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EFFECT OF SOIL CONTAMINATION WITH FLUORINE ON THE CONTENT OF PHOSPHORUS IN BIOMASS OF CROPS

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Abstract

The purpose of this study has been to determine the effect of soil contamination with fluorine on the content of phosphorus in crops. Alongside the simulated fluorine soil pollution, substances neutralizing this xenobiotic, such as lime, charcoal and loam, were applied to soil.

Depending on the sensitivity of the plants, the degree of soil pollution with fluorine was:

- 1) 0, 20, 40 and 60 mg F kg⁻¹ of soil under sensitive crops, i.e. narrow-leaf lupine;
- 2) 0, 50, 100 and 150 mg F kg⁻¹ of soil under moderately sensitive crops, i.e. seed lucerne;
- 3) 0, 100, 200 and 300 mg F kg⁻¹ of soil under more tolerant crops, i.e. maize, winter oilseed rape, spring triticale, black radish and phacelia.

The content of phosphorus varied, depending on the level of soil contamination with fluorine and substances applied to inactivate this element, as well as on the species and organ of the examined plants. An increasing degree of soil pollution with fluorine contributed to raising the phosphorus content in black radish, in aerial biomass of yellow lupine and in roots of spring triticale. Regarding the maize roots, a reverse dependence was recorded. The highest phosphorus content appeared in roots of winter oilseed rape (8.16 g P kg⁻¹ d.m.) and black radish (7.33 g P kg⁻¹ d.m.), while the lowest one was in roots of spring triticale (0.86 g P kg⁻¹ d.m.). Overall, the applied neutralizing substances resulted in lower concentrations of phosphorus in the analyzed plant organs, with the most univocal influence achieved in aerial biomass of yellow lupine, in roots of narrow-leaf lupine, in aerial mass and roots of black radish and in aerial biomass from the first cut of seed lucerne. In respect of the other plants, the impact of the neutralizing substances on the content of phosphorus was also significant albeit dependent on their species.

Keywords: soil contamination with fluorine, content of phosphorus, crops, lime, charcoal, loam.

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INTRODUCTION

As a compartment of the natural environment, soil is heavily exposed to various pollutants (TELESIŃSKI et al. 2010). Toxic substances released to the environment have an adverse effect on the protective function of soil and its physicochemical properties, depressing soil fertility and therefore limiting the growth, development and yields of crops (WYSZKOWSKI, SIVITSKAYA 2014).

Fluorine compounds are counted among numerous poisonous substances penetrating the natural environment (REDDY, KAUR 2008). Industrial plants tend to emit large quantities of this element into the air, from which it is deposited with atmospheric precipitations on the soil surface and subsequently permeates into deeper soil horizons, thus turning into a considerable source of this element to plants, animals and humans (SAWILSKA-RAUTENSTRAUCH et al. 1998).

The adverse influence of fluorine on plants mostly involves interfering with the phytoavailability of oxygen and the uptake and transport of water, reducing the assimilation and synthesis of lipids and carbohydrates, depressing the content of chlorophyll and changing the cellular metabolism. The effect of fluorine on plants is also manifested by inhibited assimilation and photosynthesis, lowered yields and retarded plant growth. Typical manifestations of the toxic effect of fluorine compounds include the occurrence of light brown necrotic spots progressing from the tip to the edge of leaf blades. Besides, a high content of fluorine contributes to changes in the mineral composition of plants (GADI et al. 2012).

In view of the above information, a series of experiments was conducted, in order to determine the effect of soil contamination with fluorine on the content of phosphorus in eight crops. The research additionally included soil enrichment treatments with different neutralizing substances, i.e. lime, charcoal and loam.

MATERIAL AND METHODS

Eight pot experiments completed in a greenhouse of the University of Warmia and Mazury in Olsztyn, in 2009-2011, provided data for this research. The experiments were set up on soil from the arable layer, which represented the textural class of loamy sand. The pH of the soil was 5.89 in H_2O and 4.43 in KCl; the hydrolytic acidity was 30.7 mmol(+)kg⁻¹ of soil. The content of available nutrients in the soil was as follows: 43.2 mg P, 124.5 mg K and 30.0 mg Mg kg⁻¹ of soil. The soil chosen for the experiment contained 6.0 g kg⁻¹ of organic carbon, 0.62 gkg⁻¹ total nitrogen and 125 mg kg⁻¹ of total fluorine.

The tested crops were: maize (Zea mays L.), yellow lupine (Lupinus luteus L.), oilseed rape (Brassica napus L.), spring triticale (Triticosecale

Wittm.), narrow-leaf lupine (*Lupinus angustifolius* L.), black radish (*Rapha-nus sativus*), phacelia (*Phacelia* Juss.) and alfalfa (*Medicago sativa* L.).

The experiments comprised two factors. The first order factor consisted of increasing doses of fluorine, applied in the form of potassium fluoride, which simulated the soil contamination. The second factor involved a comparison of three substances alleviating the soil contamination with fluorine.

Depending on the sensitivity of the plants, the soil contamination with fluorine was:

- 1) 0, 20, 40 and 60 mg F kg⁻¹ of soil under sensitive plants, i.e. narrow-leaf lupine;
- 2) 0, 50, 100 and 150 mg F kg⁻¹ of soil under moderately sensitive plants, i.e. alfalfa;
- 0, 100, 200 and 300 mg F kg⁻¹ of soil under relatively tolerant plants, i.e. maize, winter oilseed rape, black radish and phacelia.

Yellow lupine, which was sown as a catch crop after maize harvest, was another example of a plant sensitive to fluorine pollution. In respect of this plant, the residual effect of soil contamination with fluorine, previously applied under maize, was tested.

Regarding two experiments, namely narrow lupine and alfalfa, lower doses of fluorine were applied because papilionaceous plants are more sensitive to the presence of various xenobiotic substances in soil. The following were applied to soil as substances neutralizing the pollution: lime (in a dose corresponding to 1 Hh of soil), charcoal and loam (both in quantities equal 3% of the soil mass in a pot).

Apart from the above substances, soil was also enriched with NPK fertilizers, in identical doses in all the pots, to satisfy the nutritional demand of the crops. Nitrogen was supplied with urea, in the amount of 111 mg N, phosphorus was used in the form of 46% triple superphosphate in the amount of 48 mg P, and potassium was given as 57% potassium salt in the dose of 111 mg K kg⁻¹ of soil. Each experiment was composed of 16 treatments with 3 replications. The above doses of fluorine, neutralizing substances and fertilizers were carefully mixed with soil and placed in appropriately tagged pots. The tested plants were sown immediately after filling the pots with soil.

During the plant growing period, the soil moisture in the pots was maintained at the level of 60% field water capacity. The plants were harvested at full technological maturity, and plant samples divided into aerial parts and roots were taken for laboratory analyses. Afterwards, the biomass obtained from the pots was aggregated into combined samples, corresponding to the individual treatments. These samples were comminuted and dried at 60°C. The content of phosphorus was determined colorimetrically by the vanadium-molybdenum method (OSTROWSKA et al. 1991). In alfalfa, the content of phosphorus was determined only in the aerial mass from the first cut. The results were processed statistically, with the help of Statistica 10.0, applying a two-factorial analysis of variance Anova, while the lowest significant differences (LSD) were determined at the level of significance $\alpha = 0.05$ according to the Duncan's test.

RESULTS AND DISCUSSION

The content of phosphorus in the analyzed plants depended on the degree of soil contamination with fluorine, the applied neutralizing substance as well as the plant species and organ (Tables 1-8). A higher level of fluorine was found in roots than in aerial parts of most plants. The highest content of this element was determined in roots of winter oilseed rape (8.16 g P kg⁻¹ d.m.) and black radish (7.33 g P kg⁻¹ d.m.), whilst the lowest fluorine concentration was detected in roots of spring triticale (0.86 g P kg⁻¹ d.m.). Nowak (2006) demonstrated that the content of phosphorus in a mixture of plants sown for reclamation purposes on a heap of phosphogypsum was within the range of 1.9 to 5.3 g P kg⁻¹ d.m. Pyś and PUCEK (1993) report that fodder plants grown in fields directly adjacent to the Fertilizer Factory in Machów

Table 1

Dose	Type of neutralizing substance							
of fluorine (mg kg ⁻¹ of soil)	without neutralizing substance	lime according to 1 Hh of soil mass of soil		im, % mass	Mean			
	Aerial mass							
0	1.72	1.41	1.62	1.	63	1.59		
100	1.82	1.50	1.72	1.93		1.74		
200	1.74	1.51	1.71	1.80		1.69		
300	1.63	1.63	1.70	1.82		1.69		
Mean	1.73	1.51	1.69	1.79		-		
	Roots							
0	1.92	1.75	1.93	2.	31	1.98		
100	1.74	1.64	2.02	2.34		1.93		
200	1.73	1.30	1.41	1.	42	1.46		
300	1.41	1.21	1.43	1.	20	1.32		
Mean	1.70	1.47	1.70	1.	82	-		
	for fluorine dose	a	aerial mass	0.04	roo	ots 0.04		
$LSD_{0.05}$	for neutralizing s	substance dose b	aerial mass	aerial mass 0.04 ro		ots 0.04		
	for $a \cdot b$ interaction		aerial mass	0.08	roo	ots 0.08		

Effect of soil pollution with fluorine on content of phosphorus in aerial and root mass of maize $(g P kg^{-1} d.m.)$

Table 2

735

	r						
Dose	Type of neutralizing substance						
of fluorine (mg kg ^{.1} of soil)	without neutralizing substance	lime according to 1 Hh	charcoal, 3% of soil mass	loa 3 of soil	ım, % I mass	Mean	
Aerial mass							
0	4.33	4.52	4.85	4.	94	4.66	
100	6.72	5.11	5.71	5.53		5.77	
200	6.50	4.92	5.70	6.20		5.83	
300	6.04	4.93	5.73	5.81		5.63	
Mean	5.90	4.87	5.50	5.62		5.47	
Roots							
0	3.22	4.21	4.03	5.	26	4.18	
100	4.03	4.24	3.82	4.10		4.05	
200	4.53	4.03	3.81	4.01		4.09	
300	4.50	4.00	3.64	4.03		4.04	
Mean	4.07	4.12	3.82	4.	35	4.09	
	for fluorine dose a		aerial mass 0.13		roc	ots 0.09	
$LSD_{0.05}$	for neutralizing s	substance b	aerial mass 0.13 ro		roc	ots 0.09	
	for $a \cdot b$ interaction		aerial mass 0.27		roc	roots 0.19	

Residual effect of soil pollution with fluorine on content of phosphorus in aerial mass and roots of vellow lupine (g P kg⁻¹ d.m.)

were characterized by a low content of phosphorus. MACLEAN et al. (1992) performed an experiment on wheat and determined more phosphorus in sprouts than in roots of this plant.

In the control series, without any neutralizing substance, the soil pollution with fluorine contributed to a higher content of phosphorus in roots of winter oilseed rape, in straw and roots of spring triticale, in both tested organs of yellow lupine and in black radish and phacelia. A reverse relationship, namely a decrease in the phosphorus content under increasing soil contamination with fluorine, was observed in both organs of maize and narrow-leaf lupine as well as in the aerial mass of winter oilseed rape, in grain of spring triticale and in the aerial mass of the first cut of alfalfa.

In the above series, i.e. without any neutralizing substance, the highest doses of fluorine, 60 mg F kg⁻¹ of soil in the experiment with narrow-leaf lupine, 150 mg Fkg⁻¹ of soil under alfalfa and 300 mg F kg⁻¹ of soil in the case of the other crops, caused a significant increase in the content of phosphorus. This growth reached 31% in straw and 42% in roots of spring triticale, 39% in the aerial mass and 40% in roots of yellow lupine, 64% in the aerial mass and 22% in roots of black radish, and finally 17% in the aerial mass and 7% in roots of phacelia.

Table 3

Dose	Type of neutralizing substance					
of fluorine (mg kg ⁻¹ of soil)	without neutralizing substance	lime according to 1 Hh	charcoal, 3% of soil mass	loa 3 of soil	um, % mass	Mean
Aerial mass						
0	4.73	4.71	4.52	4.	52	4.62
100	4.52	4.52	4.64	4.54		4.55
200	4.40	4.55	4.70	4.56		4.55
300	4.56	4.50	4.31	4.60		4.49
Mean	4.55	4.57	4.54	4.55		4.55
Roots						
0	5.72	6.13	7.35	7.	54	6.68
100	9.51	7.90	9.41	9.	42	9.06
200	9.40	7.41	9.00	8.70		8.63
300	7.95	7.33	9.03	8.73		8.26
Mean	8.14	7.19	8.70	8.60		8.16
	for fluorine dose a		aerial mass n.s. re		ots 0.21	
$LSD_{0.05}$	for neutralizing	substance b	aerial mass	aerial mass n.s. ro		ots 0.21
	for $a \cdot b$ interact	ion	aerial mass	0.22	ro	ots 0.42

Effect of soil pollution with fluorine on content of phosphorus in aerial and root mass of winter oilseed rape (g P kg⁻¹d.m.)

n.s. - non-significant difference

In the same series, as mentioned before, a decrease was observed in the content of phosphorus in response to the soil contamination with fluorine. Such a result occurred in maize (a decrease by 5% in aerial mass and by 27% in roots), winter oilseed rape aerial mass (by 4%) and finally in narrow-leaf lupine (by 17% in aerial mass and 7% in roots).

The experiment conducted by FUNG and WONG (2002) on Chinese tea showed the presence of positive correlation between the soil contamination with fluorine and the content of phosphorus in the plant. Contrary results were obtained by ELRASHIDI et al. (1998), who showed negative correlation between increasing doses of fluorine (100, 400 and 1000 mg F kg⁻¹ of soil) and the content of phosphorus in common barley plants. A negative effect of fluorine on the content of phosphorus in vine was demonstrated by ABDALLAH et al. (2006) and in maize roots by FACANHA and OKOROKOVA-FACANHA (2002). In turn, ZBIERSKA (1996) recorded a decrease in the content of phosphorus in the first cut sward in an area affected by the Phosphorus Fertilizer Plant in Luboń (Poland). Having applied a dose of fluorine equal 6736 μ M, STEVENS et al. (1998) noticed a 27% decline in the content of phosphorus in an experiment

on oat and a 25% rise in the content of this macronutrient in an experiment on tomato.

The impact of the growing soil pollution with fluorine on the content of phosphorus in plants was modified by the introduction of substances inactivating fluorine to the substrate (Tables 1-8). These substances in most of the treatments contributed to a decrease in the content of phosphorus in the biomass harvested from the tested crops.

A decrease in the phosphorus content in the aerial mass of yellow lupine ranged from 5% in the series with loam to 18% in the limed series. With respect to the roots of this plant, liming did not have influence on the average content of phosphorus, whose content remained the similar as in the control

Table 4

Dose		Type of neutraliz	ing substance			
of fluorine (mg kg ⁻¹ of soil)	without neutralizing substance	lime according to 1 Hh	charcoal, 3% of soil mass	loam, 3% of soil mass	Mean	
Grain						
0	4.12	4.02	3.63	3.63	3.85	
100	4.03	4.01	3.62	3.61	3.82	
200	4.05	4.04	3.76	3.80	3.91	
300	4.01	4.01	3.80	4.05	3.97	
Mean	4.05	4.02	3.70	3.77	3.89	
		Strav	v			
0	1.24	1.41	1.43	1.67	1.44	
100	1.61	1.22	1.72	1.62	1.54	
200	1.63	1.24	1.40	1.81	1.52	
300	1.62	1.20	1.41	1.51	1.43	
Mean	1.52	1.27	1.49	1.65	1.48	
		Roots	3			
0	0.72	0.73	0.72	0.71	0.72	
100	1.01	0.71	0.74	0.93	0.85	
200	1.01	0.73	0.93	0.92	0.90	
300	1.02	0.94	0.92	1.05	0.98	
Mean	0.94	0.78	0.83	0.90	0.86	
	for fluorine dose	a	grain 0.09	straw 0.03	roots 0.02	
$\mathrm{LSD}_{0.05}$	for neutralizing	substance b	grain 0.09	straw 0.03	roots 0.02	
	for $a \cdot b$ interaction	on	grain n.s.	straw 0.07	roots 0.04	

Effect of soil pollution with fluorine on content of phosphorus in grain, straw and roots of spring triticale (g P $\rm kg^{-1}d.m.)$

n.s. - non-significant difference

Dose	Type of neutralizing substance					
of fluorine (mg kg ⁻¹ of soil)	without neutralizing substance	lime according to 1 Hh	charcoal, 3% of soil mass	loa 3 of soil	um, % I mass	Mean
Aerial mass						
0	2.76	1.91	2.73	2.	80	2.55
20	2.74	2.05	2.62	2.63		2.51
40	2.52	2.13	2.56	2.64		2.46
60	2.30	2.04	2.21	2.51		2.26
Mean	2.58	2.03	2.53	2.64		2.44
		Roots	8			
0	4.12	3.82	3.82	3.51		3.82
20	3.81	3.61	4.06	3.	62	3.77
40	3.85	3.50	3.80	3.83		3.74
60	3.83	3.55	3.43	3.60		3.60
Mean	3.90	3.62	3.78	3.64		3.73
	for fluorine dose a		aerial mass 0.06 r		ro	ots 0.09
$LSD_{0.05}$	for neutralizing	substance b	aerial mass	l mass 0.06 ro		ots 0.09
	for interaction a	·· b	aerial mass	0.12 ro		ots 0.18

Effect of soil pollution with fluorine on content of phosphorus in aerial and root mass of narrow-leaf lupine (g P $kg^{-1}d.m.$)

series. The highest decrease in the level of phosphorus in the sward from the 1st cut of alfalfa was noticed in the series with charcoal (less by 12%), next in the limed series (10%), and finally in soil treated with loam (2%). The decrease in the concentration of phosphorus in the aerial biomass of black radish induced by the applied substances neutralizing fluorine ranged from 5% in the series with charcoal to 12% in the series with lime; in roots of this crop, the analogous decline varied from 4% in the series with lime and loam to 6% in treatments with charcoal. All the applied substances had a negative effect also on the content of phosphorus in roots of narrow-leaf lupine, with lime and loam producing the strongest limiting effect, causing a 7% decrease compared to the control series.

Of the three substances alleviating the impact of fluorine on the content of phosphorus in plant biomass, lime had the worst effect. In response to this substance, the content of phosphorus decreased by 17% in spring triticale straw and roots and 21% in aerial biomass of narrow-leaf lupine. The application of loam to soil contributed to an increase in the average concentration of phosphorus from a 3% rise in aerial parts of maize up to 24% in roots of phacelia, all in comparison with the control series.

739

Charcoal, used to neutralize soil pollution with fluorine, demonstrated the weakest influence on the content of phosphorus in biomass of the tested crops. Its positive effect on the content of phosphorus was observed in roots of winter oilseed rape. Under the influence of charcoal, the content of phosphorus in roots of this crop rose by an average 7%. A reverse dependence was noticed in aerial mass of phacelia, roots of black radish and aerial mass of alfalfa, where the concentration of phosphorus decreased by 5, 6 and 12%, respectively.

To summarize, the influence of the tested substances introduced to soil in order to neutralize the effect of fluorine as a soil pollutant on the content of phosphorus in biomass of the examined plants depended on the type of substance as well as the species of a plant and its organs.

Table 6

Dose	Type of neutralizing substance							
of fluorine (mg kg ⁻¹ of soil)	without neutralizing substance	lime according to 1 Hh	charcoal, 3% of soil mass	loa 3 of soil	ım, % mass	Mean		
	Aerial mass							
0	3.43	3.62	4.02	3.	62	3.67		
100	4.52	3.71	4.21	3.83		4.07		
200	5.11	4.40	4.50	4.51		4.63		
300	5.64	4.73	4.94	4.92		5.06		
Mean	4.67	4.13	4.42	4.22		4.36		
	Roots							
0	6.72	7.13	6.73	6.52		6.77		
100	7.23	7.15	6.81	7.	53	7.18		
200	8.24	7.61	8.22	7.91		7.99		
300	8.20	7.32	6.94	7.15		7.40		
Mean	7.60	7.30	7.17	7.28		7.34		
	for fluorine dose a		aerial mass	0.11	ro	ots 0.19		
$LSD_{0.05}$	for neutralizing	substance b	aerial mass	0.11 ro		ots 0.19		
	for $a \cdot b$ interaction	ion	aerial mass 0.22 roo			ots 0.38		

Effect of soil pollution with fluorine on content of phosphorus in aerial and root mass of black radish (g P kg⁻¹d.m.)

Table 7

	una	foot mass of phas						
Dose								
of fluorine (mg kg ⁻¹ of soil)	without neutralizing substance	lime according to 1 Hh	ng charcoal, loam 3% 3% of soil mass of soil r		n, 6 mass	Mean		
Aerial mass								
0	5.12	5.13	5.44	5.53		5.30		
100	5.61	5.32	5.65	6.11		5.67		
200	5.85	5.54	5.61	6.24		5.81		
300	6.00	5.81	4.62	5.62		5.51		
Mean	5.64	5.45	5.33	5.87		5.57		
	Roots							
0	1.61	1.42	1.82	1.6	5	1.62		
100	1.62	1.61	1.80	2.3	0	1.83		
200	1.80	1.63	1.91	2.2	1	1.89		
300	1.73	1.21	1.73	2.22		1.72		
Mean	1.69	1.47	1.81	2.09		1.76		
$LSD_{0.05}$ for fluorine dose <i>a</i> for neutralizing substance <i>b</i> for <i>a</i> x <i>b</i> interaction			aerial ma 0.13 0.13 0.27	ss	1	roots 0.04 0.04 0.09		

Effect of soil pollution with fluorine on content of phosphorus in aerial and root mass of phacelia (g P $kg^{-1}d.m.$)

Table 8

Effect of soil pollution with fluorine on content of phosphorus in aerial mass of the first cut of alfalfa (g P kg^{\cdot1}d.m.)

Dose					
of fluorine (mg kg ⁻¹ of soil)	without neutralizing substance	lime according to 1 Hh	charcoal, 3% of soil mass	loam, 3% of soil mass	Mean
0	3.32	2.73	2.52	2.83	2.85
50	2.71	2.51	2.31	2.71	2.56
100	2.74	2.56	2.54	2.62	2.61
150	2.70	2.50	2.70	3.11	2.75
Mean	2.87	2.57	2.52	2.82	2.69
	for fluorine dose	a	0.06		
$\mathrm{LSD}_{0.05}$	for neutralizing substance b		0.06		
	for a b interaction	on	0.13		

CONCLUSIONS

1. The effect of the increasing degree of soil contamination with fluorine on the content of phosphorus in the biomass of examined plants depended on the species and organs of those plants.

2. Under the influence of soil pollution with fluorine, the content of phosphorus in roots of winter oilseed rape, in straw and roots of spring triticale and in both organs of black radish, phacelia and yellow lupine increased, while decreasing in roots of maize, aerial biomass of winter oilseed rape and in both organs of narrow-leaf lupine and in aerial mass of alfalfa.

3. The soil application of lime, charcoal and loam caused the biggest changes in the content of phosphorus in aerial mass of yellow lupine, in roots of narrow-leaf lupine, in aerial mass and roots of black radish and in aerial mass of the first cut sward of alfalfa. These changes were negative in character and were most distinctly seen after soil liming.

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