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ADAPTABILITY OF *PINUS NIGRA* ARN. DEPENDING ON SOIL pH

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Summary. A pot experiment was carried out to study the adaptability of two-year-old saplings of *Pinus nigra* Arn. grown on a light gray forest soil at pH 4.8, 5.1, 6.1, 7.1 and 7.4 modified by soil acidity neutralization with calcium carbonate. Criteria for evaluating the adaptability were the acidic and sorption properties of roots, stems and needles. Content of H^+, Ca^{2+}, Mg^{2+} and K^+ ions in the liquid and adsorption phase of organs' tissues and capacity values of acidic ion-exchangers in needles were determined. A tolerance of the saplings was established under acidic and alkaline soil conditions manifested in the following adaptive mechanisms at pH variation: gradual change of the cations' content and independent character of the relative distribution of cations in organs; maximum organic acids and dominant share of strongly acidic ion-exchangers in needles; dynamic ion-exchange of strongly acidic and weakly acidic biopolymers in needles.

Key words: adaptability, acidic and sorption properties of tissues, *Pinus nigra* Arn., soil pH

Abbreviations: CEC_A – cation exchange capacity of weakly acidic ion-exchangers in needles, CEC_{SA} – cation exchage capacity of strongly acidic ion-exchangers in needles, CEC_{SA+A} – total cation exchange capacity of needles

Introduction

The exchangeable acidity and bases' insufficiency in forest soils are pointed among the main reasons for forest ecosystems' damages (Goodbold et al., 1988; Kazda and Zvacec, 1989; Wiegel, 1989; Rehfuess, 1991). Forest trees react with different sensitivity to soil acidity. Soil pH is of importance especially for young saplings because their roots grow in the upper soil horizons characterized with higher acidification and toxic elements' accumulation.

Pinus nigra Arn. is considered to be more tolerant to soil pH compared to other coniferous despite the natural acid medium in the forest soils. Our aim was to study some adaptive mechanisms of saplings of *Pinus nigra* Arn. depending on soil pH which determines its tolerance under acidic and sorption conditions. The criteria for evaluating the adaptability were the acidic and sorption properties of saplings' organs.

Materials and Methods

Needles, stems and roots were taken from two-year-old saplings of *Pinus nigra* Arn. grown in a pot experiment on a light gray forest soil (Albic Luvisols). The following physico-chemical characteristics of the soil were determined by physico-chemical methods according to Ganev and Arsova (1980): pH (H_2O) – 4.8; exchangeable acidity (exch. Al) – 2.4 mequ/100 g; total acidity (exch. $H_{8.2}$) – 8.4 mequ/100 g; exchangeable bases (exch. Ca^{2+} + exch. Mg^{2+}) – 16.2 mequ/100 g; cation exchange capacity ($CEC_{8.2}$) – 24.6 mequ/100 g.

pH was modified by soil acidity neutralization with $CaCO_3$ (g per kg soil) according to the scheme:

pH 4.8 variant Ca_0 – 0.0 g (control);
pH 5.1 variant Ca_1 – 0.6 g (neutralized 0.5 exch. Al);
pH 6.1 variant Ca_2 – 2.5 g (complete neutralization of exch. Al);
pH 7.1 variant Ca_3 – 8.5 g (overliming – neutralized exch. Al + exch. $H_{8.2}$);
pH 7.4 variant Ca_4 – 28.5 g (overliming – variant Ca_3 + 2% $CaCO_3$)

Soil pH of samples was measured in water suspension 1: 2.5.

The content of H^+, Ca^{2+}, Mg^{2+} and K^+ ions in water soluble and exchange adsorbed state in dry biomass of organs as well as the cation exchange capacity of strongly acidic (CEC_{SA}) and weakly acidic (CEC_A) ion-exchangers in needles were determined by analytical methods according to Ganev and Arsova (1982, 1989).

Cations in water soluble state were extracted with 3 M glycerin and cations in exchange adsorbed state were desorbed with 0.5 N NaCl. Ca^{2+}, Mg^{2+} and H^+ ions were determined titrimetrically with EDTA and NaOH, respectively, and K^+ ions – by FAAS methods.

The determination of the capacities of acidic ion-exchangers in biopolymers was based on a saturation of strongly acidic positions with calcium indicator cations and weakly acidic positions with hydrogen indicator cations (calcium acetat-lactat buffer, pH 5.0). After desorption of both cations (sodium acetat-maleinat buffer, pH 8.2), H^+ and Ca^{2+} ions were determined acidimetrically and complexometrically, respectively.

The results have been statistically processed by the method of dispersion analysis.

Results and Discussion

The multiaspect study of coniferous is of importance from an ecological point of view (Petkova and Dimitrova, 1998; Kurteva and Gateva, 1998). Results about qualitative parameters and nutrient balance in some coniferous have been reported recently (Nilsen and Abrahamsen, 1995; Stoykov, 1998). The investigations concerning physico-chemical characteristics of coniferous are still insufficient. In the present study some possible mechanisms of adaptation of *Pinus nigra* Arn. are suggested on the basis of the results concerning the acidic and sorption properties of saplings.

Cations content (mequ/100 g) in water soluble and exchange adsorbed state in saplings' organs depending on soil pH is presented in Table 1. The relative distribution of cations in the liquid and adsorption phase is shown in Fig. 1 and Fig. 2, respectively.

First must be noticed the gradual change of the cations' content although pH varied significantly from 4.8 (Ca_0) to 7.4 (Ca_4). The fact expresses a saplings' reaction to maintain the internal acid-base balance. A similar effect has been reported about other plants (Ganev and Arsova, 1985) and it is most likely an universal compensative mechanism of plant adaptability to the external medium.

The increasing pH ($Ca_0 \rightarrow Ca_4$) diminished H^+ ions in water soluble state (dissociated mainly from organic carbonic acids – RCOOH) by 8–14% in different organs and enhanced Ca^{2+} ions needed for neutralization of carbonic acids by 9–14% (Fig. 1). Both cations, however, changed to a different extent – calcium increase was higher than the proton's decrease. For example, H^+ ions in needles decreased by 10 mequ (12%) from Ca_0 to Ca_4 variant, while Ca^{2+} ions increased by 14 mequ (14%). The fact suggests that higher soil pH activates synthesis of carbonic acids (concentration of H^+, respectively) and their neutralization by additional amount of Ca^{2+} ions. In the same direction ($Ca_0 \rightarrow Ca_4$) K^+ ions diminish because of Ca–K competition. The total electrolytic content (sum of cations content in the liquid phase) shows a tendency to increase slightly at higher pH. It could be assumed that soil pH influences the amount carbonic acids (RCOOH) and, mainly, their calcium salts in organs.

In the direction root $\rightarrow$ needles H^+, Ca^{2+} ions and electrolytic content in the liquid phase increased to a different extent depending on soil pH. For example, H^+ ions in needles compared to roots increased with 3% (Ca_0 and Ca_1), 5% (Ca_2 and Ca_4) and 6% (Ca_3). In almost the same extent was the increase of Ca^{2+} ions towards the needles with increasing soil pH. The accumulation of H^+ ions and formation of maximum electrolytic content in the liquid phase of needles is a specific reaction of *Pinus nigra* Arn. different from other plants characterized by maximum H^+ ions in roots (Arsova, 1989). The transport of H^+ ions toward needles is most likely an adaptive mechanism of saplings grown under natural acidic conditions in forest soils avoiding a high proton concentration in the roots.

The relative distribution of cations in the liquid phase in organs (Fig. 1) showed a dominant share of H^+ ions in the electrolytic content that determined high tissues' acidity:

$$H^+ > Ca^{2+} > K^+ >> Mg^{2+}$$

Table 1. Cations in water soluble and exchange adsorbed state (mequ/100 g) in organs of *Pinus nigra* Arn. depending on soil pH. Values are given as mean average from three replications.

Treat-ments	Organs	H^+	Ca^{2+}	Mg^{2+}	K^+	Σ	H^+	Ca^{2+}	Mg^{2+}	K^+	Σ
		in water soluble state					in exchange adsorbed state				
Ca_0	needles	48.0	24.0	3.5	19.8	95.3	13.6	16.8	3.0	0.9	34.4
	stems	42.4	18.5	3.0	21.4	85.3	15.0	16.0	2.0	1.1	34.1
	roots	36.4	18.0	3.5	20.8	78.7	14.6	16.0	2.2	1.2	34.0
Ca_1	needles	44.4	29.0	3.5	19.0	95.9	13.2	18.8	3.0	0.9	35.9
	stems	40.2	18.5	3.2	21.0	82.9	15.0	17.5	2.1	1.1	35.7
	roots	32.4	18.5	3.6	20.0	74.5	12.8	17.3	2.3	0.9	33.3
Ca_2	needles	42.4	32.0	3.7	18.5	96.6	12.8	21.3	3.1	0.8	38.0
	stems	37.2	21.0	3.5	20.2	81.9	11.6	18.0	1.9	1.0	32.5
	roots	28.8	19.5	3.5	20.0	71.8	12.0	19.0	2.3	1.0	34.3
Ca_3	needles	40.4	35.5	4.1	18.0	98.0	12.0	22.8	3.1	0.7	38.7
	stems	36.0	23.0	3.7	20.0	82.7	11.0	19.2	2.0	1.0	33.2
	roots	26.0	22.5	3.8	19.6	71.9	11.2	20.5	2.4	1.0	35.1
Ca_4	needles	38.0	38.0	4.4	18.0	98.4	11.2	24.5	3.4	0.7	39.8
	stems	34.2	25.5	4.0	20.0	83.7	10.4	21.4	2.2	0.9	34.9
	roots	24.0	25.0	4.0	19.0	72.0	10.8	21.8	2.4	1.1	36.1
$SD_{average}$		±1.13	±1.04	±0.11	±1.06		±0.55	±0.29	±0.20	±0.15	
LSD 1%		2.23	2.35	0.27	2.27		1.23	0.66	0.34	0.26	
5%		1.40	1.75	0.17	1.81		0.91	0.49	0.28	0.19	

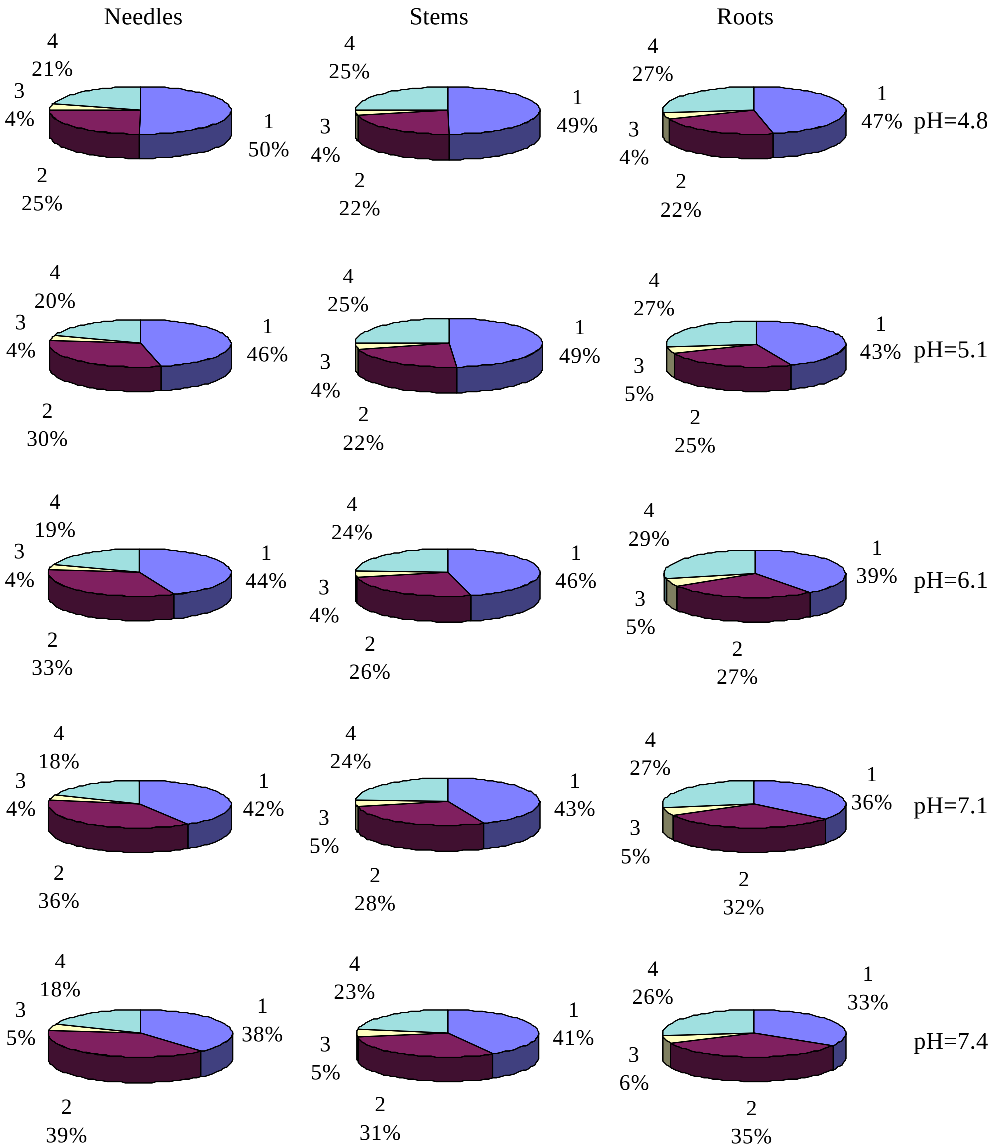

Fig. 1. Distribution of cations in water soluble state in organs of *Pinus nigra* Arn. at different soil pH. 1 – H^+, 2 – Ca^{2+}, 3 – Mg^{2+}, 4 – K^+.

It could be noticed that the character of the cations' distribution in the liquid phase of organs is independent of soil pH variation that is probably another mechanism of saplings' adaptability under acidic and alkaline conditions in the soil.

The influence of soil pH on the content of cations adsorbed on ion-exchange positions of biopolymers in saplings' organs (carboxylic groups in pectin, phosphate

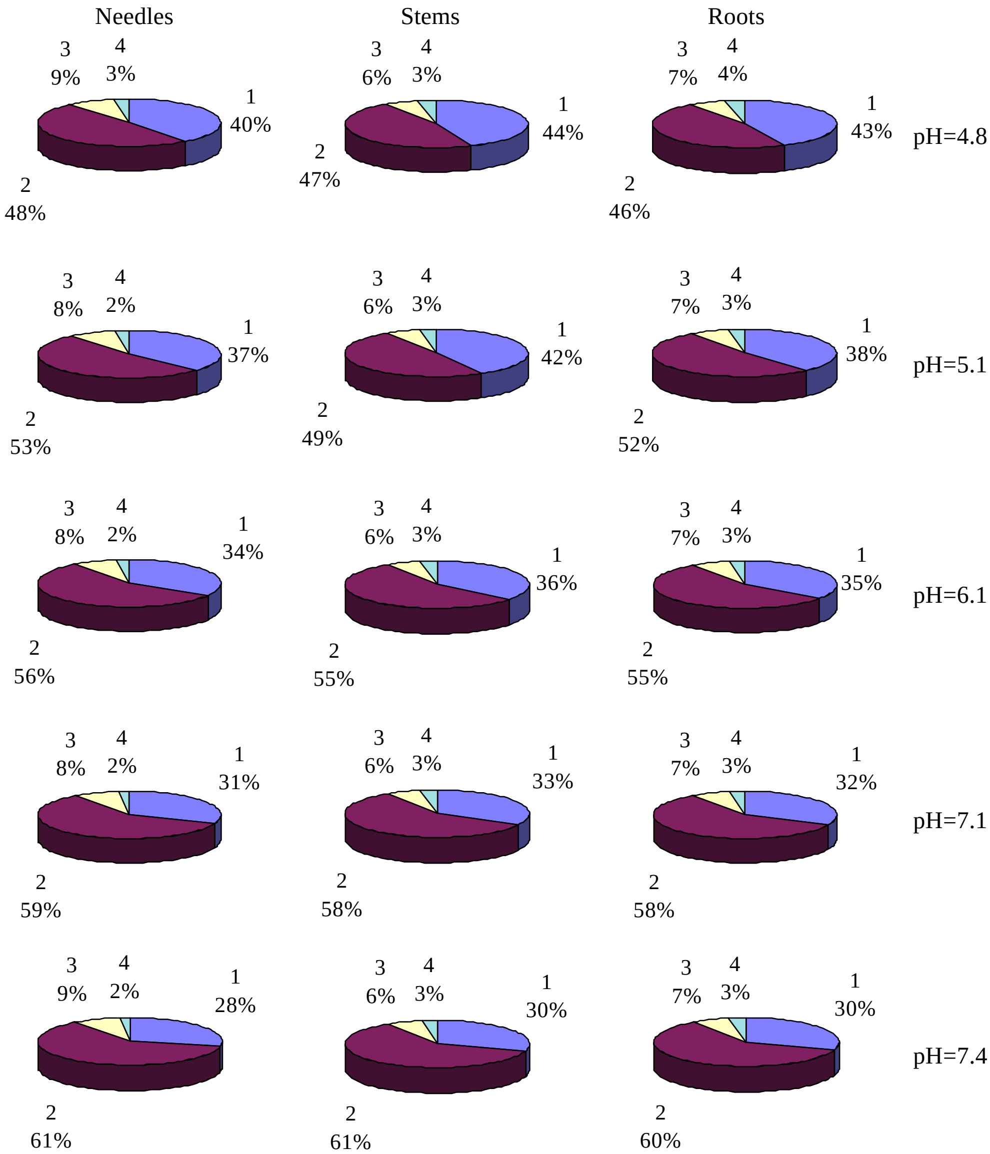

Fig. 2. Distribution of cations in exchange adsorbed state in organs of *Pinus nigra* Arn. at different soil pH. 1 – H^+, 2 – Ca^{2+}, 3 – Mg^{2+}, 4 – K^+.

groups in phospholipides and nucleic acids, amino groups in proteins, etc.) was similar to those in the liquid phase (Table 1). The relative distribution of cations in the adsorption phase is shown in Fig. 2. Decreasing soil acidity diminished H^+ ions and enhanced Ca^{2+} ions. For example, H^+ ions in needles decreased from 13.6 mequ/100 g (Ca_0) to 11.2 mequ/100 g (Ca_4) that is 12% and Ca^{2+} ions increased from 16.8 mequ/100 g

(Ca_0) to 24.5 mequ/100 g (Ca_4) that is 13%. In the roots, respectively, the proton decrease was 13% – from 14.6 mequ/100 g to 10.8 mequ/100 g and the calcium increase is 14% – from 16.0 mequ/100 g to 21.8 mequ/100 g.

In root → needles direction basic cations in exchange adsorbed state (Ca^{2+} and Mg^{2+}) increased summarily with 2–3% and H^+ ions decreased with 1–2%. H^+ ions in the adsorption phase contrary to the liquid phase were maximum in the roots because of their ion-exchange function. We observed a similar effect in the roots of other plants (Arsova, 1989).

Increasing soil pH raised the cation exchange capacity of organs calculated by the sum of exchange adsorbed cations (Table 1). For example, the capacity of needles increased from 34.4 mequ/100 g (Ca_0) to 39.8 mequ/100 g (Ca_4) and, respectively, in roots – from 34.0 mequ/100 g to 36.1 mequ/100 g. Besides, the capacity enhanced in the direction root → stems → needles that most likely facilitated the upward cation transport. We have reported the same fact about other plants (Arsova, 1989). The increase of the capacity at higher pH is due to the increasing adsorption of bases (mainly Ca^{2+} ions) on the biopolymers. The relative share of calcium in the capacity of saplings' organs was dominant (Fig. 2):

$$Ca^{2+} > H^+ >> Mg^{2+} > K^+$$

Increased soil pH did not influence the relative distribution of the cations in the adsorption phase of organs similarly to the liquid phase which, probably, is also a saplings' adaptive reaction.

Biopolymers in plant tissues react in cation exchange as strongly acidic and weakly acidic structures according to the degree of H^+ ionization in dependence of pH. The strongly acidic ion-exchangers (functional groups of phospholipides, polyuronic acids, etc.) and weakly acidic ion-exchangers (functional groups of pec-

Table 2. Strongly acidic (CEC_{SA}) and weakly acidic (CEC_A) ion-exchangers and cation exchange capacity (CEC_{SA+A}) in needles of *Pinus nigra* Arn. depending on soil pH. Values are given as mean average from three replications.

Treatments	CEC_{SA}	CEC_A	CEC_{SA+A}	CEC_{SA}	CEC_A
	mequ / 100 g			% of CEC_{SA+A}	
Ca_0 pH 4.8	28.4	5.6	34.0	83.5	16.5
Ca_1 pH 5.1	30.0	5.3	35.3	84.5	15.0
Ca_2 pH 6.1	32.3	4.7	37.0	87.3	12.7
Ca_3 pH 7.1	36.4	2.6	39.0	93.3	6.7
Ca_4 pH 7.4	38.0	2.0	40.0	95.0	5.0
$SD_{average}$	±0.60	±0.34			
LSD 1%	1.35	0.32			
5%	0.65	0.20			

tin, proteins, etc.) take part in the proton-basic exchange with the nutrient medium. It could be expected that the acidic biostructures are related to the plant adaptive reactions as well.

Capacity values of strongly acidic (CEC_{SA}) and weakly acidic (CEC_A) ion-exchangers in needles and their sum that is the total cation exchange capacity (CEC_{SA+A}) are presented in Table 2. Logically, the capacity of needles determined by the sum of the acidic ion-exchangers is almost equal to that determined by the sum of exchange adsorbed cations (Table 1 – needles). Increasing soil pH enhanced significantly the strongly acidic ion-exchangers (CEC_{SA}) from 28.4 mequ/100 g (Ca_0) to 38.0 mequ/100 g (Ca_4). The weakly acidic ion-exchangers (CEC_A) decreased in a much lesser extent – from 5.6 mequ/100 g (Ca_0) to 2.0 mequ/100 g (Ca_4). As a result total cation exchange capacity (CEC_{SA+A}) increased from 34.0 mequ/100 g (Ca_0) to 40.0 mequ/100 g (Ca_4).

The relative share of CEC_{SA} dominated in the total capacity. It varied from 85% (Ca_{0-2}) to 93% (Ca_{3-4}). The share of CEC_A is much smaller – about 15% (Ca_{0-2}) and 6% (Ca_{3-4}). The large share of strongly acidic biostructures in needles distinguishes *Pinus nigra* Arn. from other plants (Ganev and Kalichkova, 1992; Arsova, 1995). The fact is most likely a specific characteristic of *Pinus nigra* Arn. conditioning its adaptability to the natural acid forest soils with bases' deficit. The large share of CEC_{SA} improves the adsorption of bases in these soils. The participation of weakly acidic biostructures (CEC_A) in the cation exchange is of importance at higher pH. The share

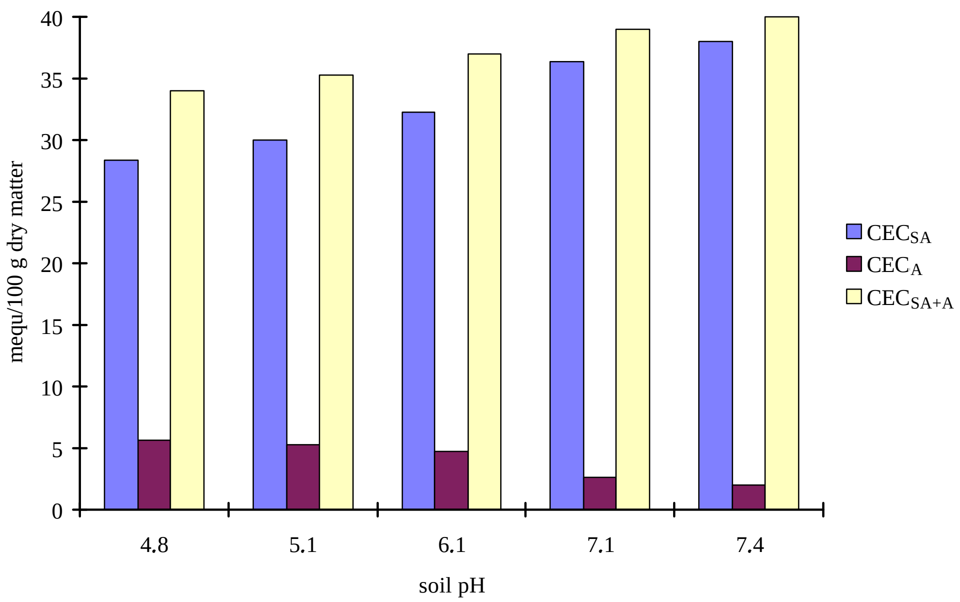

Fig. 3. Strongly acid (CEC_{SA}) and weakly acid (CEC_A) ion-exchangers and cation exchange capacity (CEC_{SA+A}) of needles of *Pinus nigra* Arn. depending on soil pH

of CEC_A in the total capacity of needles is small even under alkaline conditions – about 6% at pH>7.0. It means that the strongly acidic ion-exchangers (CEC_{SA}) are decisive for cation exchange.

The share of strongly acidic ion-exchangers depends on the adsorbed protons on biopolymers. It could be assumed that the increase of CEC_{SA} at higher soil pH is due to the adsorption of H^+ ions produced in metabolism. Therefore, the increase of the total capacity of needles in alkaline medium results from an exchange of such protons with Ca^{2+} ions, mainly on the strongly acidic ion-exchangers in biopolymers.

The capacity values of biopolymers in needles change dynamically depending on soil pH (Fig. 3). The fact provides a dynamic ion-exchange of tissues that, probably, is another adaptive mechanism conditioning saplings' tolerance under acidic and alkaline conditions in the soil.

On the basis of data presented here it is difficult to generalize the observed effects on other coniferous, that requires additional investigations.

Conclusions

A tolerance was established of two-year-old saplings of *Pinus nigra* Arn. at soil pH 4.8–7.4 manifested in the following mechanisms of adaptability:

gradual change of the content of cations in water soluble and exchange adsorbed state and independent type of their relative distribution in organs;

accumulation of maximum organic acids in needles;

large share of the strongly acidic ion-exchangers dominating in the cation exchange capacity of needles;

dynamic ion-exchange of strongly acidic and weakly acidic biostructures in needles.

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