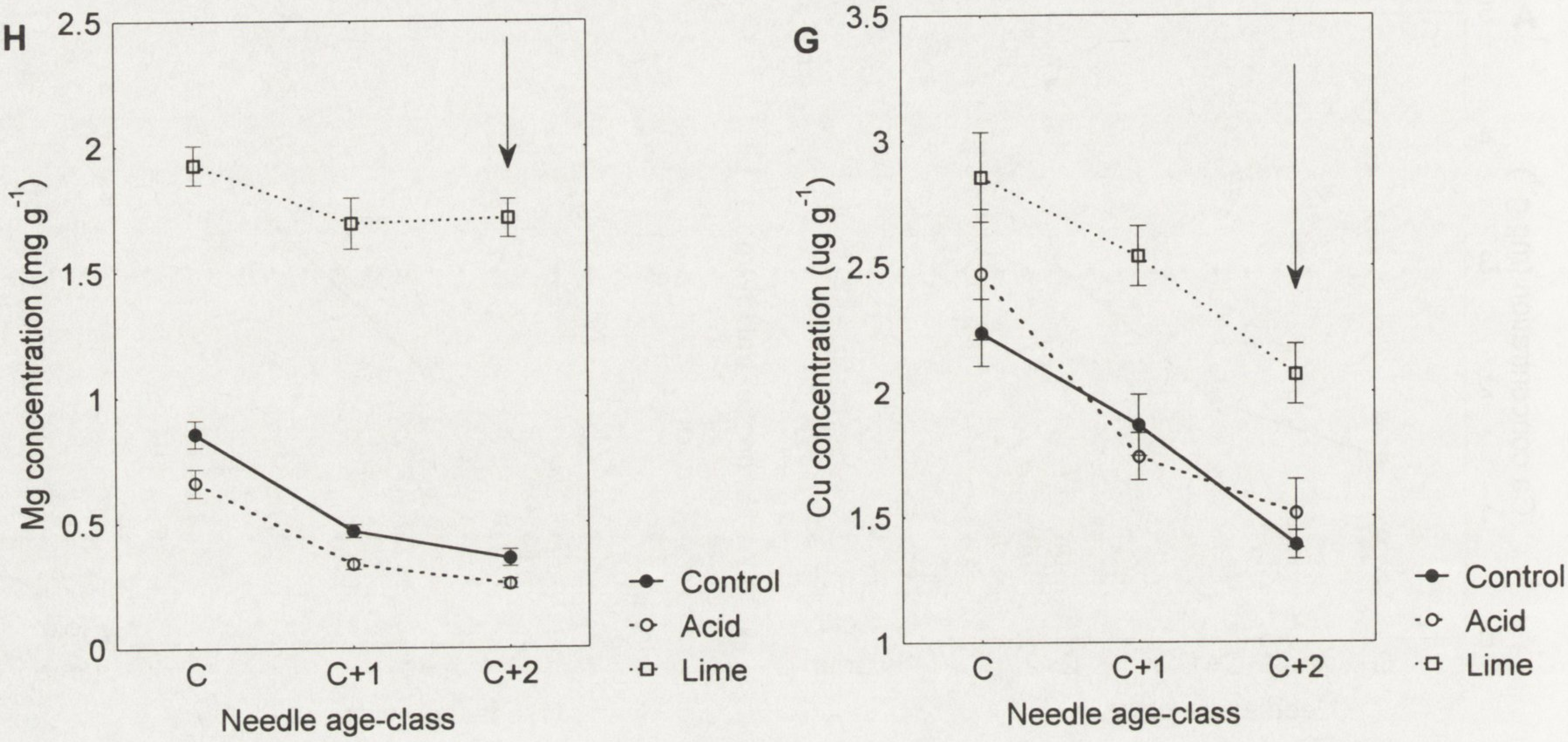
Acid
Lime



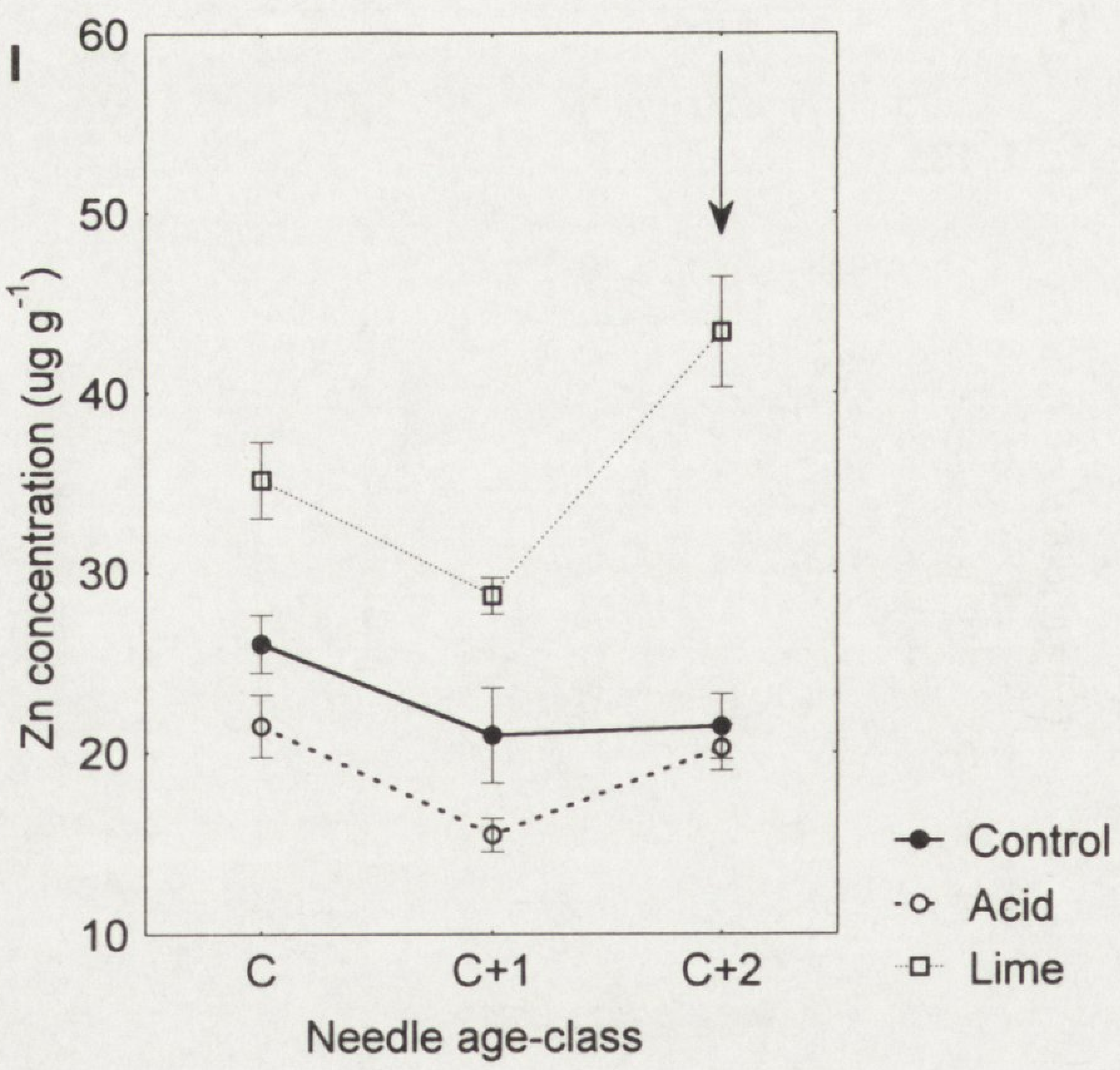


Fig. 1. Changes in concentrations of the analysed metals with age of pine needles. Symbols represent seasonal means (±SE), n=8. Treatment year (1991) is marked with the arrow.

while lower for Cd (1.5) and Fe (1.3). The rate of change in Zn concentration was 1.0 (i.e. no change), whereas Cu and Mg decreased, on average, by factor of 1.5 (Table 3).

Although the tendencies described above were generally consistent across the treatments, some metals changed their concentrations at different rates depending on the substance added to the soil (Fig. 1). This was most evident for Mn and Al (Fig. 1B, C). Aluminium increased from 19.5 in current to 56.6 g g^{-1} in two-year-old needles, i.e. almost 3 times, at the acidified plot, whereas from 15.7 (C) to only 25.2 μg g^{-1} (C+2) at the limed plot (1.6-fold increase). The control plot exhibited an intermediate rate of the Al increase (Fig. 1C). It can thus be stated that the rate of the increase in Al concentration was the higher, the higher was the mean foliar level of the element and the more Al-saturated was the soil.

A similar picture was characteristic of Mn. Manganese increased from 0.36 to 1.02–1.19 mg g^{-1} at the Control and Acid plots, and from 0.30 to 0.69 mg g^{-1} at the Lime plot (Fig. 1B). Thus, the increase in Mn concentration was more pronounced in the acid-treated and control plots, where foliar

Mn was similarly high, while less pronounced in the limed plot, where the mean Mn level was lowered (Table 2). It should be noticed that concentrations of both Al and Mn in current needles did not differ among the treatments, though C+2 concentrations varied much (Fig. 1 B, C).

A similar pattern was also observed for lead (Fig. 1F). Its concentration at the control plot was almost unchanged regardless of needle age, whereas at the limed plot Pb level was higher in older needles, while lower in current ones. At the same time, Pb concentration in the youngest needles did not differ between the Control and Lime plots (Fig. 1F). Changes in concentrations of the remaining metals were not so diversified across the examined sites.

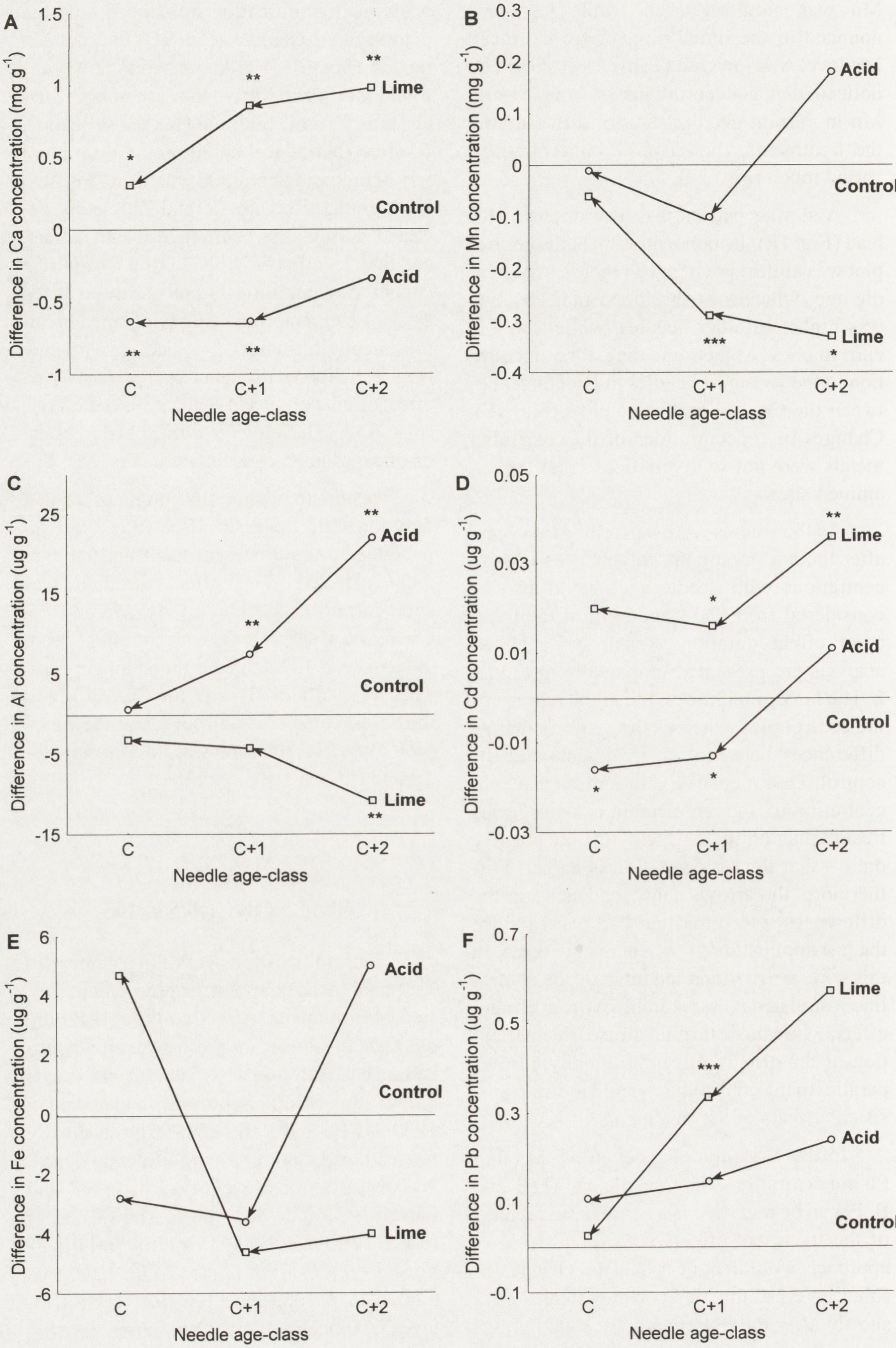
As the studies were performed two years after the soil treatment, the changes in concentrations with needle age should also be considered from the standpoint of the treatment effect duration. Results of such an analysis are presented graphically in Figure 2. The horizontal line on the graph represents the control plot, whereas the symbols denote differences between the treatments and the control. Thus, negative values mean that concentration of a given element is lower in the treated than untreated site, while the positive ones – that the concentration is higher. Furthermore, the arrows show tendencies in the differences with time that had passed since the last application of the chemical agents. In this way, arrows directed towards the control line would denote weakening of the treatment effect, while those turning away – intensification of the effect with time. Finally, arrows parallel to the control line would indicate persistent effects of the treatments.

In this way, the changes in Al, Mn and Pb concentrations with needle age (Fig. 2C, B, F) can be regarded in a sense of weakening of the treatment effects with time. Such an approach would suggest that the changes in foliar levels of the metals were affected only shortly after the treatments. As stated previously, soil acidification influenced only the pattern of Al changes (Fig. 2C), but not Mn nor Pb (Fig. 2B, F). Another regularity was found for Ca and Mg. In the case of both metals, the effect of soil liming tended to decline, whereas that of soil acidification – to intensify or at least to continue with time (Fig. 2A, H). Liming effect on Cd and Zn clearly declined during first year since the treatment, and then levelled off (Fig. 2 D, I). Changes in copper concentrations were hardly affected by the treatment, this being confirmed by almost negligible tendency to decline with time (Fig. 2G). Soil acidification had practically no effect on changes in Cd, Zn, Cu concentrations (Fig. 2D, G, I). Neither treatment had an effect on changes in Fe concentration (Fig. 2E).

To sum up, it should be emphasised that duration of the treatment effect may differ depending on the treatment itself and the element affected. The effect duration was short-lasting in the case of Al, Mn and Pb, whereas Ca, Mg and Cu concentrations seem to have been affected over much longer time. This was particularly true for Ca and Mg at the acid-treated site, and for Cu at the limed plot. The effect duration was intermediate for Zn and Cd.

4. DISCUSSION AND CONCLUSIONS

The results of this work have confirmed the phenomena commonly observed in acidified environments. Although the soil pH did not change significantly after the acid application, base saturation, which is a good measure of soil acidification (de Vries *et al.* 1989, Hüttl and Schaaf 1995), was greatly reduced, and that of Al – significantly raised. As expected, foliar level of Al increased, and those of Ca and Mg – decreased (Table 2) (e.g. Oren *et al.* 1989, Johnson and Lindberg 1992). Concentrations of the latter two metals in current needles (0.82 and 0.66 mg g^{-1}, respectively) reached deficiency lev-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Difference in Ca concentration (mg g-1)
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-1
*
**
**
**
**
Lime
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Acid
C
C+1
C+2
Needle age-class
B
Difference in Mn concentration (mg g-1)
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0
-0.1
-0.2
-0.3
-0.4
Acid
Control
Lime
***
*
C
C+1
C+2
Needle age-class
C
Difference in Al concentration (ug g-1)
25
15
5
-5
-15
**
**
Acid
Control
Lime
**
C
C+1
C+2
Needle age-class
D
Difference in Cd concentration (ug g-1)
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0.03
0.01
-0.01
-0.03
**
Lime
*
Acid
Control
*
*
C
C+1
C+2
Needle age-class
E
Difference in Fe concentration (ug g-1)
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4
2
0
-2
-4
-6
Acid
Control
Lime
C
C+1
C+2
Needle age-class
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Difference in Pb concentration (ug g-1)
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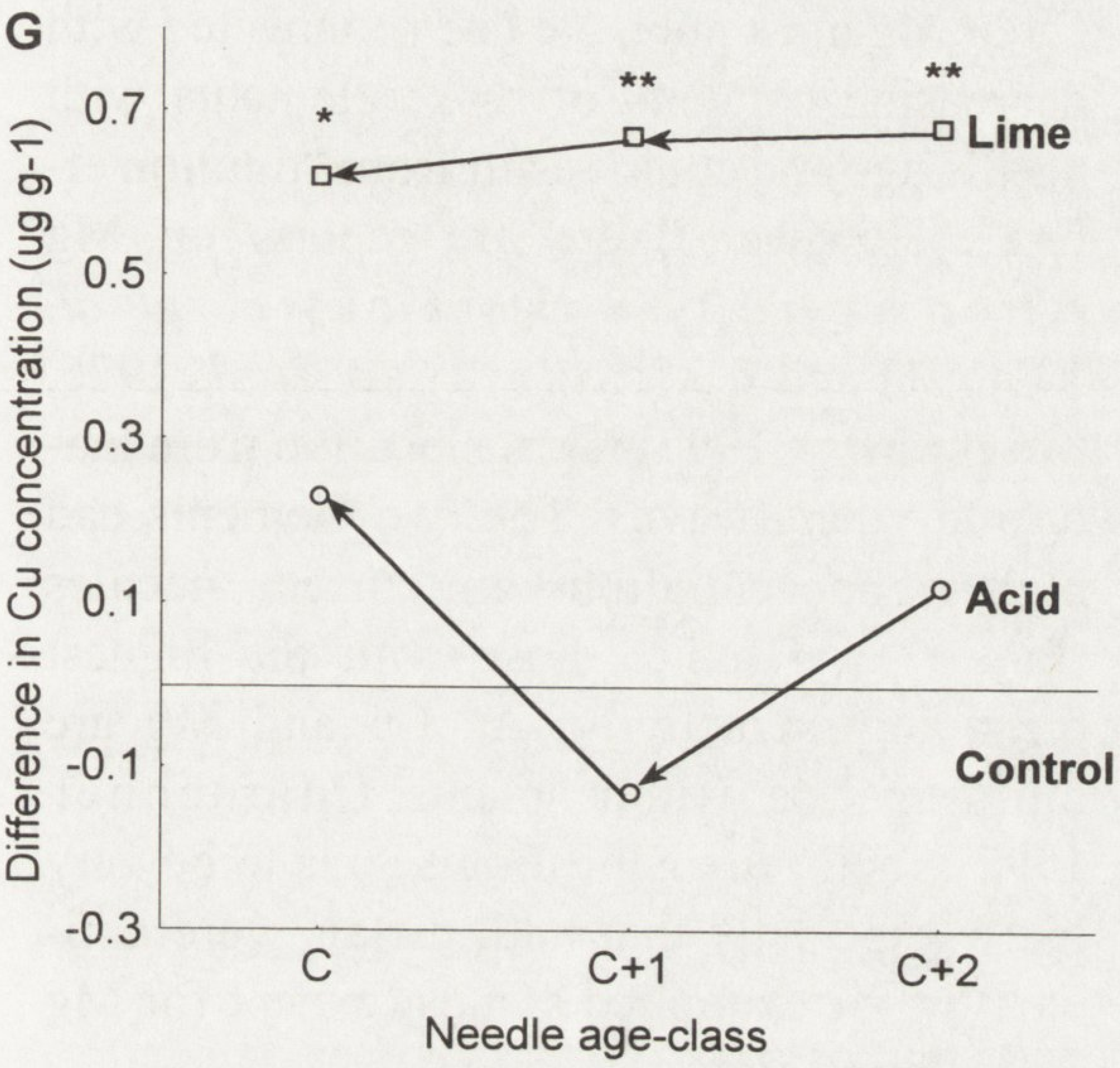
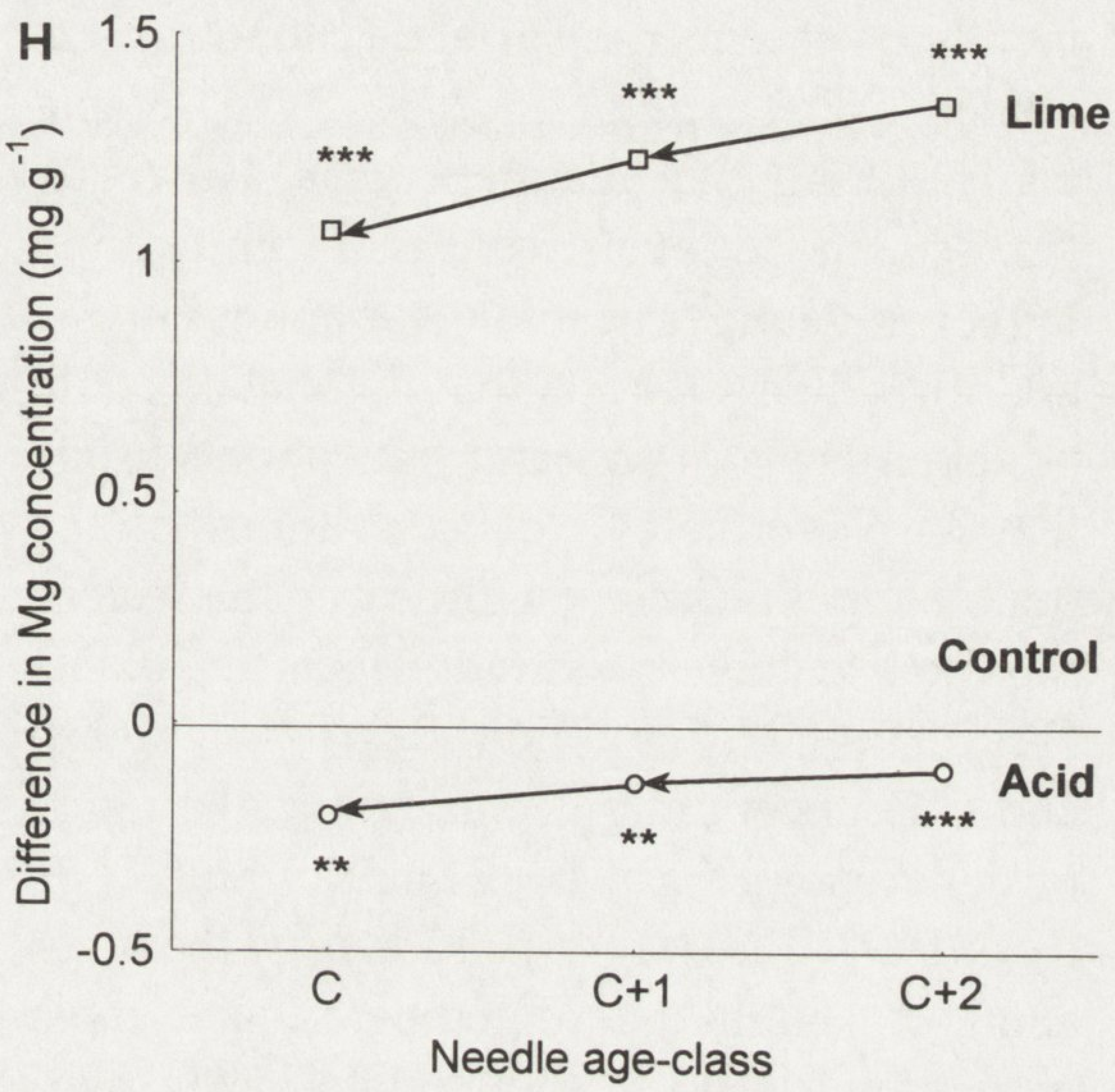
Needle age-class





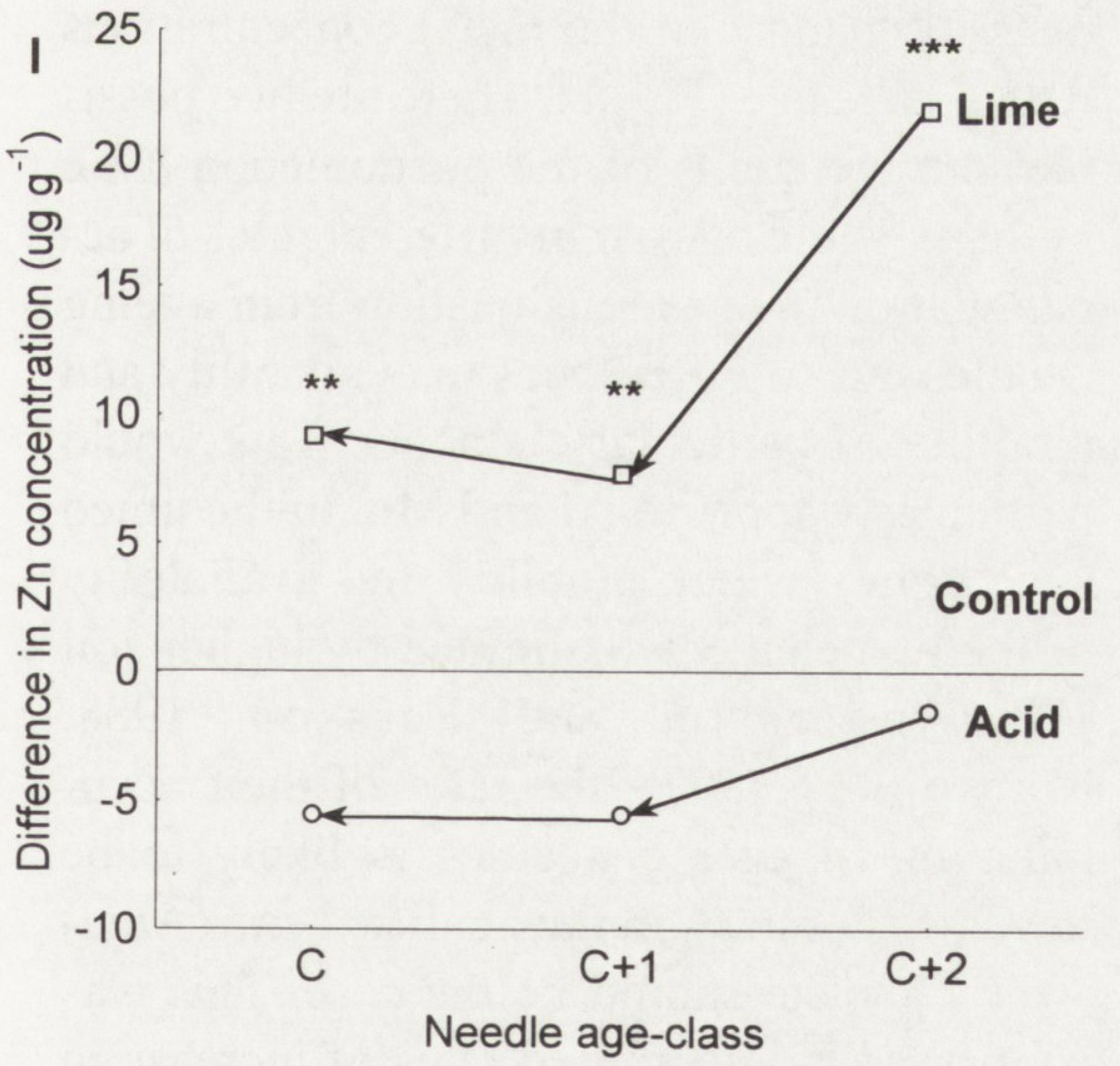


Fig. 2. Differences in metal concentrations between the treatments and the reference plot. Concentrations at the control plot were assumed constant (the horizontal line). Arrows denote tendencies with time since the last application of the chemical agents. Statistically significant differences between the treatments and the control are marked with stars according to paired t-test for consecutive sampling dates ($n = 8$) (* – $P < 0.05$, ** – $P < 0.01$, *** – $P < 0.001$)

els (Johnson *et al.* 1992, Thelin *et al.* 1998).

Soil liming resulted in an increase in Mg and Ca at simultaneous decrease in Al and Mn, which has also been well documented in the literature (e.g. Andersson and Persson 1988, Dreyer *et al.* 1994, Kreutzer 1995). Magnesium concentration in current needles (1.93 mg g^{-1}) exceeded the upper sufficiency level (Johnson *et al.* 1992, Thelin *et al.* 1998). Although significant, the increase in Ca level was not large in relation to the exceptionally large dose of lime applied or to the reported increase in base saturation of the soil (cf. Tables 1 and 2).

More attention should be given to the unexpected increase in foliar levels of Cu, Zn, Cd and particularly Pb following soil liming (Table 2). The only reasonable explanation of the phenomenon seems to be lime contamination with the trace metals. Although the substances applied to the soil were not chemically analysed, this might be the case as lime fertilisers are often by-products of zinc and lead works (Kabata-Pendias and Pendias 1993). Because needles were not washed before analysing, deposition of the metals on the needle surfaces cannot be excluded (Wyttenbach *et al.* 1985), especially during the treatment year. However, Cu, Zn and Cd levels were also significantly higher in younger needle generations (Figs 1 and 2), which suggests that the metals could be taken up *via* roots and transported to the leaves. Nevertheless, concentrations of the trace elements were much lower than those reported to have negative effects on plants (Kabata-Pendias and Pendias 1993), and Cu concentration remained in the range of deficiency (Kabata-Pendias and Pendias 1993, Thelin *et al.* 1998). On the other hand, it should be remembered that most trace metals tend to accumulate in the rizosphere and the forest floor (Dürr and Münnich 1991, Göransson and Eldhuset 1991, Lamersdorf *et al.* 1991), which may pose a threat to the plant roots and the soil biota.

It appeared that most trace metals tend to increase their concentrations with needle age, which is particularly true for Mn and Al. The same applies to calcium, which is an exception among macronutrients in that it is hardly mobile, tends to precipitate as oxalates and continues to accumulate in foliage (Marschner 1997). Then, Mg and Cu tend to decrease their concentrations during the needle lives. Zinc was the only metal, the concentration of which decreased, and then increased resulting in little overall changes (Table 3). The results presented in this work are in a good agreement with those described by Wyttenbach *et al.* (1995) for concentrations of the metals in Norway spruce needles.

Because needles become thicker and heavier per unit of length as they age (Tarabuła and Żero 1997), it can be concluded that increasing (or constant) concentration means increasing content of an element. This relates certainly to such metals as Ca, Mn, Al, Pb, Cd, Fe and probably to Zn, which would support the common opinion of accumulation of the trace metals in ageing leaves (Wyttenbach *et al.* 1995, Marschner 1997). On the other hand, decreasing concentrations of Cu or Mg must not have been connected with decreasing contents of these elements with needle age and could result from "dilution effect". However, there are reports on Mg (Oren *et al.* 1988, Le Goaster *et al.* 1990/91) and Cu (Loneragan *et al.* 1976, Marschner 1997) retranslocation from mature to young leaves. The two elements had highest concentrations in current needles (Fig. 1 G, H), i.e. those with the highest physiological activity. As Cu and Mg are fairly mobile within plants (Marschner 1997), their retranslocation seems to be very likely especially that both metals were deficient in the examined stands (except for Mg at the limed plot).

The treatments differed with regard to rates of changes in the metal concentrations with needle age (Fig. 1). There are two possible interpretations of the phenomenon. One of them would consist in different rates of accumulation in or retranslocation from ageing needles due to differences in availability and mobility of particular elements. This would particularly apply to Al and Mn. In the limed site (Lime), where mobility and availability of the two elements is limited by higher soil pH (Andersson and Persson 1988, Marschner 1997), the rates of their accumulation in ageing needles is likely to be lower. In contrast, in the acidified site (Acid) – the opposite should be the case. This was confirmed by diversified rates of increase in Al and Mn concentrations with the needle age, which were much lower at the Lime than Acid plot (Fig. 1B, C). However, the above explanation would be satisfactory enough if the chemical substances had been applied to the soil in the year of the study. Because the soil was last treated in 1991 (when C+2 needles were the current ones), another interpretation seems to be more reasonable, i.e. weakening of the treatment effects with time. In this way, greatly diversified Al and Mn levels in two-year-old needles could reflect initially large differences in the metal availability (and uptake). With time, the differences have become smaller and almost disappeared in current needles (i.e. 2 years after application of the chemical substances) (Figs 1B, C and 2B, C). The same was true for Pb at the limed plot (Figs 1F and 2F). On the other hand, although the differences in Ca, Mg and Cu, as well as those in Zn and Cd concentrations tended to decline at the limed plot, the treatment effect was still evident after two years after the lime application (Figs 1 and 2). Moreover, at the acid-treated plot, the effect on Ca and Mg displayed even a tendency to increase with time (Fig. 2A, H). Such a picture would suggest that duration of the treatment effect depends on the treatment type and the elements affected. In this context, Al and Mn seem to have been affected for a relatively short time (about 1–2 years), whereas Cu, Ca, Mg, Zn and Cd – for a longer period. Moreover, the effect of soil acidification on Ca and Mg seems to have been slightly intensified with time.

The results obtained during one-year-study do not allow to decide which one of the two presented explanations reflects true reasons of the between-site differences in the rates of changes in the metal concentrations. The effects observed could result from either one or both factors at the same time. Nevertheless, it is obvious that chemical substances entered into an ecosystem modify nutritional status of plants. It can be expected that even if acid substances are no longer introduced, calcium and magnesium can still be deficient if their depletion rates through leaching losses from the soil exceed inputs from weathering and atmosphere (Johnson and Lindberg 1992). On the other hand, although soil treatment with magnesium lime substantially improved Mg and Ca nutrition, a side effect of liming, i.e. introduction of heavy metals may occur. Regardless of whether the metals are taken-up or deposited on the plant and soil surfaces, their presence in the environment poses a potential threat to the ecosystem, especially when the positive lime effect on soil pH ceases.

ACKNOWLEDGEMENTS: I would like to thank to Professor J.R. Zimka and Assistant Professor A. Stachurski for discussions and valuable comments on the manuscript, and to K. Zielska and B. Królak for their help in performing chemical analyses.

5. SUMMARY

In this work, influence of soil treatment with sulphuric acid and magnesium lime on foliar concentrations of Ca, Mg, Mn, Cu, Zn, Fe, Cd, Pb and Al and their changes with needle age were analysed. The studies were performed in a Scots pine thicket in NW Poland in 1993, i.e. two years after last application of the chemical substances.

Soil acidification significantly increased Al and decreased base saturation (Table 1), which was reflected by significantly increased foliar level of Al, and decreased Mg and Ca concentrations (Table 2). In contrast, soil liming reduced saturation with Al, and raised that with basic cations (Table 1). As a consequence, Al concentration in needles was significantly lower, and those of Ca, and particularly Mg – substantially higher than recorded at the untreated plot (Table 2). Additionally, soil liming reduced foliar Mn level. Unexpectedly, mean concentrations of Zn, Cu, Cd, and particularly Pb in live needles significantly increased following lime application (Table 2), which was attributed to contamination of the fertiliser.

It has been found that concentrations of Ca, Mn, Al, Fe, Cd and Pb tend to increase their concentrations with needle age, whereas those of Cu and Mg decline with the needle age. Zn concentration decreased and then increased, resulting in no change from current to two-year-old needles (Table 3). On the basis of the literature, the changes were attributed to accumulation in (Ca, Mn, Al, Fe, Cd, Pb, Zn) and retranslocation from (Cu, Mg) ageing needles.

The general pattern of changes in concentrations of the metals with needle age was modified by the soil treatments. This was manifest by diversified rates of the changes (Fig. 1). The most pronounced departure from the overall pattern was characteristic of Al, Mn and Pb (Fig. 1). This could be attributed to differences in availability and mobility of the elements, and hence, to different accumulation rates of the elements in ageing needles. Alternatively, a more plausible explanation was proposed, consisting in a fairly rapid weakening of the treatment effects. The latter possibility implies that different treatments may affect concentrations of particular elements for a shorter (Mn, Al, Pb) or longer time (particularly Ca and Mg in the acidified site, but also Cu, Zn, Cd, Mg, Ca in the limed stand) (Fig. 2).

6. REFERENCES

Andersson F., Persson T. 1988 – Liming as a measure to improve soil and tree condition in areas affected by air pollution – Report 3518, National Swedish Environmental Protection Board, Solna, Sweden, 131 pp.

Bergkvist B. 1986 – Leaching of metals from spruce forest soil as influenced by experimental acidification – Water, Air, Soil Pollut. 31: 901–916.

Cronan C. S., April R., Bartlett R. J., Bloom P. R., Driscoll C. T., Gherini S. A. 1989 – Aluminium toxicity in forests exposed to acidic deposition: the ALBIOS results – Water, Air, Soil Pollut. 48: 181–192.

Dreyer E., Fichter J., Bonneau M. 1994 – Nutrient content and photosynthesis of young yellowing Norway spruce trees (*Picea abies* L. Karst.) following calcium and magnesium fertilisation – Plant Soil, 160: 67–78.

Dürr H., Münnich K.O. 1991 – Lead and cesium transport in European forest soils – Water, Air, Soil Pollut. 57–58: 809–818.

Göransson A., Eldhuset T.D. 1991 – Effects of aluminium on growth and nutrient uptake of small *Picea abies* and *Pinus sylvestris* plants – Trees 5: 136–142.

Huettl R. F.1989 – Liming and fertilization as mitigation tools in declining forest ecosystems – Water, Air, Soil Pollut. 44: 93–118

Hüttl R.F., Zöttl H.W. 1993 – Liming as mitigation tool in Germany's declining forests–reviewing results from former and recent trials – For. Ecol. Manage. 61: 325–338.

Hüttl R.F., Schaaf W. 1995 – Nutrient supply of forest soils in relation to management and site history – Plant Soil, 168–169: 31–41.

Johnson D.W., Lindberg S.E. 1992 – Atmospheric deposition and nutrient cycling in forest ecosystems: A synthesis of the Integrated Forest Study – Ecol. Stud. 91 – Springer–Verlag, New York, 707 pp.

Kabata-Pendias A., Pendias H. 1993 – Biogeochemia pierwiastków śladowych [Biogeochemistry of trace elements] – PWN Warszawa, 364 pp. (in Polish).

Katzensteiner K., Glatzel G., Kazda M., Sterba H. 1992 – Effects of air pollutants on mineral nutrition of Norway spruce and revitalization of declining stands in Austria – Water, Air, Soil Pollut. 61: 309–322.

Katzensteiner K., Eckmuellner O., Jandl R., Glatzel G., Sterba H., Wessely A., Hüttl R. F. 1995 – Revitalization experiments in magnesium deficient Norway spruce stands in Austria – Plant Soil, 168–169: 489–500.

Kreutzer K. 1995 – Effects of forest liming on soil processes – Plant Soil, 168–169: 447–470.

Lamersdorf N. P., Godbold D. L., Knoche D. 1991 – Risk assessment of some heavy metals for the growth of Norway spruce – Water, Air, Soil Pollut. 57–58: 535–543.

Le Goaster S., Dambrine E., Ranger J. 1990/91 – Mineral supply of healthy and declining trees of a young spruce stand – Water, Air, Soil Pollut. 54: 269–280.

Loneragan J. F., Snowball K., Robson A. D. 1976 – Remobilization of nutrients and its significance in plant nutrition. (In: Transport and transfer processes in plants, Eds. I. F. Wardlaw, J. B. Passioura) – Academic Press, New York, pp. 463–469.

Marschner H. 1997 – Mineral Nutrition of Higher Plants. Academic Press, 889 pp.

Meiwes K. J. 1995 – Application of lime and wood ash to decrease acidification of forest soils. Water, Air, Soil Pollut. 85: 143–152.

Nouri P. A., Reddy G. B. 1995 – Influence of acid rain and ozone on soil heavy metals under loblolly pine trees: A field study – Plant Soil, 171: 59–62.

Oren R., Schulze E.–D., Werk K.S., Meyer J. 1988 – Performance of two *Picea abies* (L.) Karst. stands at different stages of decline. VII. Nutrient relations and growth – Oecologia, 77: 153–173.

Reddy K. J., Wang L., Gloss S. P. 1995 – Solubility and mobility of copper, zinc and lead in acidic environments – Plant Soil, 171: 53–58.

Rengel Z., Robinson D. L. 1989 – Competitive Al^{3+} inhibition of net Mg^{2+} uptake by intact *Lolium multiflorum* roots. I. Kinetics – Plant Physiol. 91: 1407– 1413.

Shortle W.C., Smith K.T. 1988 – Aluminium-induced calcium deficiency syndrome in declining red spruce – Science, 240: 1017–1018.

Szujecki A. 1990 – Założenia metodyczne eksperymentu modelowego [Methodological assumptions of the experiment] (In: Reakcje ekosystemów leśnych i ich elementów składowych na antropopresję [Responses of forest ecosystems and their components to anthropopressure] (Ed. A. Szujecki) – CPBP 04.10, Synteza Nr II, Wyd. SGGW–AR, Warszawa: pp. 173–178.

Tarabuła T. 1996 – Reakcja boru sosnowego na zakwaszenie gleby w warunkach umiarkowanego dopływu atmosferycznego pierwiastków [The response of a Scots pine forest to soil acidification under conditions of moderate atmospheric input of elements] (In: Chemizm i oddziaływanie kwaśnych deszczy na środowisko przyrodnicze [Chemistry and impact of acid rain on natural environment] (Eds. B. Walna, L. Kaczmarek, J. Siepak) – Sesja naukowa Poznań – Jeziory 1996, pp. 160–165.

Tarabuła T., Żero A. 1997 – The effect of soil liming, acidification and urea fertilisation on distribution, biomass and accumulation of foliage within a Scots pine stand – Ecol. pol. 45: 361–383.

Thelin G., Rosengren-Brinck U., Nihlgard B., Barkman A. 1998 – Trends in needle and soil chemistry of Norway spruce and Scots pine stands in South Sweden 1985–1994 – Environm. Pollut. 99: 149–158.

Ulrich B., Mayer R., Khanna P.K. 1980 – Chemical changes due to acid precipitation in a loess-derived soil in central Europe – Soil Sci. 130: 193–199.

de Vries W., Posch M., Kämäri J. 1989 – Simulation of the long-term soil response to acid deposition in various buffer ranges – Water, Air, Soil Pollut. 48: 349–390.

Wyttenbach A., Bajo S., Tobler L., Keller Th. 1985 – Major and trace element concentrations in needles of *Picea abies*: levels, distribution functions, correlations and environmental influences – Plant Soil, 85: 313–325.

Wyttenbach A., Schleppi P., Tobler L., Bajo S., Bucher J. 1995 – Concentrations of nutritional and trace elements in needles of Norway spruce (*Picea abies* [L.] Karst.) as functions of the needle age class – Plant Soil, 168–169: 305–312.

(*Received after revising November 1999*)