MULTIELEMENT ANALYSIS OF TREATED PINE SEEDLINGS

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A comparison study concerning the effects of acid rain on pine seedlings has been performed. Two different X-ray fluorescence methods, PIXE and IXRF were employed to produce multielement analyses of the samples.

Seedlings were treated for 3 months with watering of pH=7 or pH=3 liquids on the needles and on the roots. One year and two years old needles of the seedlings were inspected for changes in photosynthetic rate as well as for changes in elemental concentration.

Twelve elements from Si to Zn were compared in the samples. The PIXE results show that the amounts of most of these elements in the needles of the seedlings grown in sand increase, when treated with acid water. This growth is more clear, when acid treatment is effected on the roots.

The elemental concentrations of the needles in the seedlings grown in soil on the other hand decrease slightly.

INTRODUCTION

The use of fossil fuels around the globe has increasingly addes to the burden of pollutants in the atmosphere. In considering the effects of these pollutants sulfur dioxide is sulfur dioxide interacts with other sizes (HANSEN et al. 1978). constituents in the atmosphere, thus also e.g. affect the true influence of these pollutants.

The transformation of sulfur dioxide in the atmosphere produces compounds with different oxidation states. It is difficult to specify

absorbed in liquid droplets, but may also be released continuously during evaporation process. Sulfites and sulfates as well as sulfuric acid are found in air (Proceedings . . . 1978). frequently recognized as the most serious in The sulfuric acid occurs first in the form of the northern hemisphere. The total effects of ultrafine particles, but after transformation man-made pollutants have, however, not yet by condensation to sulfates it is present also been the subject of systematic scientific in droplets of size diameter less than 2μ m. studies. It is on the other hand, known that The sulfite is thought to occur in all particle

The presence of gaseous and solid sulfur with fine particles emitted or otherwise compounds simultaneously in the atmopresent in air. After transport over long sphere, and the dynamics involved with their distances complex sulfur containing aerosols transport and transitions, reflect the need for and chemical species are deposited on the diversified analysis. Most of the effects of ground and on the vegetation. The physical sulfur compounds must be coupled also with state and variations in the reactions under changes in nutrient mobility in the soil. All different meteorological conditions should these effects are almost impossible to trace with sufficient precision. Some main aspects can, however, be revealed by simple field

In the following a simulation experiment the transformation exactly. The SO2 in air is on young pine seedlings treated with acid probably adsorbed on solid particles or water is described. The analyses of the seedlings were performed multielementally. Care should, however, be taken in drawing direct conclusions from the results achieved

herein. As such, the results reflect only the suitability of multielemental X-ray fluorescence methods in delicate ecological research.

SAMPLES

In the experiments, altogether 40 seedlings of three year old pines (Pinus sylvestris L.) were subjected to controlled treatment. Half of the plants were growing in sand, the other half in mould soil. In each group of seedlings a reference subgroup was watered with neutralized water, pH=7, (group A), part of the seedlings were treated with an acid water, pH=3, sprayed on the shoots (group B), and the remainder watered with an acid water, pH=3, on the soil (group C). See fig. 1.

The treatment was carried out continuously during three months in the summer of 1978 at the Hyytiälä Forestry Station of the University of Helsinki. During the study period the seedlings were under the influence daily meteorological conditions. The photosynthetic rates, respiration rates and damage on the needles were measured continuously. At the end of the treatment period, growth of the seedlings and radiative reflection characteristics of the groups A, B and C, at 410 to 950 nm wavelengths (JAAKKOLA et al. 1980), were measured. The present experiments contributed towards a research project concentrating more fully on the effects of air pollutants on the Finnish forests (Contract . . . 1979).

Representative samples consisting of one to two years old needles of the seedlings were

processed for analysis. The needles were dried in 105°C for 24 hours, then ground by an ultracentrifuge into fine powder of particle size less than $50 \mu m$. From this powder~1 mm thick pellet with a diameter of 10 mm was compressed into a polyacetalic support. Use of plastic materials is necessary to maintain a low background in the analysis (RAUNEMAA et al. 1980).

The sample compositions were scanned through two separate methods: by radioisotope excited X-ray fluorescence, IXRF, and by particle induced X-ray fluorescence, PIXE. As both these methods are nondestructive, the samples can be stored after analysis for reuse in any way.

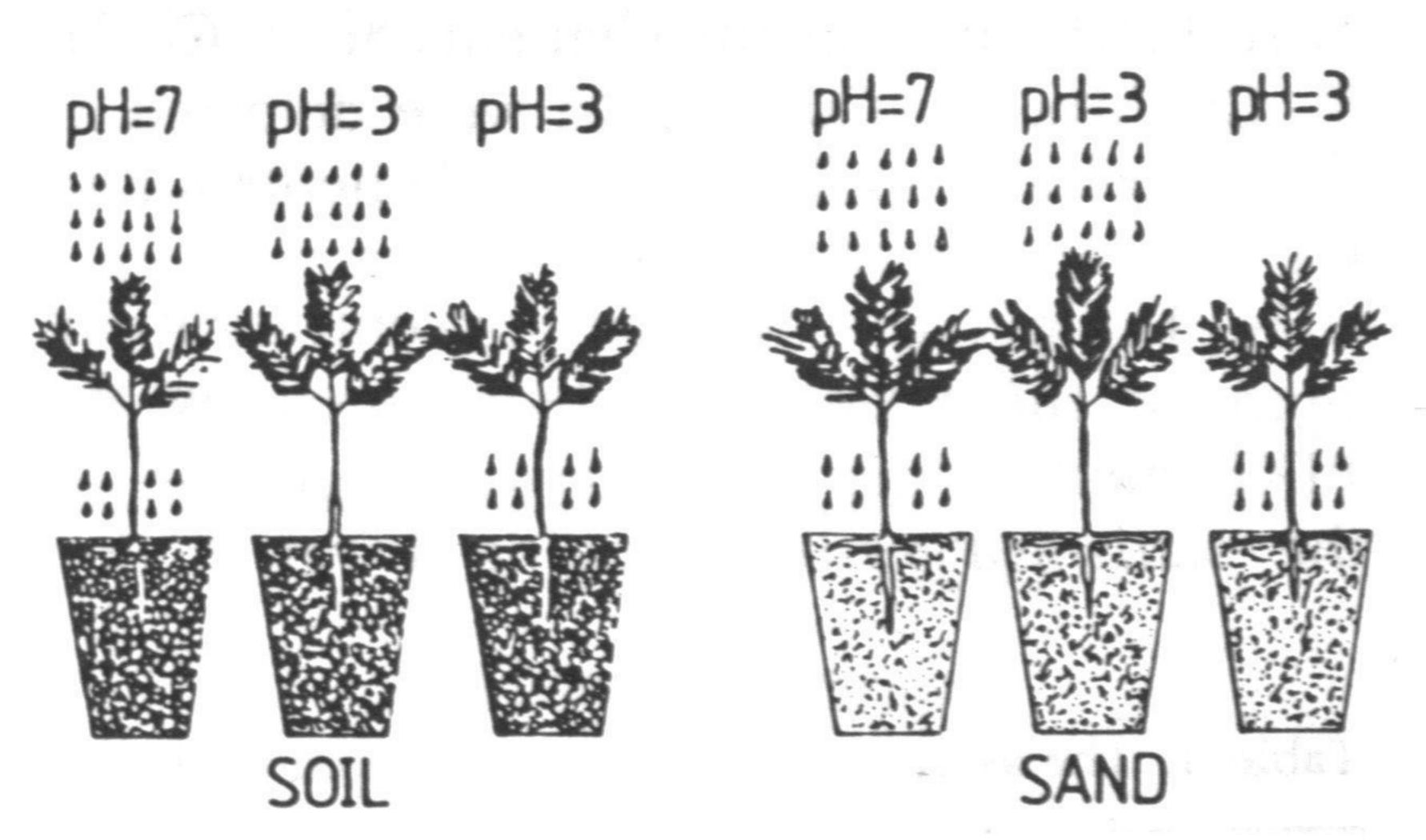


Fig. 1. Watering of the seedlings.

THE EXPERIMENTAL METHODS

X-ray fluorescence effect

In X-ray fluorescence electromagnetic interaction is employed to produce momentary radiation which is characteristic to each element. The yield of the X-ray production can be calculated using refined theoretical formulations (MASSEY and BURHOP 1936). Howewer, when high analytical applicabi-

lity is required, different semiempirical methods must be applied. In practice, the X-ray fluorescence method determines the elemental composition of any sample in a measurement which is non-destructive and takes only a few minutes. However, the data processing requires that large computer programs (KAUFMANN et al. 1980) must be utilized to obtain well analyzed final results.

When using the isotope excited fluores- _1 _______/ cence method (IXRF) X-rays were produced by the MnK-radiation from an Fe-55 2 MeV PROTONS radioactive source. This radiation induces fluorescence up to the element vanadium. In the facility used here other sources enclosed in the equipment can be used to study the elements up to lead semiquantitatively (RAUNEMAA et al. 1978). A careful IXRF measurement takes 15 to 30 minutes to this method with varying sensitivities. execute.

PIXE

the Van de Graaff accelerator of Helsinki description of the PIXE facility is given University were used (fig. 2.). The elements elsewhere (RAUNEMAA et al. 1980).

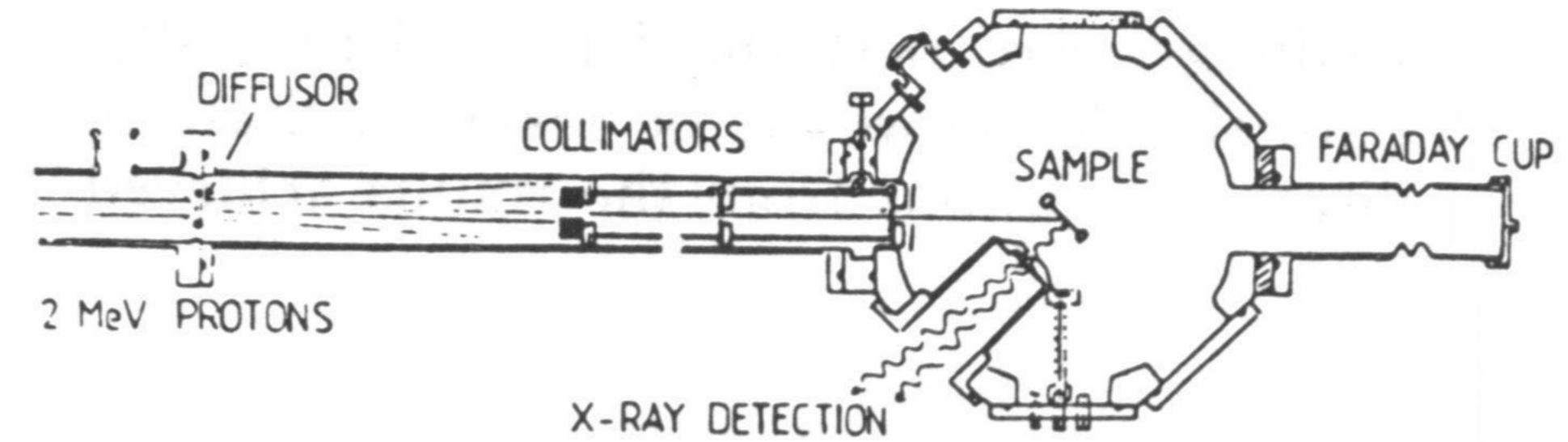


Fig. 2. The PIXE facility in Helsinki University.

from aluminum up to lead can be studied in

In the present experiments a proton beam with 1.5 mm diameter and an average 2 nA current was employed. This implies that ~1010 protons/s strike the sample, which means about 1013 protons in an average In the PIXE method 2.0 MeV protons from experiment lasting 10 minutes. A detailed

The fluorescence spectra arising from the IXRF and PIXE method are presented in Fig. 3. In PIXE analyses the elements Si, P, Cl, Ti, V, Cr, Mn, Fe, Cu and Zn were detected in the samples in addition to the elements K and Ca obtained in the IXRF analyses.

In Table 1 the average concentrations in ppm of the needles as determined by the PIXE method are tabulated. In addition to the statistical errors ranging from 1 (for

element K) to 30 (element Cr) percent of the values shown in Table 1, a 10 percent systematic error should be included.

As no calibration standards were measured with the IXRF method, only element intensity changes between the different seedling groups can be compared with those due to PIXE determinations. The K/Ca ratios (Fig. 4. and Table 2) show that a rather good agreement between the IXRF and PIXE results was

Table 1. The average concentrations in ppm of the needles determined by PIXE analysis using 2.0 MeV protons.

	A													
Tre	atment	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Cu	Zn
Re	ference													
Α	Sand	115	197	185	116	1430	414	2	1	3	63	32	14	1
	Soil	238	407	686		3130		3					65	14
Ac	d sprinkling													
В	Sand	118	164	281	119	1540	460	3	1	4	58	43	9	_
	Soil	197	345	735	202	2580	709	3	2	7	200	73	20	12
Ac	id watering													
_	Sand	253	424	601	383	4080	863	4	2	12	208	101	63	20
	Soil	244	350	629	262	2710	995	19	4	7	251	55	25	16

Statistical erros are 1 % (K, Ca) to 30 % (Cr)

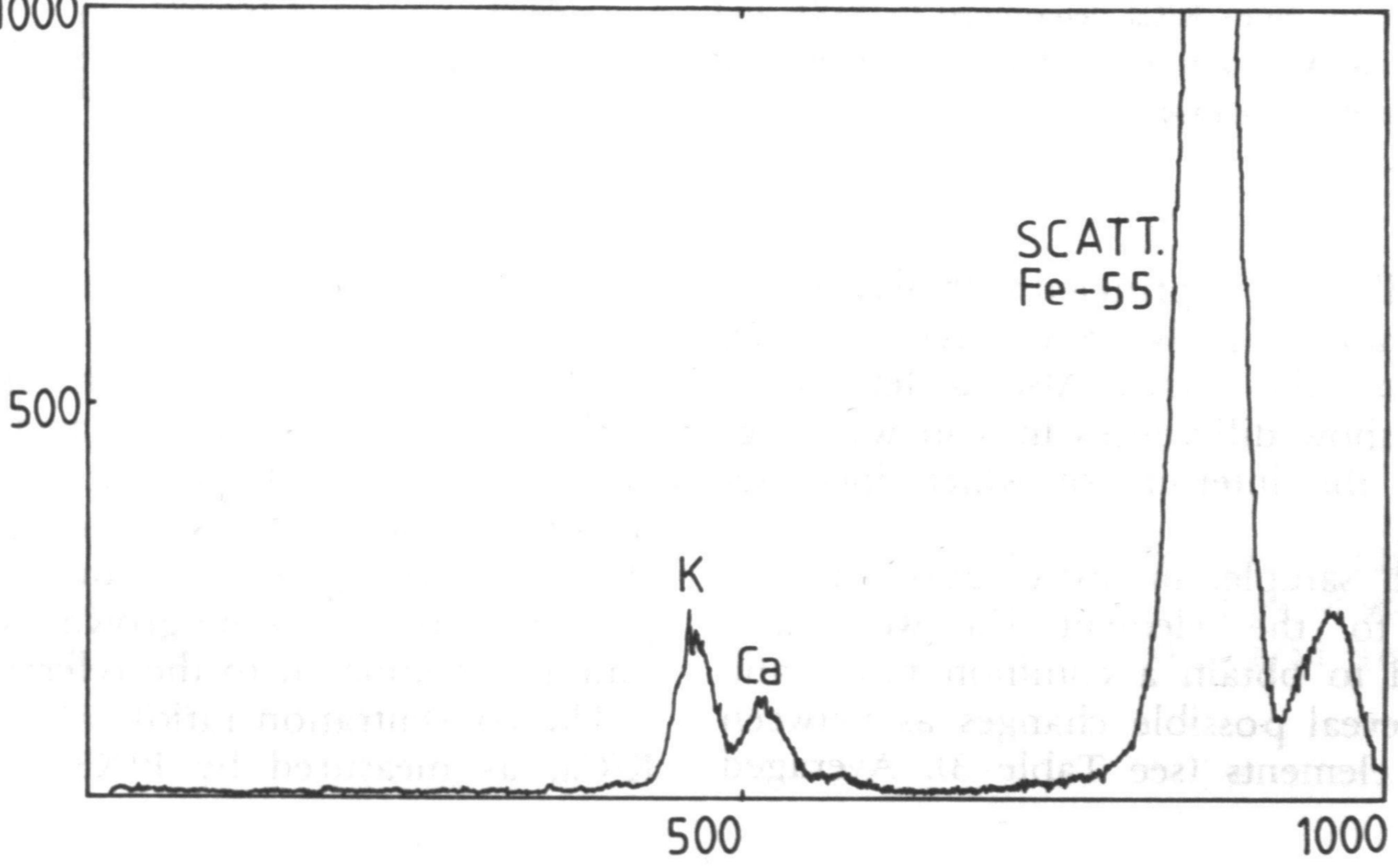


Fig. 3. X-ray fluorescence spectra of a treated pine needle sample by PIXE method (above) and by IXRF-method (below).

achieved.

Some general conclusions can be drawn from the PIXE results. Firstly, the amounts of different elements in the two year old needles do not change much, only by +5 percent, when considering the seedlings grown in sand and sprinkled on the shoots, but increase considerably, by a factor of 3.0, when acid are sprinkled, all element intensities except treatment is effected on the roots. The sulfur decrease by 24 percent, and when the concentration of sulfur behaves differently, roots are watered, the decrease is 12 percent, increasing by 50 percent when the shoots are as compared to the reference groups. The sprinkled. The most intense change in sand sulfur behaves again differently; its concen-

the concentration of which increases by a factor of 20 when the seedlings are watered with acid water on the roots.

Secondly, the amounts of the elements in the needles slightly decrease when we consider the seedlings grown in soil and subjected to acid treatment. When the shoots seedled pines occurs with the element zinc, tration increases somewhat (~ 7 percent)

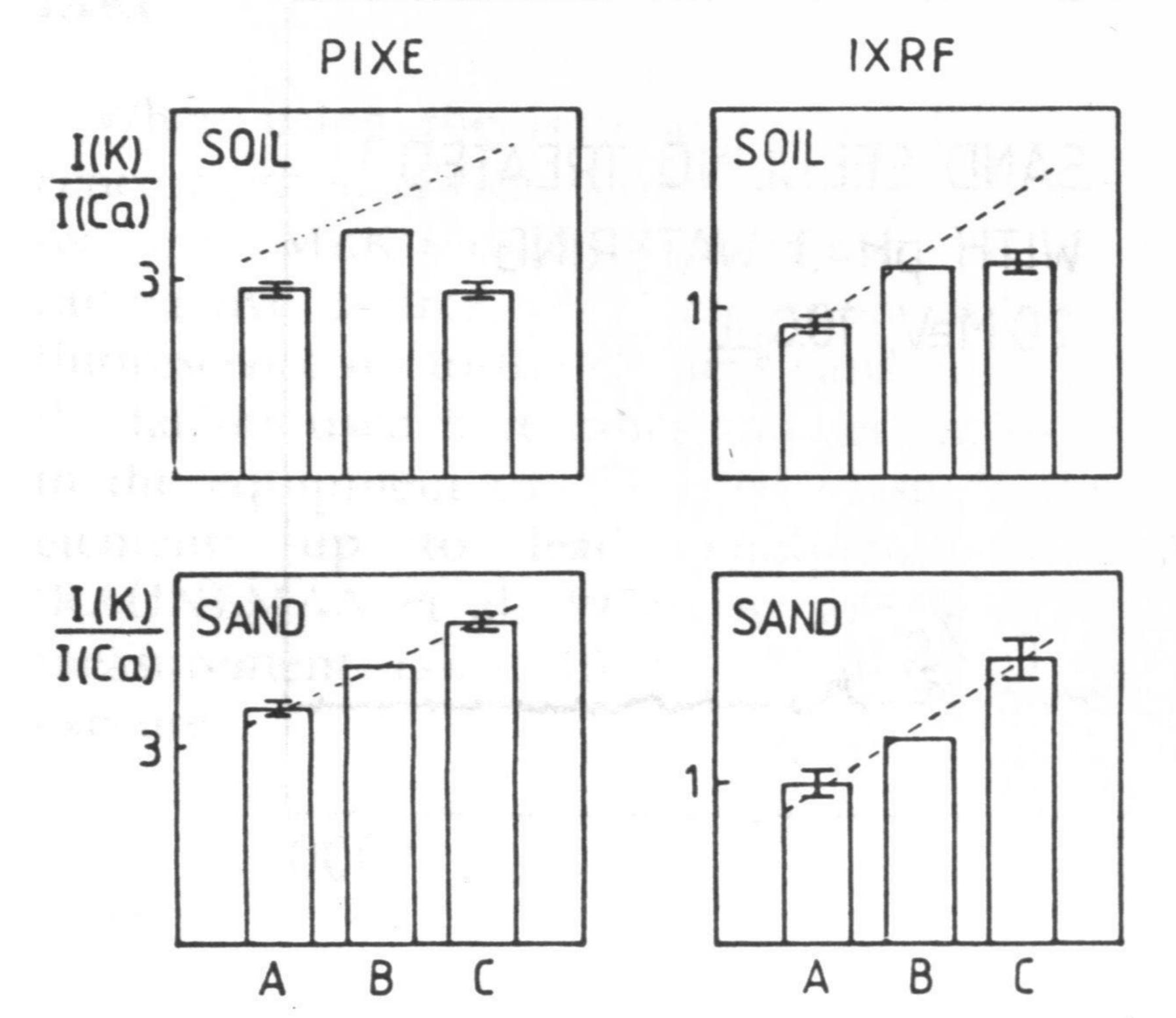


Fig. 4. Intensity ratios K/Ca determined by PIXE and IXRF methods. A broken line is drawn in the figure to show the trend of increase.

Table 2. Intensity ratios K/Ca determined by PIXE and IXRF methods. In IXRF studies no transformation to concentration values were carried out.

Treatment	PIXE I(K)/I(Ca)	IXRF I(K)/(Ca)
Reference Sand A Soil	3,52±0,07 2,80±0,05	0,99±0,08 0,92±0,06
Acid sprinkling Sand B Soil	4,21±0,14 3,70±0,05	1,23±0,09 1,26±0,09
Acid watering Sand C Soil	4,83±0,09 2,76±0,04	1,71±0,13 1,28±0,08

when seedlings are sprinkled with acid water, slightly.

In each sample, intensity ratios of each element to the element Ca were also calculated to obtain a common norm and also to reveal possible changes as between different elements (see Table 3). Averaged K/Ca, as measured by PIXE method, are

over each group of seedlings these ratios show but decreases slightly (~8 percent), when that the elements Cl, K, V, and Mn change watered on the roots. Also a few other similarly to the element S both in sand grown elements show differences in acid watering; and in soil grown groups. In acid sprinkling, e.g. zinc, the intensity of which increases an average of 20 percent increase was obtained in both groups. In acid watering no change in soil grown, but an average of 48 percent increase in sand grown seedlings was found as compared to the reference group.

The concentration ratios S/Ca, Cl/Ca and

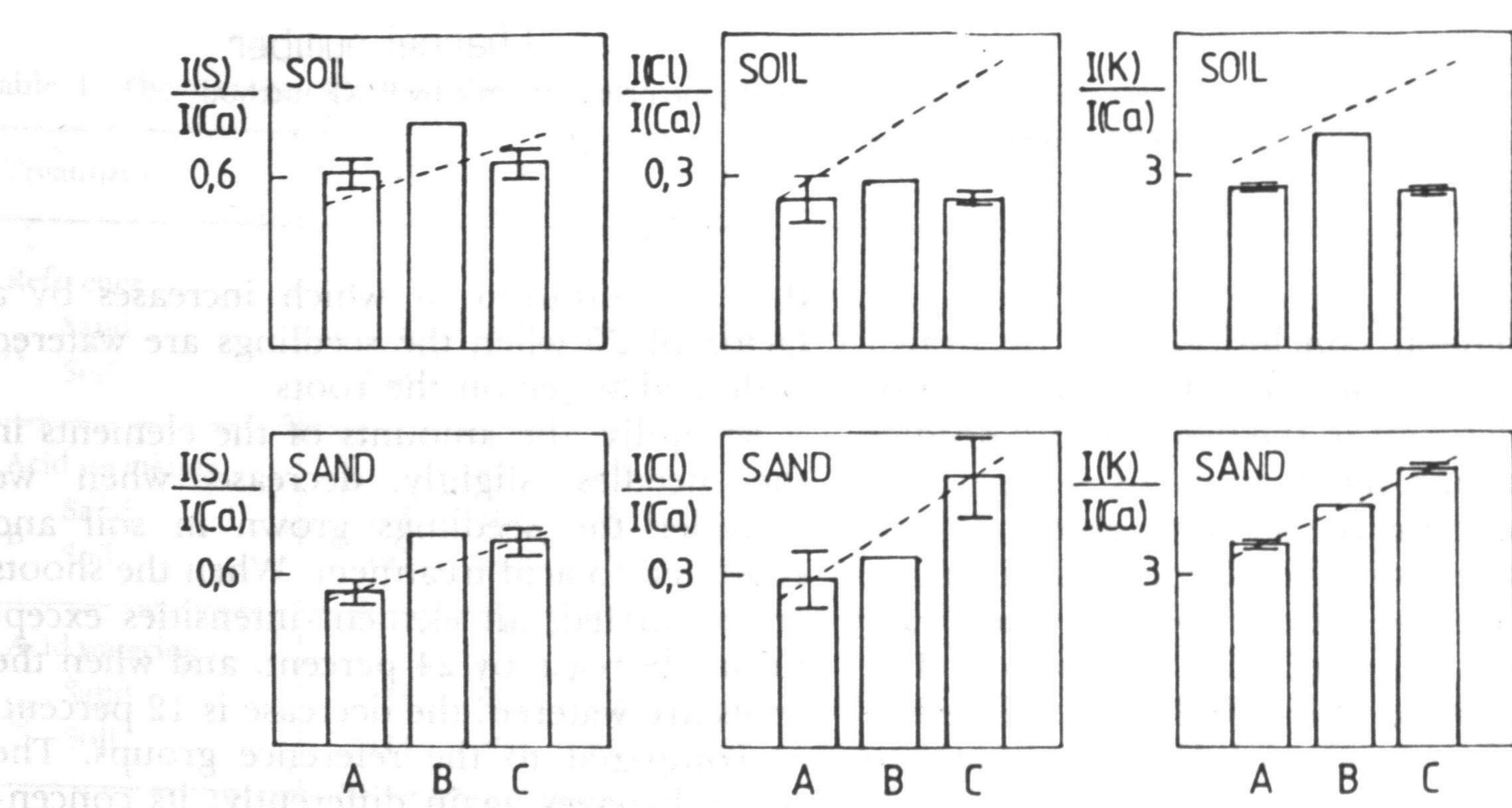


Fig. 5. The concentration ratios S/Ca, Cl/Ca and K/Ca determined by PIXE met-

Table 3. The ratios of elemental concentrations to element Ca determined by PIXE method.

Treatment	Si/Ca _{ave}	P/Ca _{ave}	S/Ca _{ave}	Cl/Ca _{ave}	K/Ca _{ave}
Reference					
Sand	0.28 ± 0.02	0.51 ± 0.05	0.54 ± 0.04	0.29 ± 0.05	3.52 ± 0.07
A Soil	0.23 ± 0.04	0.36 ± 0.03	0.62 ± 0.05	0.26 ± 0.04	2.80 ± 0.05
Acid sprinkling					
Sand	0.31 ± 0.07	0.45 ± 0.11	0.74 ± 0.05	0.33 ± 0.10	4.21 ± 0.14
B Soil	0.27 ± 0.01	0.49 ± 0.04	0.79 ± 0.06	0.29 ± 0.04	3.70 ± 0.05
Acid watering					
Sand	0.30 ± 0.04	0.51 ± 0.08	0.72 ± 0.05	0.47 ± 0.07	4.83 ± 0.09
Soil	0.22 ± 0.03	0.36 ± 0.04	0.65 ± 0.05	0.26 ± 0.01	2.76 ± 0.04
D C	Ti/Ca _{ave}	V/Ca _{ave}	Cr/Ca _{ave}	Mn/Ca _{ave}	Fe/Ca _{ave}
Reference	(F A 1 1 C) 10-5	1 /0 0 1 0 F) 10-8	/O 4 1 'O E) 10-8	0 1 7 1 0 0 1	0.000 1.0001
A		$(2.9 \pm 0.5) 10^{-3}$			0.080 ± 0.001
Soil		(2.4 ± 0.3) "	(11 ± 3)	0.26 ± 0.02	0.088 ± 0.004
Acid Sprinkling		2 (0 0 . 0	/ O O I O O O O O O O O O O O O O O O O		
B Sand		$(3.3 \pm 0.5) 10^{-3}$	20) 20 - 20 - 20 - 20 - 20 - 20 - 20 - 20 -		0.11 ± 0.03
Soil	(2.2 ± 0.8) "	(2.8 ± 0.9) "	(9.1 ± 1.0) "	0.28 ± 0.03	0.10 ± 0.01
Acid watering					
CSand		3 (4.3 \pm 0.4) 10^{-3}			0.14 ± 0.02
Soil	(5.3 ± 2.9) "	(2.2 ± 0.2) "	(6.8 ± 0.5) "	0.26 ± 0.01	0.060 ± 0.002

presented in Fig. 5.

The ratios of the elements Si, P and Ti to Ca have almost constant values in each group and in each treatment. The ratios of the

elements Fe and Cr to Ca increase in sand seedling groups, but decrease in soil seedling groups when subjected to acid treatment.

DISCUSSION

needles show that when the seedlings are seedlings. This coupling may be deduced sprinkled with acid water the sulfur concentration increases independently of the growth environment. When the acidifying is effected through watering on the roots, the growth environment may affect the needle composition; in sand the mineral content is effectively increased, in moulded soil no large change occurs. This may be due to differences in the mineral leaching.

coupled with the apparent increase in for this purpose. concentration of all elements in sand grown

The elemental concentrations of pine and the moderate decrease in soil grown through the observed growth changes, which showed decrease in sand, and respectively, increase in soil grown seedlings.

An optimal equilibrium between the mineral content and growth of the needle biomass may be possible. Verification of the existence of this equilibrium requires further careful examination. The results achieved so far by this study indicate that multielemental The decrease in photosynthesis must be PIXE analyses can be beneficially put to use

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