Full Paper

Distribution of nutrients and trace elements in annual rings of pine trees (*Pinus silvestris*) as an indicator of environmental changes

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Received 31 May 1988; accepted 18 August 1988

Summary. Annual rings of about 100-year-old pine trees (*Pinus silvestris*) from two locations of the Nürnberger Reichswald were investigated. According to the chronological distribution patterns, the elements can be divided into two groups: a) elements with decreasing concentration from the older to the younger wood: Ca, Mg, Mn, Zn, Al, Pb and Cd; b) elements with increasing concentration: K, P, S, Fe, Cu and Ni. These changes of the element uptake occur at both locations almost parallel and this could be the result of two superimposed tendencies: On the one hand, it indicates increasing immission of pollutants; accordingly for several elements increasing deposition can be observed. On the other hand, sulphur dioxide causes progressive acidification of the soil and the biosphere, followed by increasing washing out of elements. The industrial development, especially the emission of sulphur dioxide, is assumed to be the cause of at least part of these effects. According to our interpretation, sulphur seems to be the key-element for understanding both tendencies.
Key words. Acid deposition; air pollution; annual rings; nutrients; sulphur dioxide; trace elements.

Introduction

The importance of anthropogenic immissions (carried into the forest ecosystems by the air) for the widespread decline of forest trees[1-6] has been discussed with increasingly convincing arguments in the last years[7]. The most important air pollutants (acid-forming gases, ozone and heavy metals) and their main emittants (industry, trafic, power plants and domestic heatings) are known[7-9]. Yet, so far no clear cause-and-effect relationship has been proved and a number of hypotheses are still in discussion[5,6,10-13].
Air pollutants generally produce a change a) of the pH and other physico-chemical properties of the soil[2,4,7,14], b) of the solubility and availability of several essential and potentially toxic elements[13-15] and, as a result, c) of the uptake of elements into the plants[16]. There is evidence that not a single substance or environmental parameter is the key factor to cause the forest decline[7]. Rather, coactions and interactions of a number of factors appear to be responsible, and additionally indirect effects must be considered. Therefore, present research tries to focus on such indirect effects of several air pollutants and their interactions with other biotic and abiotic stress factors[1,7,14,17].
Investigations on the availability of macronutrients and trace elements for the plants and their uptake can make use of the fact that no significant translocation of elements appear to occur once they have been taken up and deposited in the corresponding annual tree ring[3,8,18,19]. Their element concentrations are supposed to reflect long-time changes of the element uptake into the trees, and provide the possibility to relate these changes to the actual level of industrial activity[3,8,18,20].
It shall be tested whether there are differences in the element concentrations in the wood of different age that can be related to long-term changes of environmental conditions. Although the Nürnberger Reichswald is far away from the centers of the European mining and metal working industry it was and is subjected to the overall increasing air pollution in Middle Europe. This ecosystem appears suitable for such investigations because as a widespread monoculture of pine trees it is rather homogenous, and the sandy soil, poor in nutrients, should be sensitive to changes in immissions.

Material and methods

In January/February 1984 two locations have been selected in the northern part of the Nürnberger Reichswald that appeared similar to each other in various respects, viz. topographical, edaphic and meteorological conditions as well as distance from emission sources. Both locations, 2.8 km apart, are covered with pine trees 100 years of age. Three pine trees each were investigated with a maximum of 20 m apart.
20 cm above ground level a slice of 10–15 cm was cut from each trunk. Short-term effects are often due to the annual fluctuation of the climatic conditions and thus cannot be correlated to air pollutions. Therefore, wood samples containing 10 annual rings were taken from four different age classes, each with distances of 10 annual rings in between. Three parallel samples were taken

from each of the four cardinal points (south, west, north, east). This amounts to 12 samples per age class and tree. The wood fragments were polished with quartz glass to avoid contamination. They were dried for 18 h at 70 °C. About 1 g of each sample was dissolved in 10 ml of 65% HNO_3 (supra pure, Merck) and about 2 ml of 30% H_2O_2 (supra pure, Merck). The clear solutions were diluted with double-distilled water to 25 ml total volume. The element concentrations were analyzed alternatively by AAS (Atomic Absorption Spectrometry), DCP- (Direct Current Discharge Plasma) and ICP-Emission Spectrometry (Inductively Coupled Plasma).

Seventeen elements were evaluated: the macronutrients calcium, magnesium, potassium, phosphorus, sulphur, and the essential and non-essential trace elements, manganese, zinc, iron, copper, nickel, aluminum, lead, cadmium (sequence as discussed later on). Additional analysis of chromium, strontium, titanium and vanadium did not yield reliable results, as these elements were too close to the thresholds of detectability (data not shown).

Each column in figures 1–3 represents 36 measurements (3 parallel samples at 4 cardinal points in 3 trees). The results were compared, for each age class (i.e., each investigated decade) concerning the differences between the means at the two locations, and between the means of the age classes at either location. The differences were examined with the t-test.

Results

The long-time tendencies of five macronutrients and eight trace elements are summarized in figures 1–3. The trace elements are separated, according to present knowledge, in essential (fig. 2) and non-essential (fig. 3) elements. For all investigated elements either of two tendencies can be found: a) elements with increasing concentrations from the older to the younger wood. This covers the macronutrients K, P and S (fig. 1) and the trace elements Fe, Cu and Ni (fig. 2); b) elements with decreasing concentrations from the older (inside) to the younger

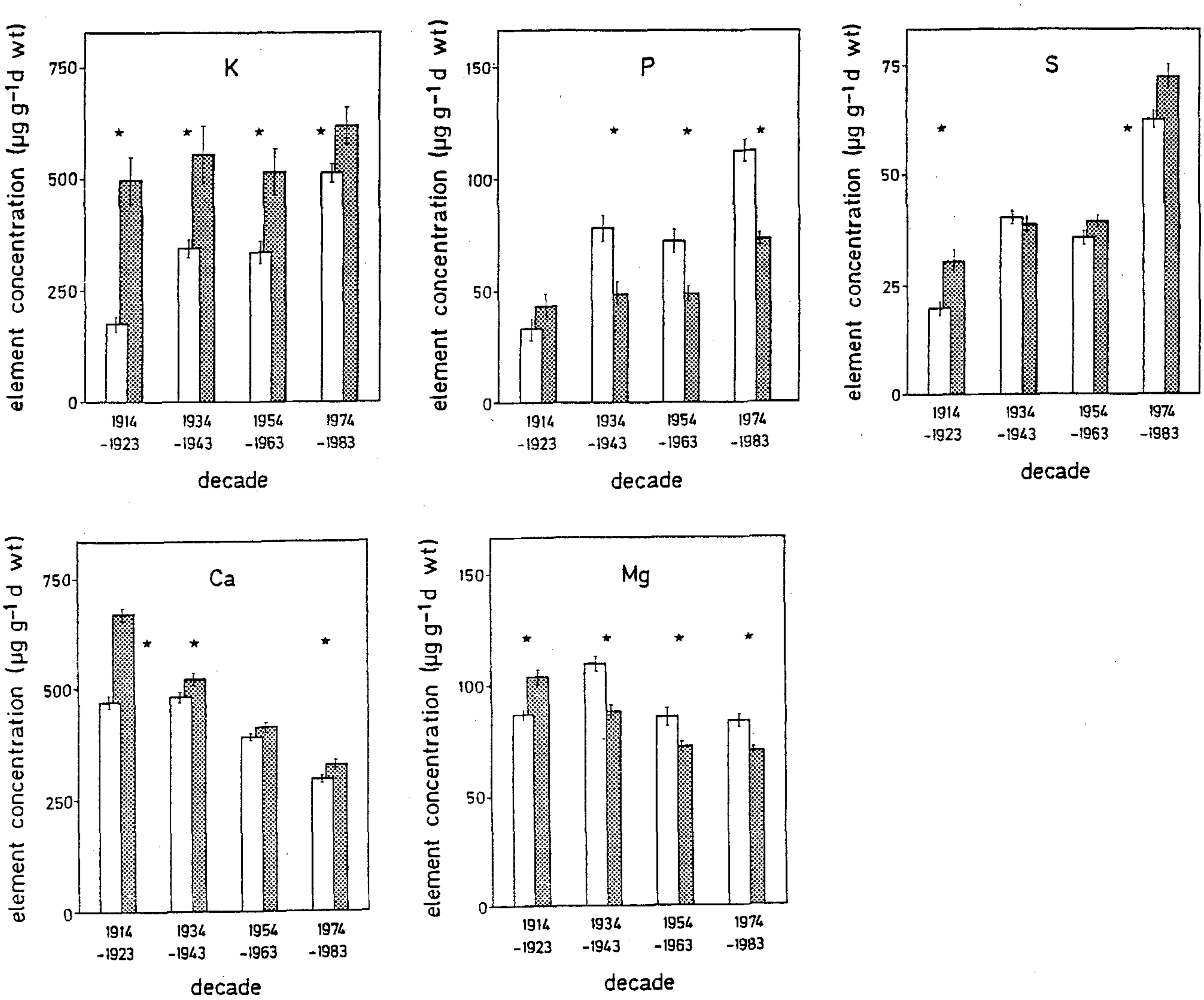

Figure 1. Concentration of nutrients in the wood of *Pinus silvestris* from 1914/23 to 1974/83. Each column is the average of 36 samples; each sample contains 10 annual rings as indicated at the abscissa. Location A, white columns, location B, hatched columns. Notice the different scales of the ordinates. Additional information in the text.

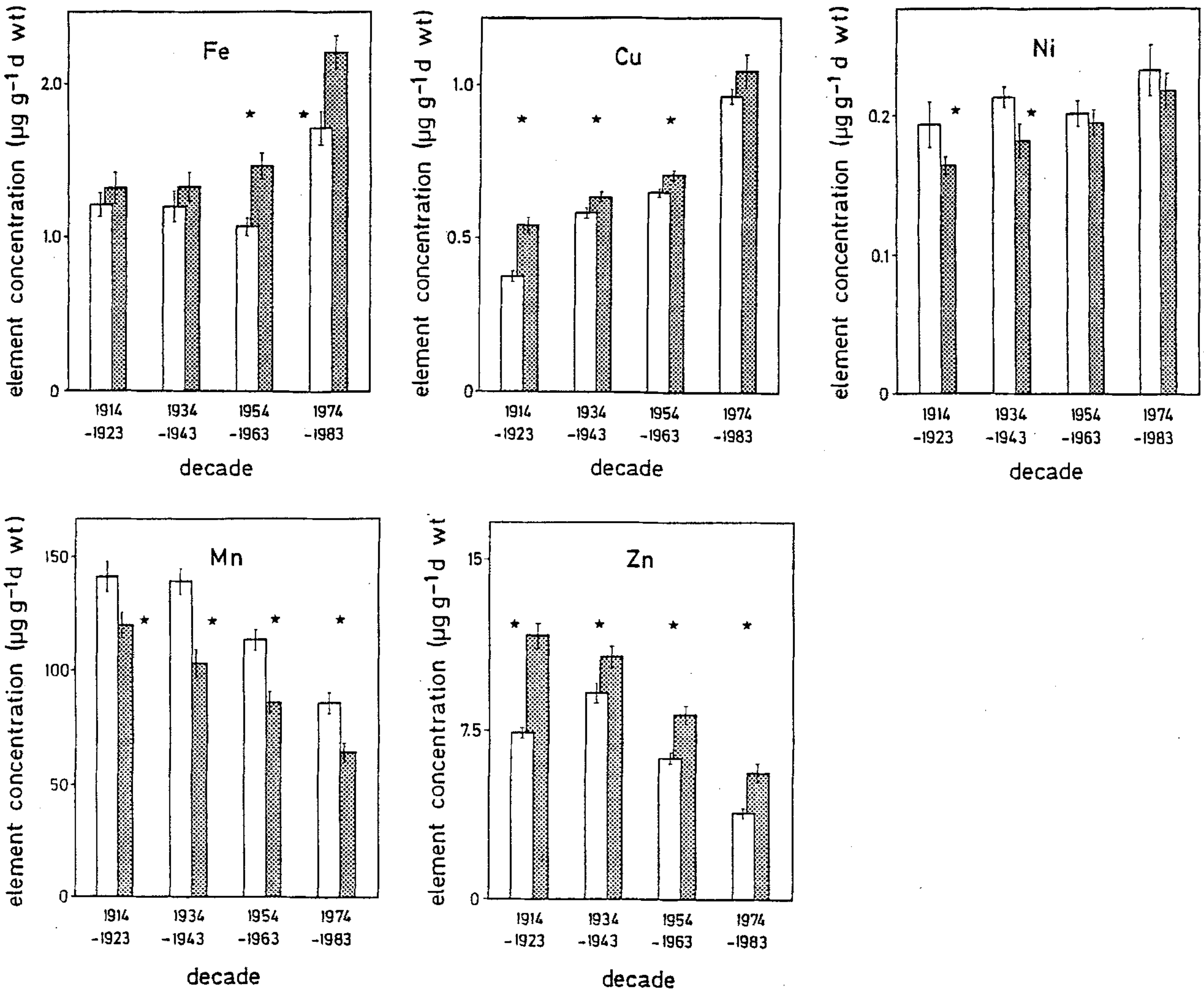

Figure 2. Concentration of (essential) trace elements in the wood of *Pinus silvestris* from 1914/23 to 1974/83. Otherwise as in figure 1.

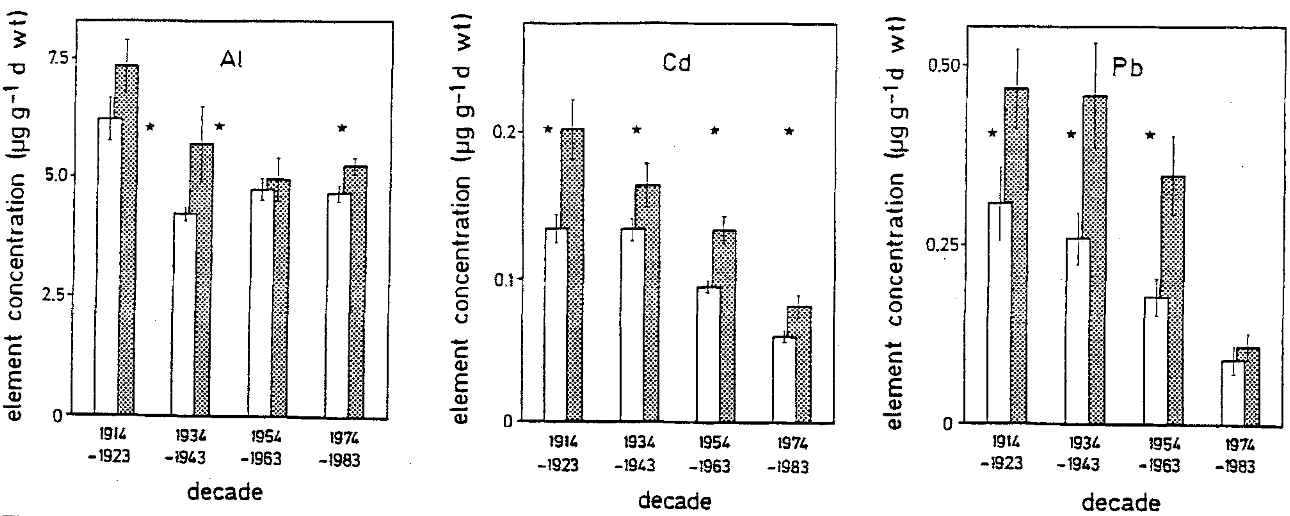

Figure 3. Concentration of (non-essential) trace elements in the wood of *Pinus silvestris* from 1914/23 to 1974/83. Otherwise as in figure 1.

Number of significant and not significant differences for the 13 investigated elements between age classes (decades) at both locations (thus 26 samples per age class). t-test-based comparisons are made between two neighboring as well as between the oldest and the youngest age classes.

Number of	Differences between decade 1914/23 and 1934/43	1934/43 and 1954/63	1954/63 and 1974/83	1914/23 and 1974/83
Significant differences	12 [a]	12	19	23
Not significant differences	14	14	7	3
Total	26	26	26	26

[a] Two of these significant differences are in the opposite direction, viz. Mg and Zn, each for location A (figs 1 and 2).

wood (outside). These are the macronutrients Ca and Mg (fig. 1) and the trace elements Mn, Zn, Al, Cd and Pb (figs 2 and 3).
The general tendencies, e.g., increase or decrease from 1914/23 to 1974/83, correspond at both locations. And this is also true, in principle, for each individual tree (data not shown). Increasing as well as decreasing tendencies lead to significant differences at least between the oldest and the youngest wood at both locations (except for K and Ni, which show significance of the differences only at one location, and Mg, which at location A does not decrease at all). This is summarized in the last column of the table. Even the changes of the element concentrations from decade to decade occur mainly in the same direction, occasionally observed opposite tendencies, however, are hardly significant with two exceptions (table).
The elements Mg, P, Mn and Ni show higher concentrations in the trees of location A as compared to B, with one exception for Mg and with non-significant difference for P in the oldest decade. All other elements (Ca, K, S, Zn, Fe, Cu, Al, Cd and Pb) are found in higher concentrations in the trees at location B, with one exception for S (not significant) in the decade 1934–1943. Although all these differences in our samples are relatively small, hardly reaching a factor of 2:1 or 1:2, a high percentage of them are significant at the 95% level, as indicated by the asterisks in figures 1–3.
Assuming that the observed differences are due to environmental factors, our data should also give information about the strength of these environmental influences at different periods. Therefore, the table shows the number of significant differences of all 13 elements at each location from age class to age class, i.e., from decade to decade. The proportions of significant and non-significant differences are approximately equal (12:14) between the decades 1914/23 and 1934/43 as well as 1934/43 to 1954/63. But in the period from 1954/63 to 1974/83 the significant differences amount to 19 out of 26 (Mg, Ni and Al at both, K at one location), and non of them is in the 'wrong' direction. This indicates a strong change of the element concentrations in respect to their incorporation in the most recent time.
The comparison of the element concentrations at both locations between the oldest and the youngest wood –

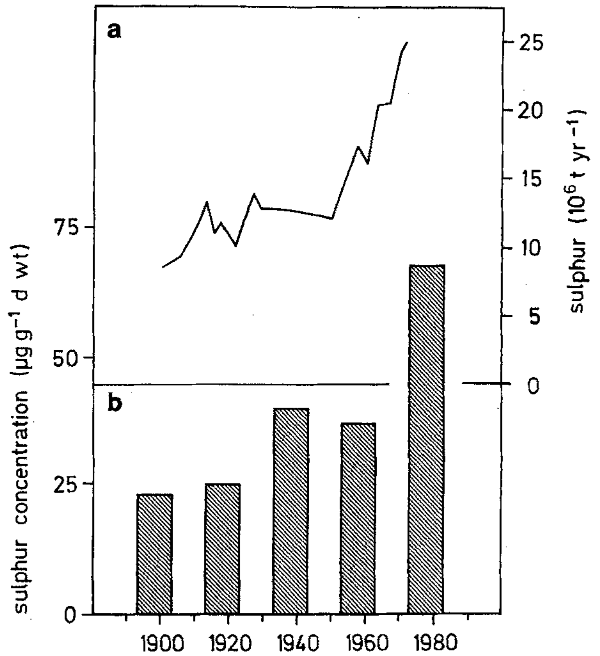

Figure 4. Concentration of sulphur in the wood of *Pinus silvestris* from 1894/1903 to 1974/83. Each column represents the average of the two respective columns in figure 1, thus being an average from 6 trees with 12 samples each. The 1894/1903 value has been obtained accordingly. Curve on top: Emission of sulphur dioxide in Europe (taken from Ulrich[4], changed).

i.e., the differences within the left and right pair of bars in figures 1–3 – show that for six elements (Ca, K, Zn, Cu, Cd and Pb) the differences between the two locations are smaller in the youngest than in the oldest wood.
The concentration of sulphur in the wood is characterized by a nearly identical change at both locations and an especially strong increase from 1954/63 to 1974/83 (fig. 1). The data have been replotted, averaging those of the two locations and including additional results from the period 1894/1903 (fig. 4a); for comparison (fig. 4b), the figure contains the sulphur emission in Europe[8]. The concentration of sulphur in the wood parallels to the increasing sulphur dioxide in the atmosphere (fig. 4). Thus, the content of sulphur in the annual rings of the investigated pine trees reflects nicely the industrial development even in a forest ecosystem that is far away from the great European industrial centers.
The potentially toxic elements Al, Cd and Pb (fig. 3) show a surprisingly decreasing tendency: especially the two heavy metals decrease strongly and simultaneously by a factor of 2–4 during the whole period of 70 years. Yet, the decrease of Cd and Pb in the wood is stated by other investigations[21] and especially in relation to the Nürnberger Reichswald by Rein (in preparation).

Discussion

Preliminary investigations have been focused on a single tree[22] or on trees grown at the same location[3]. We have chosen two locations in the Nürnberger Reichswald to be able to separate specifically local and general aspects, typical to the region.

The trees have been classified by various optical criteria (e.g., degree of damage of the crown, number of age classes of the needles, percentage of precocious loss of needles, degree of discoloration of the needles; Tendel and Hoffmann, in preparation). Although significant differences between the locations A and B have been found for these parameters, they do not allow reliable conclusions about the different degrees of damage, as tendencies in opposite directions are noticed, depending on the particular parameter used. This is valid also for the abiotic conditions of the Nürnberger Reichswald, as, e.g. climatic, edaphic, and geological qualities that have been investigated by Reigber[23].

Our analytical results are similar: neither the macronutrients nor the essential trace elements show overall higher or lower concentrations at one location. Yet, small but significant differences have been found between the locations for some of these elements (figs 1 and 2). On the other hand, the concentrations of the non-essential elements Al, Cd and Pb are always higher in B than in A (fig. 3). Summarizing our data, none of the two groups of pine trees seem to have an effectively higher overall level of nutrients whereas the higher burden of potentially toxic metals at location B does not result in significant signs of damage. Growth and vitality of the pine trees at both locations of the Nürnberger Reichswald are obviously neither supported nor impaired in a different way. They undergo the same long-term influences during the period from 1914/23 to 1974/83 and could have been influenced by two superimposed and divergent environmental tendencies. Therefore, we expect no simple correlation between increasing air pollutants and element concentrations in the wood.

A clear correlation between industrial development and the consumption of fossil fuels has been shown and on this basis the combustion of sulphur dioxide has been calculated[3,11,18,24]. Sulphur dioxide is ejected worldwide in large quantities and is widespread in the whole atmosphere. It has been proven to be a very good indicator of industrial activity[4], a main component of the increasing acidification of forest ecosystems[9] and in general an indicator of other air pollutants[11]. According to these aspects, the emission of sulphur dioxide in the atmosphere and the sulphur content of the wood can be related to the differences from one age group to the next, as shown in figure 4.

The industrialization in Europe reached a first maximum at the beginning of the century, followed by an economic stagnation during and after World War I. As can be seen, the sulphur content of our samples (wood, grown from 1893–1904 and 1914–1923) remain nearly constant. The time before and at the beginning of World War II was a period of increasing industrial activity; it is represented by the wood that grew from 1934–1943 and reflects the increasing emission of sulphur dioxide. The time from 1953–1964 is part of the period of reconstruction after the destruction of the European economy and, in comparison with the former period, a phase of industrial stagnation, while the following decades are characterized by an incomparable, nearly exponential increase in industrial activity. Accordingly, the emissions of sulphur dioxide and the sulphur content in the wood remained at first nearly unchanged, followed by a drastic increase, too.

The strong increase of the sulphur concentration in the wood, the similar time course at both locations and the corresponding emission of sulphur dioxide show that the influence of the air pollutants to the pine trees became stronger at both locations, especially from the period 1954/63 to 1974/83. Thus, it appears justified to use the integrated emission data of sulphur dioxide instead of the more relevant local data, which are not available. Sulphur seems to be the key to interpret the change of the other investigated elements in the pine trees of the Nürnberger Reichswald.

It is known that air pollutants are a very important source of a number of nutrients and trace elements[4–6,25] and accompanied with S, the elements K, P, Fe, Cu and Ni show also increasing concentrations in the annual rings. It can realistically be assumed that for these elements, too, the immission has increased, especially in most recent time (excepted Fe). Thus, the pine trees in the Nürnberger Reichswald are supposed to be exposed to larger amounts of those elements and take up more of them, especially in the last decade.

We agree with other investigations to explain the increase of iron with a progressive acidification of the soil and its increasing mobilization at lower pH[4,8,16,26]. However, it is hard to explain our iron data by this mechanism, as we could not find a similar increasing uptake for Al, which is mobilized at lower pH, too[8]. Thus, detailed investigations of structure, pH and other physico-chemical soil properties and their dynamics are required.

In contrast, the elements Ca, Mg, Mn, Zn, Al, Cd and Pb show clearly decreasing concentrations in the pine trees, although it is known that deposition of air pollutants can contribute to the pool of these elements in the soil[4,6,25]. To explain this apparent contradiction, a number of effects – induced by progressive acidification of the soil – have been discussed[2,5,14,21,22,27]. Important are the influences on those soil microbiota that are responsible for the decomposition of organic matter. On the average, microbial numbers, growth and activity are reduced by soil acidification[2]. But additional investigations are necessary to prove that this mechanism works in the Nürnberger Reichswald.

On the other hand, a progressive acidification of the soil has been shown in many forest stands of Central Europe[7,16,17,28]. This acidification is mainly due to a higher immission of acid-forming gases such as sulphur dioxide. Accordingly, the increasing sulphur concentration in the wood could be taken as indication for increasing concentration of sulphur dioxide and other pollutants in the atmosphere as well as for a progressive acidification of the soil. This process can lead to decreasing element concentrations, especially shown to Ca, Mg, Mn and Zn[4,13,22,27]. Indeed, we have likewise found decreases in the Nürnberger Reichswald. Thus, the postulated reinforced washing out of soluble elements from the soil[6,26] could easily explain our results.

Apart from details of their decreasing tendency we can assume reinforced washing out also for Al, Pb and Cd (fig. 3). However, further investigations must show, whether this mechanism applies indeed to the potentially toxic elements. Altogether, the load of these elements is comparatively small at both locations, i.e. their concentrations are below the thresholds that are considered to be toxic, and in consequence the extent of these stress factors appears to be small[6,29]. Our results agree also with Reigber et al.[23], who investigated in 1982 the elements in needles of pine trees at the same locations. They could not register corresponding and unequivocal signs of damage though they recorded sometimes much higher concentrations.

Our results seem to support the hypothesis that air pollutants are the major factor in the changes of the element content in the wood, as stated[4-6,25]. So, we are able to add a 'missing link' to the argumentation of Meisch et al.[8], who did not investigate the sulphur concentration in the wood. We have shown a good correlation of industrial activity and emission of sulphur dioxide on the one hand, and element concentrations in the wood on the other hand. Furthermore, it is remarkable that a similar change of the element concentrations could be shown at two different tree species (*Fagus silvatica* and *Pinus silvestris*), growing in two widely distant regions (Saarland and Nürnberger Reichswald) under entirely different growth conditions. Thus, the similar element changes could be interpreted as a sign that both regions are dominated by similar long-time influences of air pollutants. Nevertheless, further investigations at additional locations have to confirm our results before they can be generalized to the whole Nürnberger Reichswald.

Significant changes in the concentrations of 15 elements during the long period of 70 years in the wood of the investigated pine trees have been proved. We conclude that a strong change in the environmental and growth conditions at the two locations of the Nürnberger Reichswald took place. Nevertheless, there is no evidence that damages are caused by these changes. The reduction of the width of annual tree rings, as having been undiscovered for a long time, has now retrospectively been interpreted as a gradual loss of the vitality of the trees during the last decades. The changes of the element concentrations in forest trees may indicate in a similar way long-term physiological mechanisms[3]. Yet, further investigations must show whether changes in element concentration can generally be used as indication of three damage, long before severe symptoms can be observed.

Acknowledgment. The investigations were supported by the Gesellschaft für Strahlen- und Umweltforschung (München/Neuherberg), Dept. Zentrale Analytik (Head: Dr P. Schramel). We would like to thank Prof. Haupt for his critical remarks.

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0014-4754/88/11-120975-06$1.50 + 0.20/0