



Fluoride accumulation by plants grown in acid soils amended with flue gas desulphurisation gypsum

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ABSTRACT

The application of flue gas desulphurisation (FGD) gypsum as an acid soil ameliorant was studied in order to establish the possible detrimental effects on plants and animals feeding on them caused by the high fluoride content in this by-product. A greenhouse experiment was conducted under controlled conditions to determine the F accumulation by two plant species (alfalfa (*Medicago sativa* L.) and ryegrass (*Lolium perenne* L.)) grown in acid soils amended with different FGD gypsum doses (0–10%). The F concentrations in plant aerial parts were comprised in the range 22–65 mg kg⁻¹, and those in plant roots varied from 49 to 135 mg kg⁻¹. The F contents in the above-ground plant tissues showed to decrease with the FGD gypsum application rate, whereas an inverse trend was manifested by plant roots. The increase in the soil content of soluble Ca as a result of the FGD gypsum addition seemed to play an important role in limiting the translocation of F to plant aerial parts.

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1. Introduction

Coal combustion plants have been equipped with flue gas desulphurisation (FGD) systems to reduce the SO₂ emissions to the atmosphere [1–3]. In the FGD process most widely applied, i.e. the wet limestone FGD method, SO₂ is removed from the flue gas by absorption into limestone slurry, then oxidised to produce sulphate, extracted from the absorber as gypsum slurry, and finally dewatered, producing the so-called FGD gypsum. This by-product is largely employed in the wallboard manufacture or in the cement industry. Nevertheless, in many countries with natural deposits of gypsum this by-product is used in a great proportion as a landfill material in mine reclamation or just sent to landfills for its disposal. The ever-increasing production of FGD gypsum has promoted the search for alternative ways of dealing with this by-product. These mainly include its use as a construction material for roads, for waste stabilisation and as a soil ameliorant [4–9].

The agricultural benefits of gypsum or gypsum-based products are well known. These mainly involve improving soil water infiltration and storage, providing a source of nutrients (Ca, S) to plants, and lessening the effects of aluminium toxicity in acid soils [6,10–13]. In addition to such ameliorations, the use of gypsum by-products in this application can also bring about some detrimental consequences. Thus, different elements of environmental concern

(such as F, As, Se, Sb, Hg, Cd, Cr, Cu, Ni, Pb, Zn, Ba, Mo) can occur in FGD gypsum since the limestone slurry used in the FGD process acts as a scavenging system also for them. Several studies have been performed trying to elucidate the environmental risks that could be derived from the agricultural use of FGD gypsum [6,10,11,14,15]. No soil contamination problems have been found as a result of the application of FGD gypsum as a soil amendment. Likewise, no increased toxic element concentrations in plants growing in FGD gypsum-treated soils have been reported, except for molybdenum. In any case, the plant contents of Mo are not large enough to cause nutritional problems for grazing animals. In spite of such positive findings, the safe agricultural use of FGD gypsum cannot be guaranteed without assessing the risks associated with the different toxic elements occurring in this by-product. So far, the researches performed on this subject have paid no attention to fluoride. Recent studies carried out on the environmental characterisation of coal combustion by-products [16,17] have revealed critical leachable contents of F in FGD gypsum (close to 150 mg kg⁻¹), being the toxic element of greatest concern in this regard. Consequently, measures for the immobilisation of F leached from FGD gypsum have been investigated in order to minimise the risk of F dispersion into the environment when this by-product is disposed of [18–20].

Environment pollution with F may entail severe risks to mammals. Excessive intakes of F can lead to a well-defined disorder, skeletal fluorosis, which may affect the teeth and skeletal tissues, and secondarily the nervous system [21,22]. For this reason, F release into the environment has been a matter of great concern in the last decades. Thus, plant F uptake from areas receiving F

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inputs is focusing increasing attention [23–29] due to the risk of plant F accumulation and further transfer to the higher trophic levels of food chain. Different F sources have been studied in this respect, including irrigation waters, Al smelters, brick kilns and phosphorus fertilisers [23,30–33]. The atmospheric emissions of F and the use of irrigation waters polluted with this element have been proven to have a negative impact on vegetation, either limiting its growth or raising its F content up to limits not recommended for consumption. Fluoride contents in food plants vary between 0.1 and 11 mg kg⁻¹. Forage plants are likely to contain a bit more elevated amounts of F [34]. Much higher values have been reported in plants in F-polluted areas. Fluoride accumulation values in the range 29.8–65.4 mg kg⁻¹ have been found in food plants in the vicinity of brick fields [32]. Particularly high F concentrations (71–1330 mg kg⁻¹) have been reported in plant foliage in areas affected by the phosphate rock processing and Al-processing industries [31,34]. At such high F concentrations even F-tolerant plants can be injured. However, the greatest concern with increased F concentrations in plants is related to the toxicity to animals. Hence, it is essential to establish this aspect as regards the use of FGD gypsum as a soil ameliorant, which up to now remains unknown.

The main goals of this study are to evaluate the F accumulation by plants grown in acid soils amended with FGD gypsum and to assess the associated risks.

2. Materials and methods

2.1. FGD gypsum

FGD gypsum was collected from a Spanish coal-combustion power plant equipped with a wet limestone FGD scrubber. Sampling was performed on three consecutive days, obtaining three different samples that were mixed and homogenised to give a single sample. The mineralogical composition of FGD gypsum (Table 1) was determined by X-ray diffraction (XRD) using the reference intensity method (RIM). X-ray diffraction analysis was performed on a Philips 1710 diffractometer using the Cu K_α radiation. The FGD gypsum pH and electrical conductivity (EC) were analysed potentiometrically in a FGD gypsum paste saturated with water (Table 1). The chemical composition of FGD gypsum (Table 1) was determined following different procedures and/or analytical methods. For the determination of the total concentrations of most major and trace elements FGD gypsum was digested with aqua regia using a Milestone Ethos Plus microwave oven working at a temperature of 190 °C for 15 min. After digestion major elements were analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a Varian 720-ES unit, and trace elements were analysed by electrothermal atomic absorption spectrometry (ETAAS) using a Varian Spectra AA-220 instrument equipped with a GTA 110 graphite atomiser unit. The total Hg content in FGD gypsum was analysed using a mercury analyser (model DMA-80). The total F content in FGD gypsum was determined following the method described by Sager [35]. Accordingly, samples were fused with NaOH at 550 °C during 1 h, followed by dissolving the arisen residues by means of tiron (pyrocatechol-3,5-disulfonic acid, disodium salt). Fluoride analysis was performed by fluoride ion selective electrode (ISE) using a Thermo Orion ISE-meter (model 710). The leachable content of elements of environmental concern in FGD gypsum (Table 2) was determined according to the EN 12457-4 leaching standard [36]. Thus, samples underwent an agitation period of 24 h with deionised water on a vertical rotary shaker (10 rpm), using a liquid/solid ratio of 10 l kg⁻¹. Leachates derived from this process were analysed for As, Se, Sb, Cd, Cr, Cu, Ni, Pb, Zn, Ba, Mo by ETAAS, for Hg using a mercury analyser and for F by fluoride ISE after the addition of TISAB III as described by Agarwal et al. [37].

Table 1

Mineralogical and chemical characterisation of FGD gypsum (values are expressed as mean ± standard deviation of three replicates).

FGD gypsum	
Mineralogical composition	Gypsum, calcite (<5%)
pH	7.87 ± 0.19
EC (μS cm ⁻¹)	8450 ± 120
Major and trace element composition	
	wt.%
Al	0.106 ± 0.001
Ca	21.9 ± 0.2
Fe	0.080 ± 0.001
K	0.025 ± 0.001
Mg	0.317 ± 0.008
Mn	0.014 ± 0.001
Na	0.094 ± 0.004
P	0.006 ± 0.001
S	16.1 ± 0.1
	mg kg ⁻¹
As	1.81 ± 0.52
Ba	4.38 ± 0.04
Cd	0.06 ± 0.01
Cr	2.29 ± 0.18
Cu	0.78 ± 0.16
F	1419 ± 64
Hg	0.23 ± 0.02
Mo	0.19 ± 0.02
Ni	4.17 ± 0.45
Pb	1.09 ± 0.28
Sb	0.10 ± 0.03
Se	1.53 ± 0.42
Zn	3.53 ± 0.24

2.2. Soils

Two acid agricultural soils of different characteristics (Soil A and Soil B) from the central west region of Spain were selected to carry out this study. Soil A is a chromic luvisol with a loamy sand texture and Soil B is a gleyic acrisol with a sandy loam texture. Surface soils (0–20 cm depth) were sampled, then air-dried, and sieved through a 2-mm screen prior to subsequent characterisation. The main soil physicochemical properties (Table 3) were determined as follows: pH and EC were analysed potentiometrically in a soil paste saturated with water, exchangeable Al was obtained by extraction with potassium chloride following the procedure described by Mokolobate and Haynes [38], organic matter (OM) was derived by dichromate oxidation using the Tiurin method [39], and particle size distribution was analysed by the pipette method [40]. The

Table 2

Leached concentrations from FGD gypsum and leachable contents in FGD gypsum of elements of environmental concern (values are expressed as mean ± standard deviation of three replicates).

	FGD gypsum	
	mg l ⁻¹	mg kg ⁻¹
As	0.004 ± 0.001	0.04 ± 0.01
Ba	0.037 ± 0.003	0.37 ± 0.03
Cd	<0.001	<0.01
Cr	<0.001	<0.01
Cu	0.002 ± 0.001	0.02 ± 0.01
F	13.5 ± 1.1	135 ± 11
Hg	<0.001	<0.01
Mo	0.016 ± 0.002	0.16 ± 0.02
Ni	0.045 ± 0.005	0.45 ± 0.05
Pb	<0.001	<0.01
Sb	<0.001	<0.01
Se	0.018 ± 0.002	0.18 ± 0.02
Zn	0.029 ± 0.003	0.29 ± 0.03

Table 3
Physicochemical characterisation of soils (values are expressed as mean \pm standard deviation of three replicates).

	Soil A	Soil B
pH	4.40 \pm 0.03	4.67 \pm 0.05
EC ($\mu\text{S cm}^{-1}$)	375 \pm 20	100 \pm 10
F _{leachable} (mg kg ⁻¹)	4.94 \pm 0.42	6.79 \pm 0.66
Al _{exchangeable} (mg kg ⁻¹)	4.94 \pm 0.67	14.7 \pm 0.4
OM (%)	0.80 \pm 0.08	0.72 \pm 0.06
Sand (%)	87.7 \pm 3.3	76.4 \pm 2.5
Silt (%)	5.6 \pm 0.7	5.5 \pm 0.6
Clay (%)	6.7 \pm 0.8	18.1 \pm 1.4
Major and trace element composition		
	wt.%	
	Soil A	Soil B
Al	0.578 \pm 0.041	1.60 \pm 0.06
Ca	0.063 \pm 0.003	0.077 \pm 0.002
Fe	0.418 \pm 0.014	1.25 \pm 0.04
K	0.138 \pm 0.010	0.226 \pm 0.015
Mg	0.104 \pm 0.005	0.134 \pm 0.005
Mn	0.009 \pm 0.001	0.034 \pm 0.002
Na	0.076 \pm 0.006	0.089 \pm 0.006
P	0.045 \pm 0.001	0.031 \pm 0.002
S	0.018 \pm 0.001	0.014 \pm 0.001
	mg kg ⁻¹	
	Soil A	Soil B
As	1.90 \pm 0.18	5.28 \pm 0.37
Ba	26.7 \pm 1.4	76.2 \pm 3.5
Cd	0.09 \pm 0.03	0.17 \pm 0.05
Cr	5.18 \pm 0.10	14.9 \pm 0.4
Cu	4.81 \pm 0.09	10.1 \pm 0.4
F	106 \pm 7	138 \pm 11
Hg	0.03 \pm 0.01	0.05 \pm 0.01
Mo	0.65 \pm 0.12	1.62 \pm 0.19
Ni	2.66 \pm 0.48	11.7 \pm 0.4
Pb	8.60 \pm 1.87	19.0 \pm 1.1
Sb	0.10 \pm 0.03	0.07 \pm 0.02
Se	0.78 \pm 0.18	0.98 \pm 0.14
Zn	16.4 \pm 0.2	31.7 \pm 2.0

chemical composition of soils (Table 3) was determined following different procedures and/or analytical methods. For the determination of the total concentrations of most major and trace elements finely ground soil samples were digested with aqua regia following the aforementioned procedure. After digestion major elements and trace elements were analysed by ICP-AES and ETAAS, respectively. The total Hg content in soils was analysed using a mercury analyser. The total F content in soils was determined by the NaOH fusion method described by Sager [35], followed by the analysis of dissolved residues by fluoride ISE. The leachable content of F in soils (Table 3) was determined according to the EN 12457-4 leaching standard [36]. Leachates derived from this process were analysed for F by fluoride ISE after the addition of TISAB III as described by Agarwal et al. [37].

2.3. Phytotoxicity tests

A germination-elongation test was performed (in triplicate) to assess the phytotoxic effects of FGD gypsum leachates. Four different solutions were used in order to evaluate the toxicity range of FGD gypsum leachates. These were the leachate derived from FGD gypsum using the EN 12457-4 leaching standard [36] and three dilutions of this leachate (1/2, 1/5, 1/10), showing, respectively, F concentrations of 13.5, 6.8, 2.7 and 1.4 mg l⁻¹ and EC of 2770, 1770, 900 and 560 $\mu\text{S cm}^{-1}$. Although other elements of environmental concern were present in these solutions, their concentrations, even in the non-diluted leachate (Table 2), were low enough as to

not produce a significant phytotoxic effect. Ten seeds of two plant species, namely alfalfa (*Medicago sativa* L.) and ryegrass (*Lolium perenne* L.), were placed in Petri dishes on filter paper on which 2 ml of the mentioned solutions were added. The covered Petri dishes were incubated at 25 °C during 5 days in the dark. The number of germinated seeds and the average sum of the root lengths were recorded to calculate a germination index (GI) as follows [41]:

$$GI = \frac{GL}{G_c L_c} \times 100 \quad (1)$$

where G and G_c are the number of germinated seeds in the sample and the control, respectively, and L and L_c are the average sum of root lengths in the sample and the control, respectively. Deionised water was used as solution in the control.

2.4. Plant growth experiments

Plant growth experiments were conducted in soil pots in a greenhouse maintained between 18 \pm 2 °C (minimum (night) temperature) and 28 \pm 2 °C (maximum (day) temperature). Soils were fertilised with 50 mg kg⁻¹ N and 143 mg kg⁻¹ P as NH₄NO₃ and KH₂PO₄, respectively. This fertilisation was applied twice, at the beginning and after the first-half of the experimentation period. Soils were thoroughly mixed with different FGD gypsum doses (0, 1, 2, 5 and 10%). All these experiments were carried out in triplicate for each FGD gypsum treatment. Deionised water was incorporated to soil mixtures to reach the 60–70% of their water holding capacity (this condition was kept throughout the experimentation period). After 7 days of equilibration, either 10 seeds of alfalfa or 40 seeds of ryegrass were sown in each pot. Alfalfa plants were thinned to 5 per pot and ryegrass plants to 20 a few days after emergence. All the plants were harvested 90 days after sowing. Plants were separated into roots and above-ground tissues. The different plant sections were washed with freshwater, and then rinsed with deionised water in order to remove soil particles. Afterwards, plant samples were dried at 70 °C for 24 h, weighed and powdered for analysis. The plant F content was determined by the NaOH fusion method [35], followed by the analysis of dissolved residues by fluoride ISE. The accuracy of the fusion procedure and analytical method was checked with the standard reference material SRM 2695, showing analytical errors <10%. Soil samples were collected from each pot after the plant harvest, and subjected to subsequent characterisation. The analysis of soil pH was performed potentiometrically in a soil paste saturated with water. The total soluble F content, the free ionic F content and the soluble Ca content in soils were derived from soil leachates obtained according to the EN 12457-4 leaching standard [36]. The total F concentration in leachates was analysed by fluoride ISE after the addition of TISAB III as described by Agarwal et al. [37], and the free ionic F concentration was analysed by fluoride ISE after ionic strength and pH sample conditioning following the method of Agarwal et al. [37]. The Ca analysis in leachates was performed by ICP-AES.

3. Results and discussion

3.1. Phytotoxicity tests

Germination indices for alfalfa and ryegrass seeds are given in Fig. 1. The seed germination appeared quite different for the two studied species. The diverse FGD gypsum leachates hardly showed inhibitory effect on alfalfa seed germination. The corresponding GI showed values between 88 and 96%. Hence, none of the FGD gypsum leachates evidenced phytotoxicity for alfalfa, as would be indicated by GI values under 80% [41]. However, the two most concentrated solutions importantly inhibited the germination of ryegrass seeds. The corresponding GI displayed values

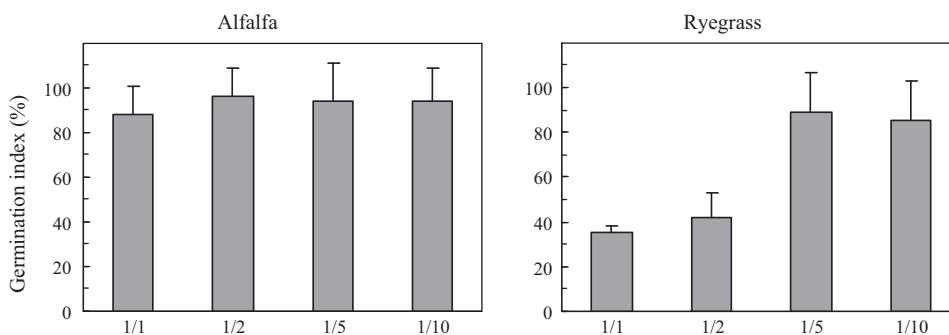


Fig. 1. Germination index of plant seeds under different FGD gypsum leachates: leachate from the EN 12457-4 leaching standard (1/1) and different dilutions of the EN 12457-4 leachate (1/2, 1/5, 1/10). (Error bars indicate standard deviation of the mean of three replicates.)

about 40%. Therefore, the ryegrass species appeared to be much more sensitive to FGD gypsum leachates than alfalfa. The germination inhibition showed by the most concentrated FGD gypsum leachates could be attributed to their higher F concentrations and also to their relatively high salinity. High salinity has been also suggested as a likely factor contributing to the ryegrass seed germination decrease found under F-containing wastewaters from the phosphate fertilizer industry [33]. Anyway, one must bear in mind that when FGD gypsum is applied to soil there is an important dilution effect. Moreover, the leachable F supplied by FGD gypsum can be immobilised in some extent by sorption processes on soil surfaces, mainly on variable charge surfaces. On the other hand, among the main mechanisms proposed to reduce the Al toxicity in acid soils by the use of gypsum and gypsum-based products is the precipitation of low soluble forms of Al, including Al-hydroxy and Al-hydroxy-sulphate compounds [12,42–45]. These compounds can act as effective immobilising systems for F due to sorption or incorporation in the Al precipitation by substitution for hydroxyl groups.

3.2. Plant growth experiments

3.2.1. Plant F contents

No visible symptoms of F toxicity occurred at any of the FGD gypsum treatments applied to soils. Throughout the growing period, either alfalfa or ryegrass did not show the typical tip or marginal leaf necrosis (“tip-burn”) manifested by plants when their accumulated F contents surpass the tolerable concentrations of F. There is a great variability in the toxic threshold concentrations of F in plants. Susceptible plants can be injured by foliar F contents between 20 and 150 mg kg⁻¹, whereas highly tolerant plants do not exhibit injury at about 500 mg kg⁻¹ [46]. In this regard, concentrations up to 2745 mg kg⁻¹ have been reported in the foliage of perennial ryegrass grown in fluorspar waste without showing visible symptoms of phytotoxicity [47]. Likewise, no chlorosis or necrosis was found in alfalfa plants with foliar F contents up to 500 mg kg⁻¹ as a result of fumigation with F during a 10-year period [48].

Fig. 2 shows the F contents accumulated in the aerial parts of alfalfa and ryegrass plants grown in the acid soils treated with

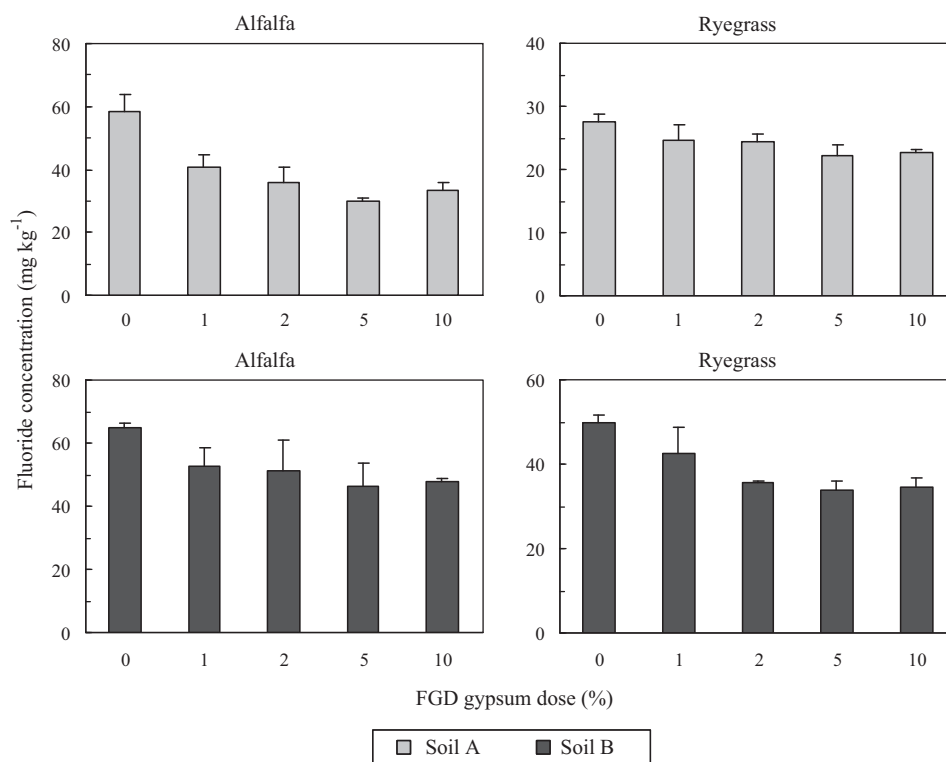


Fig. 2. Fluoride concentration in the above-ground tissues of plant species grown in FGD gypsum-amended soils. (Error bars indicate standard deviation of the mean of three replicates.)

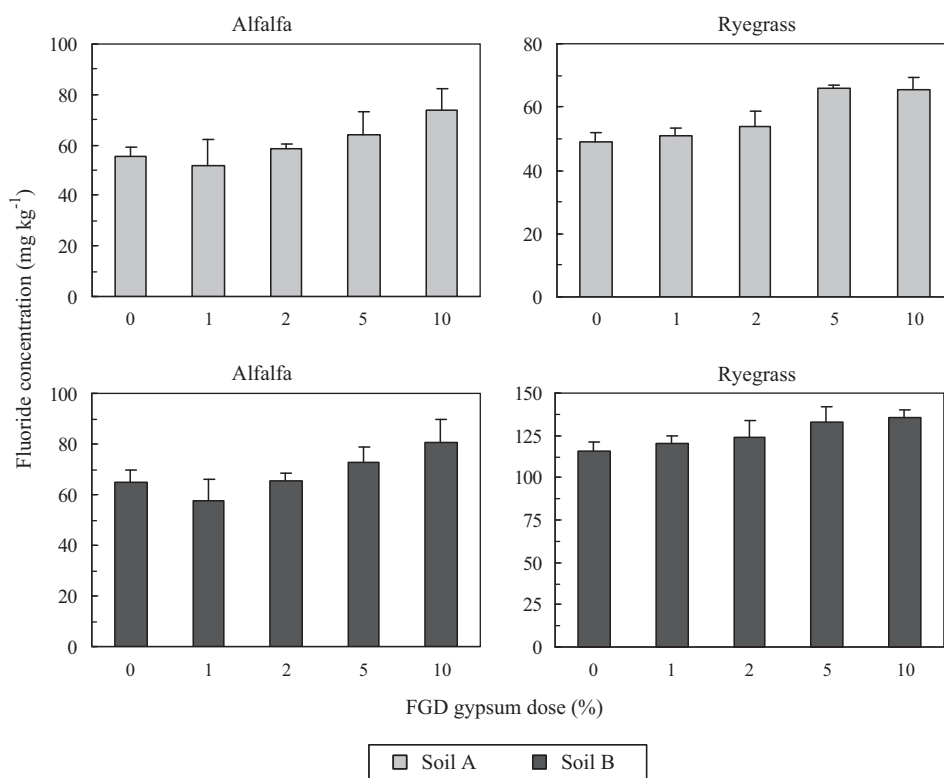


Fig. 3. Fluoride concentration in the roots of plant species grown in FGD gypsum-amended soils. (Error bars indicate standard deviation of the mean of three replicates.)

different FGD gypsum doses (0–10%). The F concentrations in the above-ground tissues of alfalfa were comprised in the ranges 30–58 mg kg⁻¹ and 46–65 mg kg⁻¹ when growing in Soil A and Soil B, respectively, whereas those of ryegrass varied from 22 to 28 mg kg⁻¹ in Soil A and from 34 to 50 mg kg⁻¹ in Soil B. These concentrations surpass the typical F content in plant tissues which ranges from 2 to 20 mg kg⁻¹ [49]. Anyway, such concentrations are far below the tolerable limits of F reported for these plant species. Concerning the toxic threshold values of F in fodder, opinions vary. Nonetheless, it has been proven that a daily intake of forage with F concentrations >100 mg kg⁻¹ can lead to fluorosis [50]. On the other hand, the maximum F content allowed in animal feed, so as to reduce its presence in the food chain, is established at 150 mg kg⁻¹ by the Directive 2002/32/EC on undesirable substances in animal feed [51]. The F concentrations found in the alfalfa and ryegrass plants grown in FGD gypsum treated-soils were below these values. Moreover, F contents were higher in plants grown in not amended soils, and decreased progressively with the FGD gypsum addition up to a certain application rate (5%) from which F contents in plants stayed more or less constant or increased slightly. These decreases attained levels up to 48% and 29% in alfalfa plants and up to 19% and 32% in ryegrass plants when growing, respectively, in Soil A and Soil B. Therefore, the application of FGD gypsum as an acid soil ameliorant at the suitable dose, rather than representing a F source to plants, limits the accumulation of F in plant aerial tissues.

Fig. 3 illustrates the F contents accumulated in the roots of alfalfa and ryegrass plants grown in the acid soils treated with different FGD gypsum doses (0–10%). The F concentrations in the roots of alfalfa were included in the ranges 52–74 mg kg⁻¹ and 58–81 mg kg⁻¹ when growing in Soil A and Soil B, respectively, whereas those of ryegrass varied from 49 to 66 mg kg⁻¹ in Soil A and from 115 to 135 mg kg⁻¹ in Soil B. An increasing trend is observed in the F concentrations of plant roots with the FGD gypsum addition to soils. Such increases attained levels up to 33% and 25% in alfalfa plants and up to 35% and 17% in ryegrass plants

when growing, respectively, in Soil A and Soil B. Plant roots showed higher F contents than plant aerial parts, except for alfalfa growing in not amended soils which accumulated similar F concentrations throughout the plant. This means relatively low translocation factor values (between 0.2 and 1), especially when soils received the highest FGD gypsum doses (5 and 10%). In such cases root F contents were the highest and F contents in the above-ground plant tissues were the lowest.

3.2.2. Plant biomass

Fig. 4 shows the biomass of aerial parts and roots of alfalfa and ryegrass plants grown in the acid soils treated with different FGD gypsum doses (0–10%). A raising trend is observed in the biomass of plants with the FGD gypsum addition to soils. These increases resulted higher for plants growing in Soil B than for those growing in Soil A. At the highest FGD gypsum dose (10%), there was a biomass enhancement of about 100% or higher when Soil B was involved, whereas biomass increases were about 25–50% when Soil A was implied. In general, higher biomass raises were found for roots. In acid soils high bioavailable Al contents inhibit root growth and nutrient uptake. With the increasing FGD gypsum dose the soil pH raised (Table 4), entailing a progressive decrease in Al bioavailability. The higher exchangeable Al content shown by Soil B could explain the greater biomass increases experienced by plants growing in Soil B. It is important to note that the increased plant growth with the FGD gypsum application rate has a dilution effect on the F accumulated in the above-ground plant tissues.

3.2.3. Relating plant F concentrations to soil parameters

The increased F concentrations found in the aerial parts of plants grown in either amended or not amended soils do not respond to elevated total contents of F in soils. Common concentrations for most soils seem to range from 150 to 400 mg kg⁻¹, although the overall variation is much broader [46]. The total F contents of studied soils (106 and 138 mg kg⁻¹ in Soil A and Soil B, respectively)

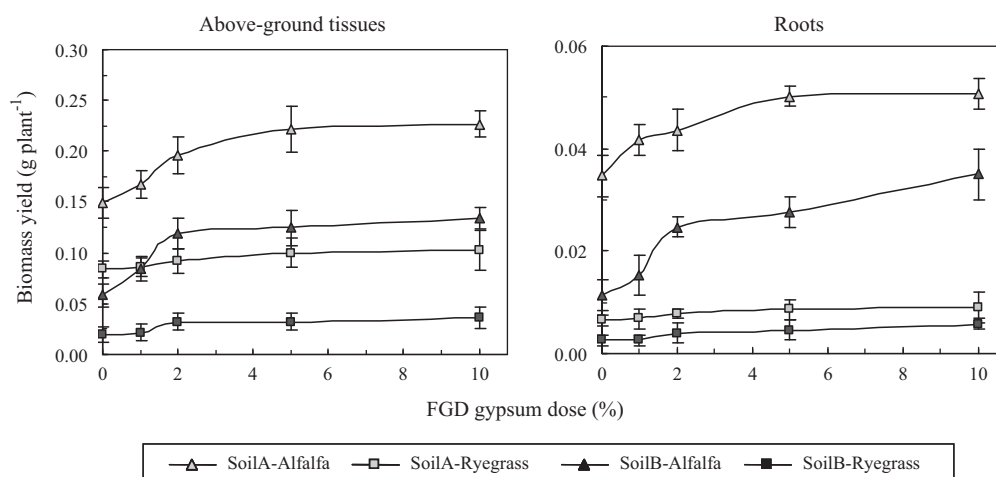


Fig. 4. Biomass yield of plant species grown in FGD gypsum-amended soils. (Error bars indicate standard deviation of the mean of three replicates.)

were below this range. This is in agreement with their textural properties; the lowest F concentrations are found in sandy soils. Even when soils were amended with the highest FGD gypsum dose (10%) the resulting total F contents (225 and 254 mg kg⁻¹ for amended Soil A and amended Soil B, respectively) stayed within the typical F range found in uncontaminated soils. Therefore, the total F content of studied soils cannot be considered critical. Moreover, generally, total F contents in soils do not correlate well with F uptake by plants, being soluble F a better indicator of F phytoavailability [52].

In normal soils soluble F is low, only 0.05% of the total F [24,32]. However, in acid soils the solubility of F increases, which facilitates its uptake by plants. The total soluble F content of soils after the plant growing period (Table 4) showed the greatest values when soils were not amended and when amended with the highest FGD gypsum dose (10%). Differently, the free ionic F content of soils (Table 4) showed an increasing trend with the FGD gypsum application rate, from concentrations about 3–4 mg kg⁻¹ up to values about 6–8 mg kg⁻¹. Anyway, neither total soluble F contents of soils nor free ionic F contents of soils appeared to be correlated with F concentrations accumulated in plant aerial parts. Nevertheless, such plant concentrations seemed to correlate positively with sol-

uble F content of soils not present as free ionic F, and negatively with soil pH.

In soil solutions of neutral to alkaline pH, F exits predominantly as the free F ion [53,54]. At slightly acid pH (<6) F is predominantly complexed with Al, whereas with decreasing solution pH the proportion of HF increases considerably [52–55]. The mobility of F in soils is variable and highly controlled by pH and sorption processes on inorganic soil constituents [56,57], with freshly precipitated Al hydroxide showing the highest F sorption capacity [58]. The mobility of F usually increases at pH below 5 and above 6. The great solubility of F under acidic conditions is explained by the formation of Al–F complexes, and under alkaline conditions by the desorption of free F ion as a result of repulsion by the negatively charged surfaces [54]. Aluminium–fluoride complexes are more easily taken up by plant roots than the free F ion due to anion exclusion by negatively charged cell walls, and HF is taken up more readily than Al–F species due to its easy diffusion across the cell membrane [52,59]. Taking into account these considerations and the pH increase experienced by soils (from values close to 4 up to values about 6) with the FGD gypsum application rate (Table 4), the accumulation trend of F in plant aerial parts could be explained. The decreasing accumulation of F in such plant tissues with the FGD gypsum application

Table 4
pH, total soluble F content, free ionic F content and soluble Ca content in FGD gypsum-amended soils corresponding to plant growth experiments (values are expressed as mean ± standard deviation of three replicates).

Soil	Plant	FGD gypsum dose (%)	pH	Total soluble F content (mg kg ⁻¹)	Free ionic F content (mg kg ⁻¹)	Soluble Ca content (mg kg ⁻¹)
Soil A	Alfalfa	0	3.46 ± 0.03	8.37 ± 0.56	3.96 ± 0.82	154 ± 20
		1	4.32 ± 0.06	6.12 ± 0.43	3.92 ± 0.76	1651 ± 137
		2	5.08 ± 0.08	5.38 ± 0.08	3.95 ± 0.06	3236 ± 283
		5	5.40 ± 0.05	5.31 ± 0.08	4.49 ± 0.08	6024 ± 161
		10	5.65 ± 0.04	6.25 ± 0.22	5.94 ± 0.13	6094 ± 153
	Ryegrass	0	3.75 ± 0.10	4.75 ± 0.30	3.38 ± 0.40	58 ± 13
		1	4.42 ± 0.02	4.16 ± 0.31	3.63 ± 0.12	1558 ± 191
		2	5.19 ± 0.03	3.83 ± 0.01	3.70 ± 0.13	3390 ± 299
		5	5.59 ± 0.06	4.43 ± 0.08	4.42 ± 0.20	6210 ± 27
		10	5.80 ± 0.06	6.67 ± 0.49	6.69 ± 0.55	6189 ± 54
Soil B	Alfalfa	0	3.74 ± 0.11	10.0 ± 0.78	4.19 ± 0.49	166 ± 17
		1	4.30 ± 0.08	7.41 ± 0.60	4.17 ± 0.14	2549 ± 261
		2	4.97 ± 0.04	6.44 ± 0.22	4.14 ± 0.06	4789 ± 421
		5	5.75 ± 0.06	7.32 ± 0.38	5.51 ± 0.35	6402 ± 210
		10	6.06 ± 0.04	9.95 ± 0.24	7.55 ± 0.24	6480 ± 207
	Ryegrass	0	3.98 ± 0.17	6.81 ± 0.81	3.50 ± 0.44	38 ± 6
		1	4.55 ± 0.03	5.88 ± 0.23	3.63 ± 0.17	1588 ± 90
		2	5.27 ± 0.11	5.65 ± 0.10	3.87 ± 0.13	4770 ± 409
		5	5.95 ± 0.07	7.24 ± 0.13	5.37 ± 0.10	6377 ± 146
		10	6.16 ± 0.02	9.24 ± 0.46	7.57 ± 0.81	6495 ± 128

Table 5

Correlation coefficient and significance level of correlations between F concentrations in plant aerial parts and different soil parameters.

	R		
	pH	[Soluble Ca]	[Total soluble F] – [free ionic F]
Soil A-Alfalfa	0.9484 ($p < 0.02$)	0.8858 ($p < 0.05$)	0.9702 ($p < 0.01$)
Soil A-Ryegrass	0.9476 ($p < 0.02$)	0.9504 ($p < 0.02$)	0.9534 ($p < 0.02$)
Soil B-Alfalfa	0.8946 ($p < 0.05$)	0.9532 ($p < 0.02$)	0.9829 ($p < 0.01$)
Soil B-Ryegrass	0.9499 ($p < 0.02$)	0.9714 ($p < 0.01$)	0.9451 ($p < 0.02$)

rate is in agreement with the pH raise experienced by soils and with the concomitant progressive decrease of Al–F complexes.

The soluble Ca content in soils (Table 4) increased sharply with the addition of FGD gypsum, from values about 50–150 mg kg⁻¹ up to values comprised between 6000 and 6500 mg kg⁻¹. The latter concentrations correspond to FGD gypsum additions of 5 and 10% for which amended soils showed similar values. Soluble Ca contents seemed to keep an inverse correlation with the F concentrations found in the above-ground tissues of alfalfa and ryegrass plants. Thus, these plant F concentrations showed to decrease gradually with the increasing soluble Ca contents in soils, pointing out the important role that must be played by Ca supplied by FGD gypsum on F uptake and translocation. In this regard, it has been reported that the addition of soluble Ca results in the formation of CaF₂ coatings on root surfaces, physically limiting the uptake of F, while if F enters the plant then it interferes with Ca deposition and partitioning within the plant [59]. This is in agreement with the generally higher F concentrations found in the roots of alfalfa and ryegrass as compared to those in the corresponding above-ground tissues. Moreover, the reduced F uptake following Ca application should not be simply due to the aforementioned mechanism. It has been suggested that Ca influences the properties of cell wall or the membrane permeability, causing a F passage decrease [60].

Statistical tests were performed to establish the correlation between F concentrations in plant aerial parts and different soil parameters (pH, soluble Ca content, total soluble F content, free ionic F content and total soluble F content minus free ionic F content). As indicated, high correlations ($R > 0.88$) were found between F concentrations in plant aerial tissues and pH, soluble Ca content and total soluble F content minus free ionic F content. The corresponding statistical fits are indicated in Table 5.

4. Conclusions

No evident symptoms of F phytotoxicity occurred on the studied plant species at any of the FGD gypsum treatments applied to acid soils (0–10%). The application of FGD gypsum as an acid soil ameliorant, rather than representing a F source to plants, limits its accumulation in plant aerial parts. Fluoride concentrations in plant aerial parts showed a high negative correlation with pH and soluble Ca content, and a high positive correlation with soluble F content, excluding that present as free ionic F. This behaviour implies an important reduction of health risks for animals feeding on plants growing in acid soils when amended with this by-product.

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