CONTENT OF FLUORINE IN BIOMASS OF CROPS DEPENDING ON SOIL CONTAMINATION BY THIS ELEMENT

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SUMMARY: The goal of this study has been to demonstrate the influence of soil contamination by fluorine on the concentration of this element in aerial biomass and roots of eight crops. Additionally, soil was enriched with substances inactivating the influence of fluorine, such as lime, charcoal, and loam. The content of fluorine in the examined plants depended on a plant species and organ, the dose of the xenobiotic element, and the type of fluorine-inactivating substance. As the degree of soil contamination by fluorine increased, so did the concentration of this element in the analyzed plants. The highest average content of fluorine was found in the aerial mass of yellow lupine (*Lupinus luteus* L.) – 15.4 mg F/kg dry matter (dm), and black radish (*Raphanus sativus* L.) – 15.0 mg F/kg dm; as for the roots, the following crops had the highest fluorine content: winter oilseed rape (*Brassica napus* L.) – 51.0 mg F/kg dm and maize (*Zea mays* L.) – 43.6 mg F/kg dm. All the neutralizing substances considerably reduced the accumulation of fluorine in the analyzed crops, with the strongest effect produced by loam and the weakest one by lime.

Keywords: Fluorine; Crops; Charcoal; Lime; Loam; Substrate contamination; Soil remediation.

INTRODUCTION

Fluorine is one of the most widespread elements in the natural environment. In fact, it is the 13th most abundant element in the Earth's crust.[1] In nature, fluorine appears in natural minerals, especially fluorite, apatite, muscovite and biotite.[2] The main anthropogenic sources of fluorine as an environmental pollutant are the gaseous emissions from aluminum smelters, coal power plants, brick manufacturers, chinaware and glassware factories, and phosphate manufacturing plants.[3] The uptake of fluorine from the substrate by crops is typically small because in soil fluorine most often occurs in a form unavailable to plants. However, when the content of fluorine in soil exceeds the background level, crops may absorb excessive amounts of this element.[4] In soils exposed to heavy emissions of fluorine, the element tends to accumulate in excessive quantities with a detrimental effect on agricultural production.[5] Noteworthy is the fact that crop species demonstrate varied tolerance to fluorine compounds. The natural content of fluorine in plants ranges from 1 to 10 mg F/kg dm.[6-8]

The objective of this study has been to determine the content of fluorine in the aerial parts and roots of plants depending on the soil contamination by this element. The substrate was enriched with some neutralizing substances, i.e., lime, charcoal, and loam, in order to reduce the phytoavailability of fluorine to plants.

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MATERIAL AND METHODS

Eight greenhouse pot experiments, conducted in 2009–2011 at the University of Warmia and Mazury in Olsztyn, provided data for the research. The experiments were set up on soil originating from the arable soil horizon, with the texture of loamy sand. The soil pH was 5.89 in H_2O and 4.43 in KCl, the hydrolytic acidity was 30.7 mmol/kg of soil, and the content of total fluorine was 125 mg/kg of soil. The following plants were grown: maize (*Zea mays* L.), yellow lupine (*Lupinus luteus* L.*)*, winter oilseed rape (*Brassica napus* L.), spring triticale (*Triticoseca Wittm.*), narrow-leaf lupine (*Lupinus angustifolius* L.), black radish (*Raphanus sativus*), phacelia (*Phacelia Juss.)* and sainfoin (*Onobrychis viciaefolia Scop.*).

Two factors were analyzed. The first order factor consisted of increasing doses of fluorine, applied in the form of potassium fluoride (commercial preparation), to simulate soil contamination. The second factor comprised three substances neutralizing the soil contamination by fluorine.

Depending on the sensitivity of the analyzed crops, the soil pollution by fluorine was: (i) 0, 20, 40, and 60 mg F/kg of soil under sensitive plants, i.e., narrow-leaf lupine; (ii) 0, 50, 100, and 150 mg F/kg of soil under moderately sensitive plants, i.e., sainfoin; or (iii) 0, 100, 200, and 300 mg F/kg of soil under tolerant plants, i.e., winter oilseed rape, spring triticale, black radish and phacelia.

Another plant sensitive to soil contamination by fluorine, examined in the present experiment, was yellow lupine, which was sown as a post-harvest crop following maize. In this trial, the residual effect of fluorine added to soil under maize was analyzed.

With respect to two other plant species, namely narrow-leaf lupine and sainfoin, the reason why they were exposed to lower doses of fluorine is that they papilionaceous plants and therefore more sensitive to a variety of xenobiotic substances.

The substances applied to soil in order to neutralize the soil contamination by fluorine were: lime (in a dose corresponding to 1 Hh of soil), charcoal, and loam, both introduced to soil in amounts equal to 3% of the soil mass in a pot. The content of total fluorine in the three applied substances was: 500, 2000, and 88 mg F/kg, respectively.

Apart from neutralizing substances, the soil was also amended with mineral NPK fertilizers, the same in all the trials, to satisfy the plants' nutritional demands. Nitrogen was applied as urea in a dose of 11 mg N, phosphorus was given as 46% triple superphosphate in an amount of 48 mg P and potassium was introduced as 57% potassium salt in a dose equal 11 mg K/kg of soil.

In total, each trial was composed of 16 treatments, including 3 replications. The set doses of fluorine, neutralizing substances and fertilizers were carefully mixed with soil and then transferred to labelled pots. Immediately after the pots had been filled with soil mixed with appropriate substances according to the experimental design, the test plants were sown. The results were submitted to statistical analysis according to the two-factorial analysis of variance ANOVA, while the least significant differences (LSD) were determined with the Duncan's test at the level of significance α=0.05.[9] All the calculations were aided by Statistica 10.0 software.

Determinations of fluorine potentially available to plants (extracted with 2M $HClO_4$) were made by the potentiometric method with an ion-selective fluoride electrode made by ORION 920. The determinations followed the protocol worked out by Szymczak and Grajeta, with the buffering solution TISAB III.[10] The content of total fluorine in soil and in the neutralizing substances was determined with the x-ray fluorescence spectrophotometry (XRF) on a Philips WD-XRF PW 2004 spectrophotometer. Each time, before the final determination of total fluorine, a preliminary analysis of the quality of a sample was carried out in order to assess the levels of interfering substances, that is sulphate (VI) ions, orthophosphate (V) ions and other ions forming hardly soluble compounds with fluorine.

RESULTS AND DISCUSSION

The content of fluorine in plant organs depended in the soil contamination by fluorine, addition of neutralizing substances as well as the plant species and organ (Figures 1–15).

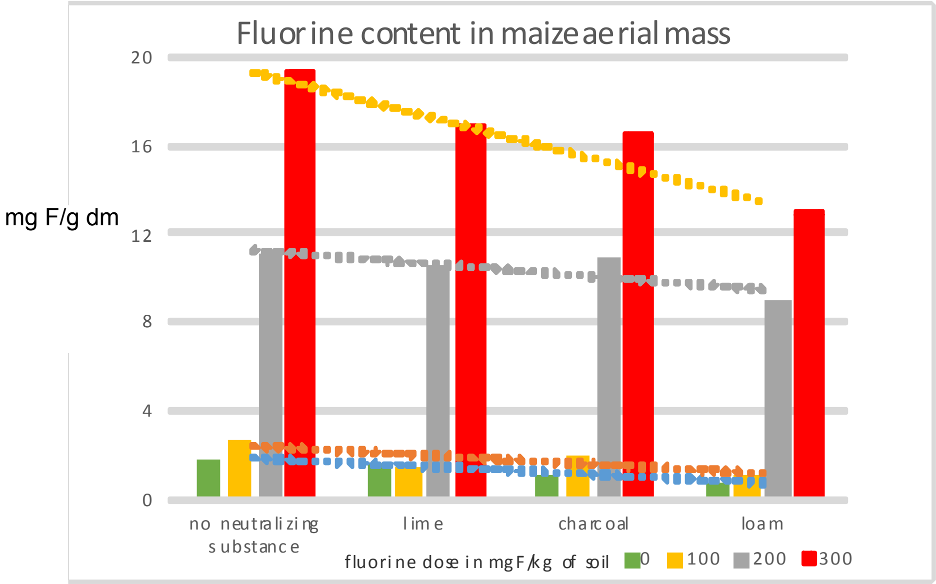

Figure 1. Concentration of fluorine in maize aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.32*; b=0.32*; a•b=0.64*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

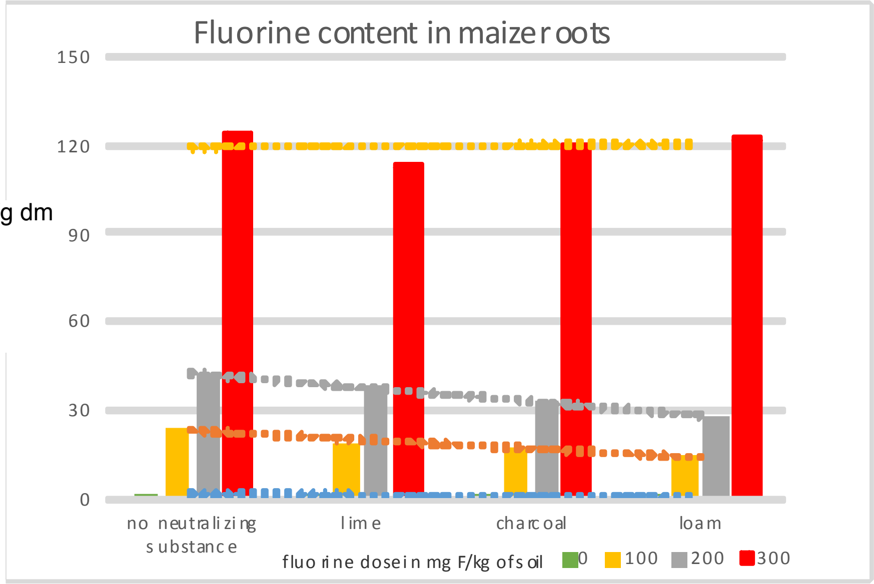

Figure 2. Concentration of fluorine in maize roots depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.71*; b=0.71*; a•b=1.43*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

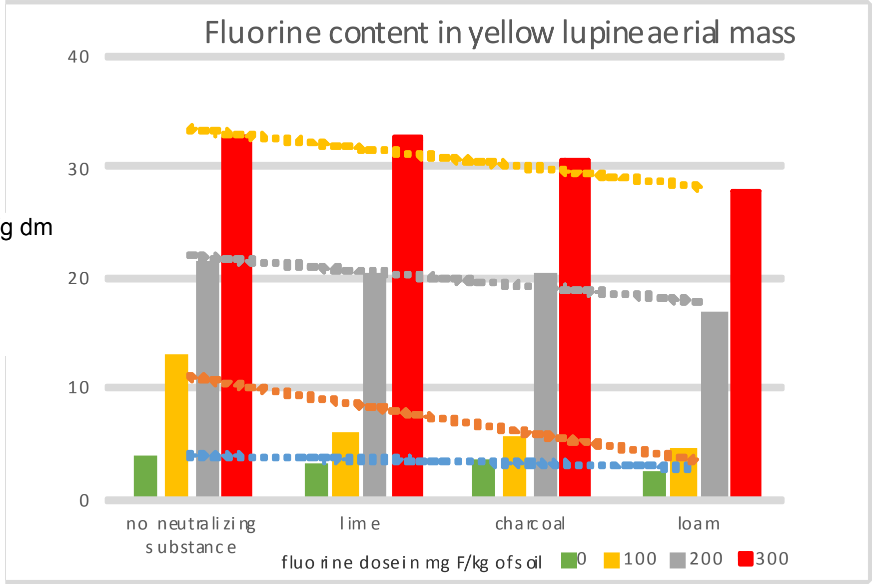

Figure 3. Concentration of fluorine in yellow lupine aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.51*; b=0.51*; a•b=1.03*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

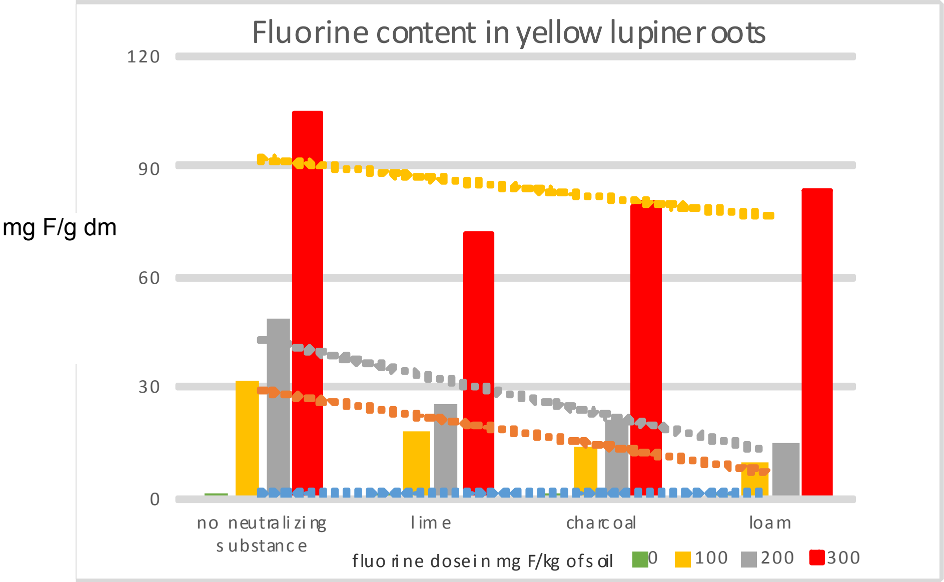

Figure 4. Concentration of fluorine in yellow lupine roots depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=1.09*; b=1.09*; a•b=2.19*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

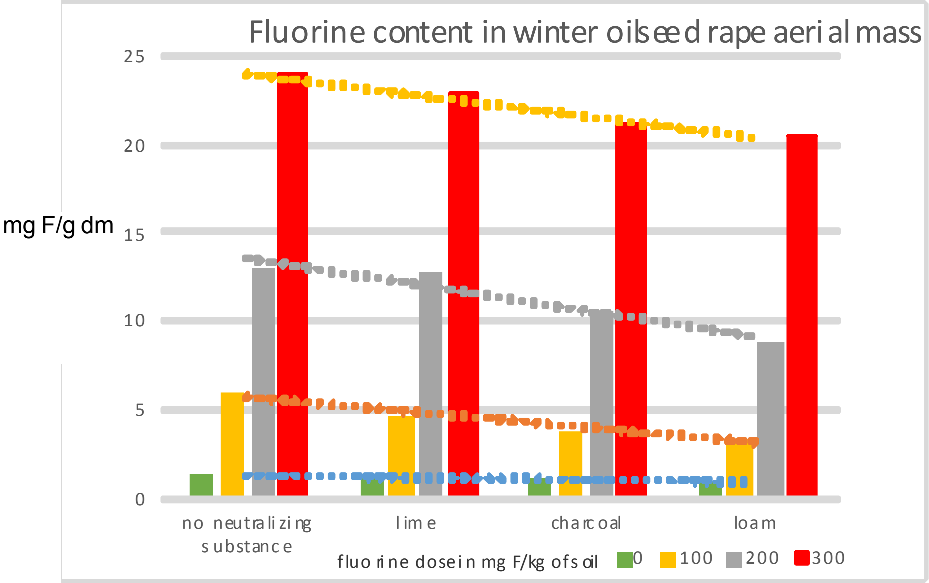

Figure 5. Concentration of fluorine in winter oilseed rape aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.37*; b=0.37*; a•b=0.74*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

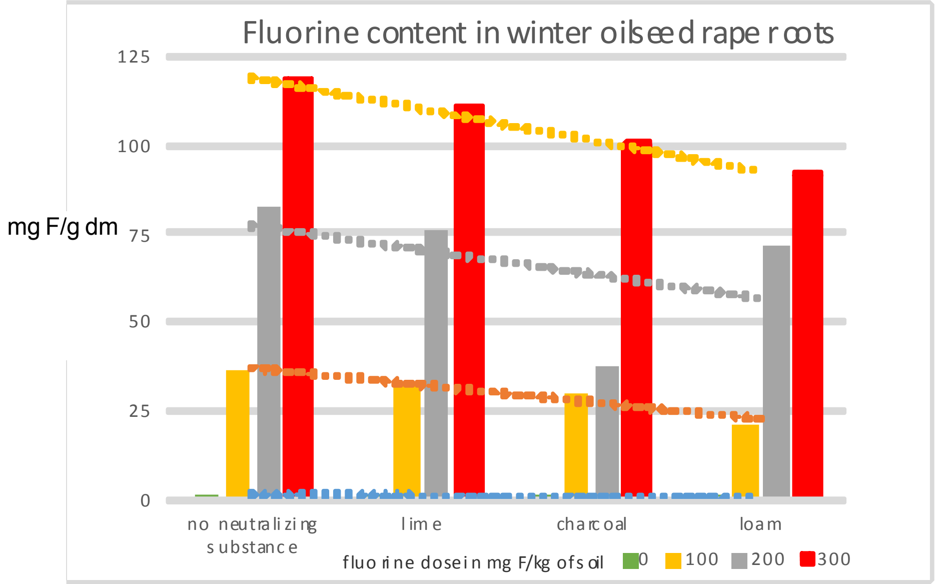

Figure 6. Concentration of fluorine in winter oilseed rape roots depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=4.52*; b=4.52*; a•b=9.04*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

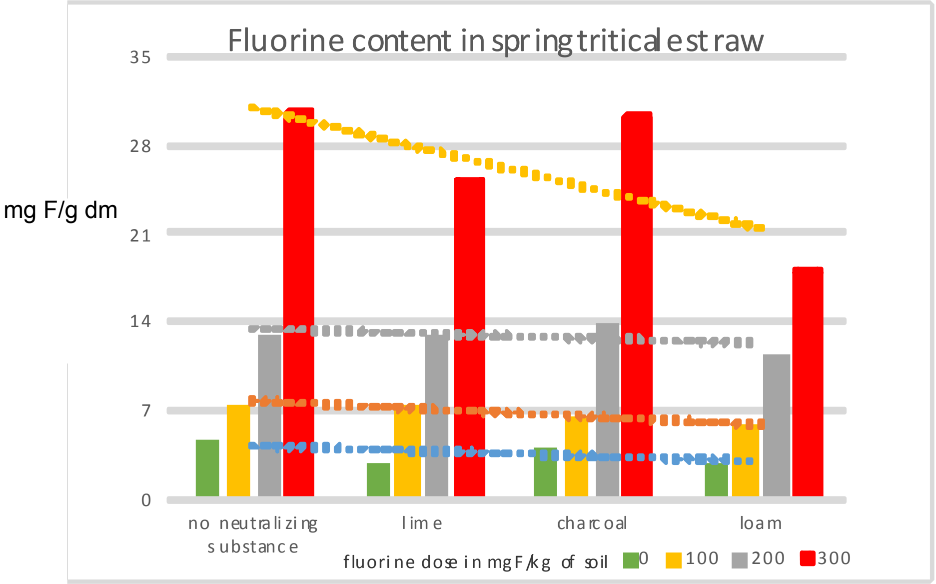

Figure 7. Concentration of fluorine in spring triticale aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.29*; b=0.29*; a•b=0.58*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

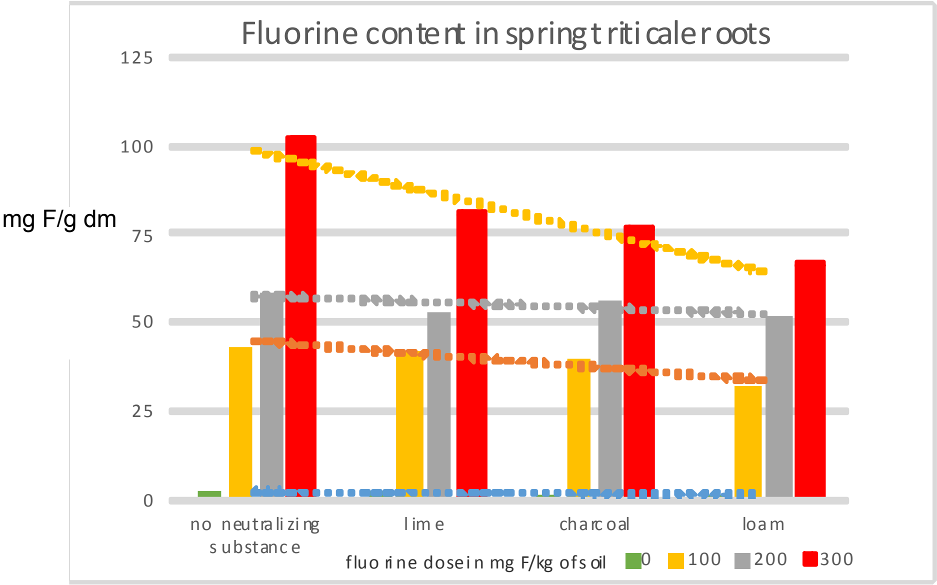

Figure 8. Concentration of fluorine in spring triticale roots depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.91*; b=0.91*; a•b=1.82*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

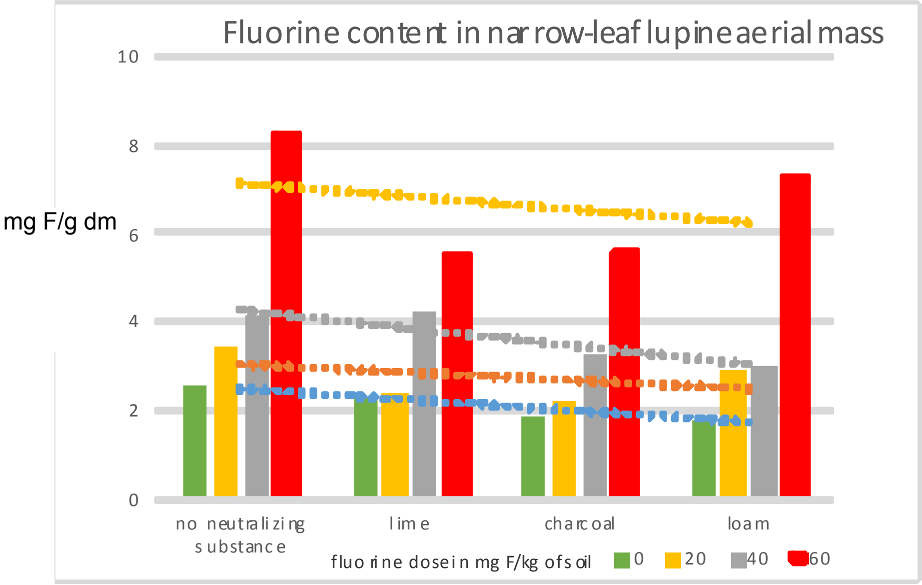

Figure 9. Concentration of fluorine in narrow-leaf lupine aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.06*; b=0.06*; a•b=0.12*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

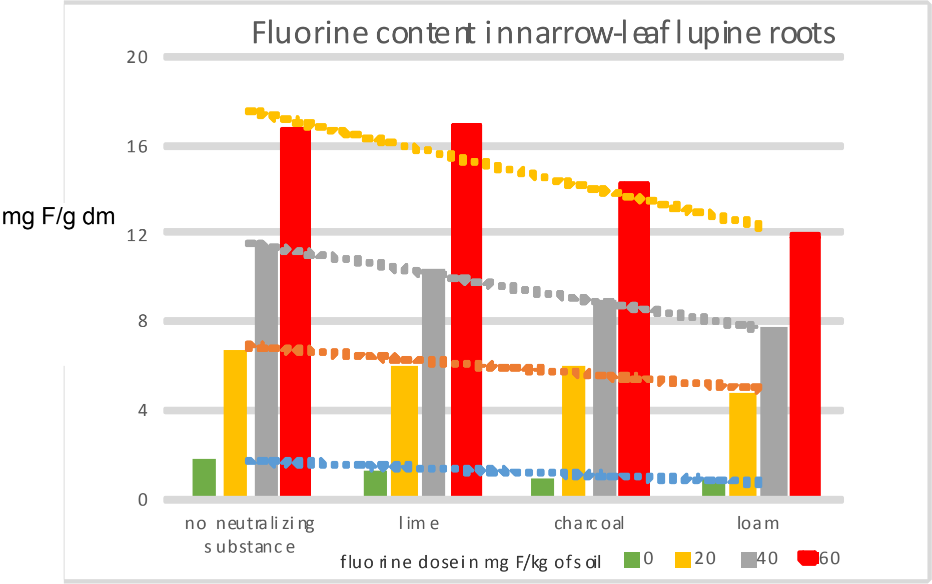

Figure 10. Concentration of fluorine in narrow-leaf lupin roots depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.43*; b=0.43*; a•b=0.87*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

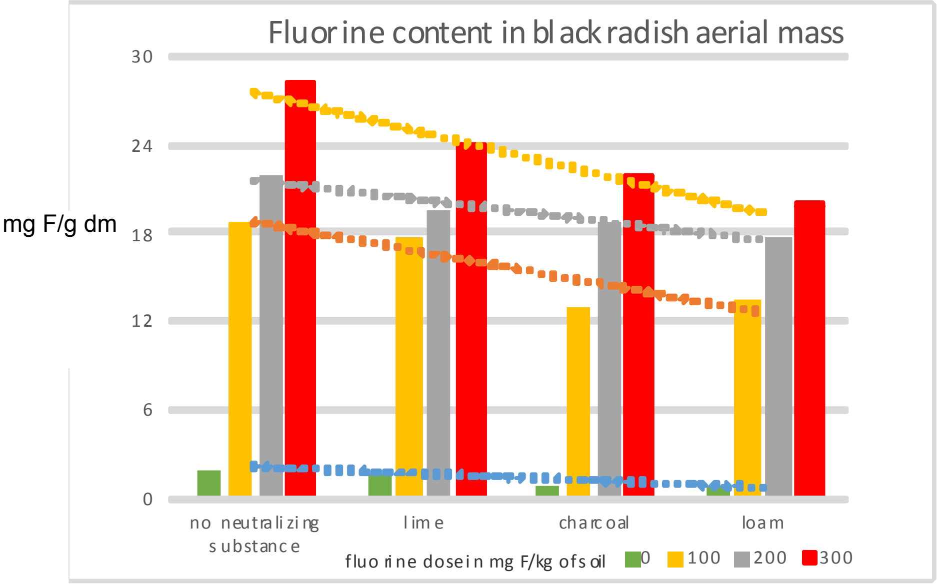

Figure 11. Concentration of fluorine in black radish aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.51*; b=0.51*; a•b=1.03*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

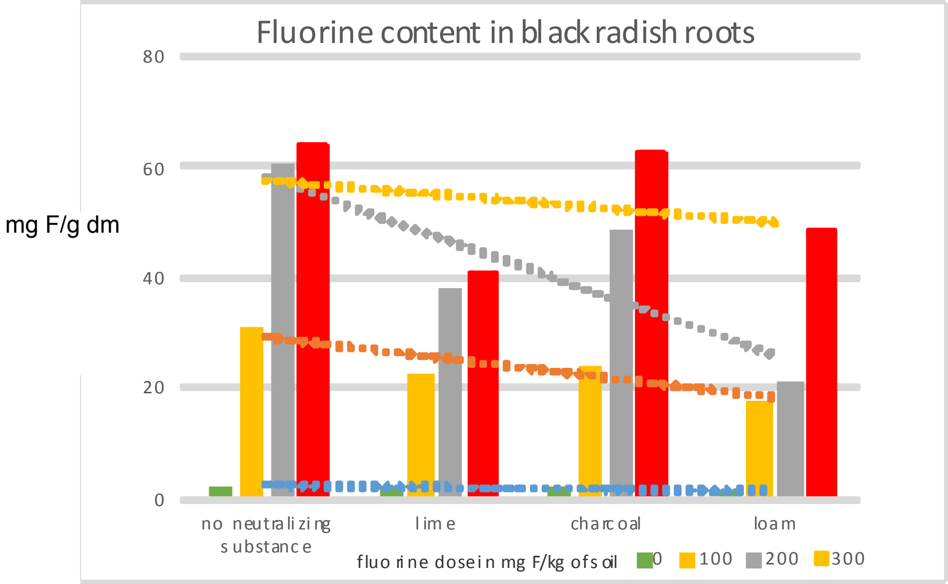

Figure 12. Concentration of fluorine in black radish roots depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=2.77*; b=2.77*; a•b=5.55*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

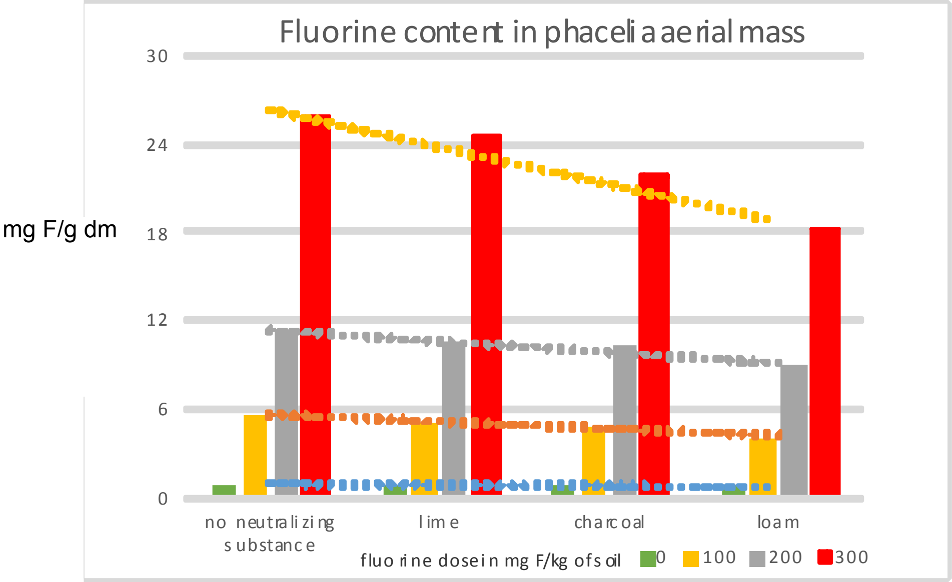

Figure 13. Concentration of fluorine in phacelia aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.48*; b=0.48*; a•b=0.96*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

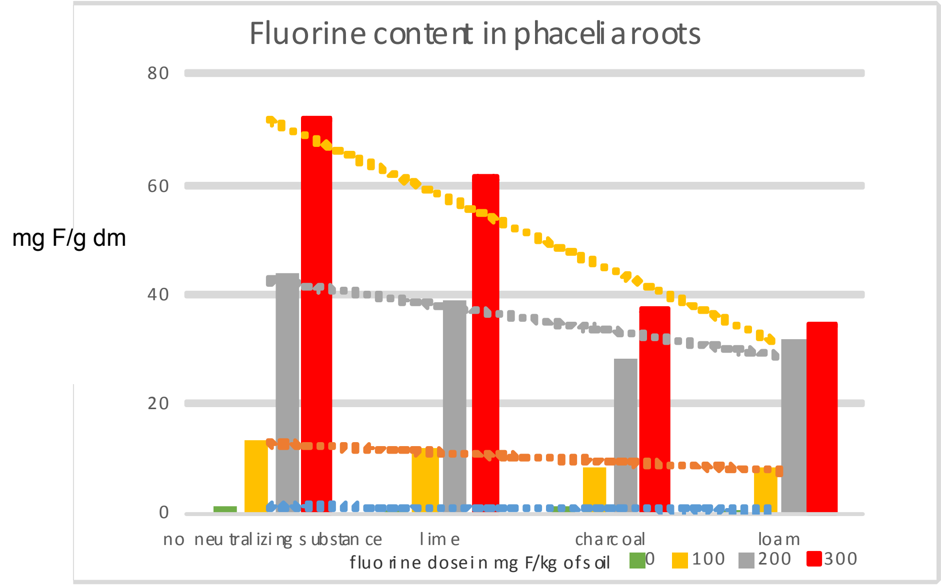

Figure 14. Concentration of fluorine in phacelia roots depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.44*; b=0.44*; a•b=0.89*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

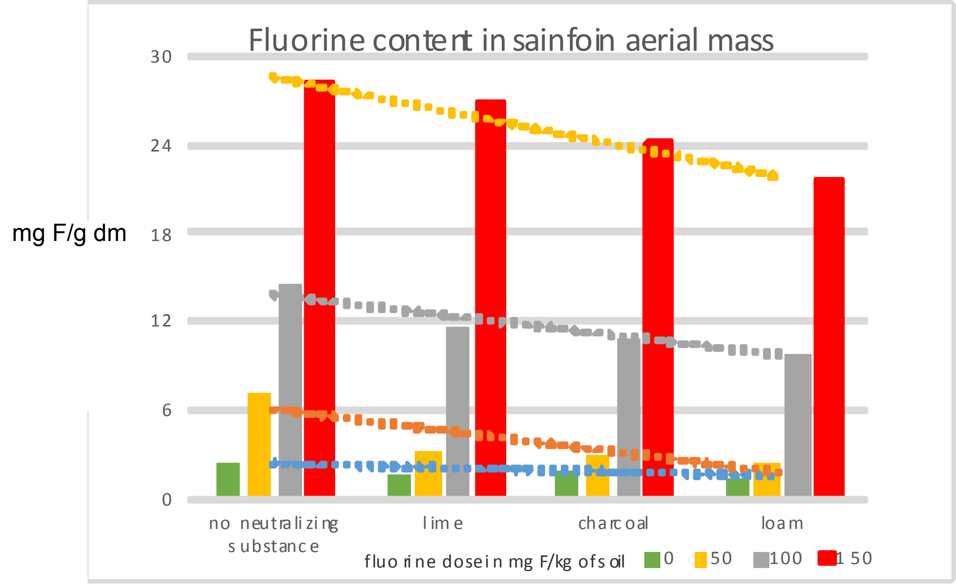

Figure 15. Concentration of fluorine in sainfoin aerial mass depending on soil contamination by fluorine and applied neutralizing substance. $LSD_{0.05}$ for a=0.39*; b=0.39*; a•b=0.79*. a=fluorine dose; b=type of neutralizing substance; *p=significant for 0.05.

All the analyzed plants were found to contain higher levels of fluorine in the roots than in the aerial parts. Maize was an outstanding plant because its roots had on average 6-fold more fluorine than the organs above the ground. This regularity was most probably a consequence of some 'biological barrier' in plants, which hinders the transport of xenobiotics to aerial parts. The highest content of fluorine was found in roots of winter oilseed rape (51.0 mg F/kg dm) and maize (43.6 mg F/kg dm).

Similar relationships were noted by Jha et al. in an experiment on *Allium cepa*,[11] Chakrabarti et al. on *Cicer arietinum*,[12] Gautam and Bhardwaj on *Hordeum vulgare*,[13] Gupta and Banerjee on *Oryza sativa*,[14] Elloumi et al. on *Amygdalis communis*,[15] and Jha et al. on *Abelmoschus esculentus*[16] as well as Davies et al. on *Vicia faba*.[17]

The relevant literature provides data to support the claim that the concentration of fluorine in plants is correlated with its content in soil.[2,18] In the current study, such dependence was verified in all the trials. As the soil contamination by fluorine increased, the concentration of this xenobiotic gradually increased in the aerial mass and in the roots of the test plants (Figures 1–15). Thus, in series without neutralizing substances, the highest increase in fluorine in the pots polluted by the highest fluorine dose, against the control, was observed in roots of maize (a 126-fold increase), winter oilseed rape (105-fold) and yellow lupine (96-fold). Elevated levels of fluorine in plants grown on F contaminated soil have also been revealed by Chakrabarti and Patra testing *Oryza sativa,*[19] Bozhkov et al. analyzing *Triticum aestivum,*[20] and Jha et al. investigating *Spinacea oleracea*.[21] However, there are also reports, e.g., by Geeson et al., which do not show significant differences between the soil content of fluorine and concentrations of this element in plants.[22]

The content of fluorine in individual organs of the test plants is a very important indicator, useful for evaluation of the effect of fluorine neutralizing soil amendments.

The authors' experiment proved that lime added to soil contributed to a decrease in the concentration of fluorine in all the examined crops. Thus, according to the mean concentrations of fluorine in the series with added lime, the biggest decrease in the plant content of fluorine appeared in yellow lupine roots (39% less than in the control), black radish roots (35%), and narrow-leaf lupine aerial organs (22%).

The positive effect of lime introduced to soil in order to reduce the bioavailability of fluorine to plants is confirmed in several references. For example, Ruan et al. reported that application of lime in the doses of 1.05 and 2.70 g/kg of soil triggered a decrease in the content of fluorine in tea leaves by 37 and 89%, respectively.[23] An experiment by Fung and Wong, also performed on tea plants, verified the beneficial influence of soil liming consisting of the limited bioavailability of fluorine to plants.[24] According to Romar et al., in soils rich in lime fluorine is bound into insoluble compounds, such as CaF_2 or to apatite compounds with similar composition, thus reducing the bioavailability of F to plants.[25] The beneficial influence of lime introduced to fluorine contaminated soil has also been shown experimentally by Arnesen on *Trifolium repens* and *Lolium multiforium*[6] and Stanley et al. on *Amaranthes viridis*.[26]

In the experiment discussed herein, positive effects were also obtained by introducing charcoal to soil. With respect to the mean concentrations of fluorine in series with added charcoal, the highest decrease in the content of fluorine versus the series without any neutralizing substance was observed in phacelia roots (42% less) and yellow lupine roots (38%). Regarding the aerial parts of yellow lupine and roots of winter oilseed rape, their content of fluorine was slightly less depressed, namely by 30% versus the control series. Gao et al. demonstrated that charcoal applied in doses of 0.5, 1.0, 2.5, and 5% of soil mass significantly decreased the concentration of fluorine in tea leaves and roots.[27] In turn, Smolik et al. showed that humus added to soil in an amount corresponding to 5–10% of soil mass had the most significant effect on diminishing the amount of fluorine available to plants.[4] Some previous study by Smolik et al. also showed that humus could be used for the sake of limiting the unwanted effect of fluorides on the soil environment.[28]

The current trials prove that the concentration of fluorine in plants can also be reduced through the soil enrichment with loam containing clay minerals. This hypothesis is supported by the fact that a lower content of fluorine was determined in all the analyzed plants, regardless of the tested organ, than in the control series, in which no neutralizing substances had been added. Our results indicate that the applied loam contributed to immobilization of fluorine in soil. Considering the average concentrations of fluorine in particular plant organs, it can be concluded that a decrease in its plant content relative to the series without the neutralizing substances was within 14% in maize roots to 44% in black radish roots. The verified positive effect of loam on limiting the phytoavailability of fluorine was most probably caused by the xenobotic element forming bonds with magnesium and calcium, which appear rather abundantly in the given neutralizing substance, thus creating hardly soluble compounds.

CONCLUSIONS

The tendency of the plants for higher accumulation of fluorine in roots than in the aerial biomass suggests that fluorine contaminated areas should be rehabilitated using plant species whose aerial organs rather than roots are treated as plant product. All the substances compared in our study and used for neutralization of soil contamination by fluorine are suitable for use in reclamation of soils polluted by this xenobiotic. However, out of the three compared substances, loam was the most effective one, followed by charcoal and lime.

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