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Sulfur metabolism in higher plants: potential for phytoremediation

Wilfried H.O. Ernst
Department of Ecology and Ecotoxicology, Faculty of Biology, Vrije Universiteit, De Boelelaan 1087, 1081 HV Amsterdam, The Netherlands

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Abstract

Sulfur is a major nutrient for all organisms. Plant species have a high biodiversity in uptake, metabolization and accumulation of sulfur so that there are potentials to use plants for phytoremediation of sulfur-enriched sites. A survey of soils enriched with sulfur either naturally or by human activities shows that a surplus of sulfur is mostly accompanied with a surplus of other chemical elements which may limit phytoremediation because these co-occurring elements are more toxic to plants than sulfur. In addition, the accumulation of the other elements makes the plant material (phyto-extraction) less suitable for the use as fodder and for human consumption.

Introduction

Clean air and clean soil legislation demands a cleaning-up of contaminated sites and has stimulated scientific and technical developments which can be summarized under key words like bioremediation and biodegradation. In the case of organic compounds it is possible to degrade them to basic elements (National Research Council 1993, Alexander 1994) resulting in the biodegradation paradigm: 'use microorganisms to degrade pollutants *in situ*' (Eddington 1994) and the environmental problem is solved. Biodegradation as 'the biologically catalized reduction in complexity of chemicals' (Alexander 1994, p.3) is restricted to organic compounds. In contrast to organics, inorganic contaminants, even if bound to organic compounds, do not give a possibility for biodegradation. Therefore, other approaches are developed ranging from physico-chemical extraction processes to biological methods.

Due to the high costs of contaminant extraction with physico-chemical methods *in situ* or *ex situ* and the difficulties in a recultivation of chemically cleaned soils (Van Gestel et al. 1992) the emphasis of management of contaminated soils has switched to phytoremediation, i.e. the decrease of the bio-availability of the contaminant *in situ* to concentrations below the limits established as safe or acceptable by regulatory agencies; this definition is similar to that of bioremediation by Alexander (1994, p. 248). Phytoremediation is mainly discussed in relation to the removal of heavy metals from the environment by plants (Salt et al. 1995) ranging from phyto-stabilization of a site up to immobilization and phyto-extraction of the element in surplus. Phyto-stabilization of a contaminated site does only revegetate the site, but it does not remove the contaminant from the site. At the revegetated site the mobility of the elements to the surroundings and the groundwater is diminished without changing the toxicity of the contaminants at the site to non-adapted organisms (Ernst 1981, 1995). Therefore, phyto-stabilization can only be effectuated by genotypes of plant species which have sufficient resistance to survive the adverse environmental situation and keep the area green (Ernst 1981). Immobilization, especially of heavy metals, has been realized by the application of materials, e.g. beringite and other zeolites, hydrous oxides of iron and manganese which diminish the bio-availability of the elements (Gworek 1992; Mench et al. 1994; Vangronsveld et al. 1995) or microorganisms (Summers 1992). Phyto-extraction is an *in situ* removal of a chemical element from the soil by plants. Effective phyto-extraction requires plants which possess a high uptake capacity for the chemical element

Table 1. Uptake kinetics of sulfate and other nutrients by barley roots. Data are calculated from Nissen (1973) and Vange et al. (1974)

Nutrient	V_{max} (μmol/g fresh wt root/hr)	Reference
sulfate	0.07 – 0.20	Vange et al. 1974
phosphate	1.17 – 3.68	Vange et al. 1974
manganese	1.30 – 2.44	Nissen 1973
potassium	2.65 – 14.20	Nissen 1973
chloride	4.10 – 12.20	Nissen 1973
sodium	5.48 – 9.00	Nissen 1973

and a high translocation rate of the element from roots to shoots or to other harvestable parts, and which produce a high biomass yield in a relatively short time (Banuelos et al. 1993; Ernst 1998). By this uptake and accumulation process the concentration of the contaminant can be diminished to a biologically acceptable level (Baker et al. 1995; Salt et al. 1995; Ernst 1996; Ebbs et al. 1997; Felix 1997). Dependent on the degree of contamination the process requires decades to centuries to be completed. After phyto-extraction the loaded plant material has to be further processed to extract the elements and to condense them for a reuse in the chemical industry, i.e. the material cycle needs to be optimized (Ayres 1992). At present, phyto-extraction is in practice nothing more than the transfer of the contaminant from the clean-up site to another storage site (Ernst 1995, 1998) although in principal a well designed procedure may result even in phyto-restoration, i.e. an attempt 'to put back exactly what was there prior to the disturbance' (Bradshaw 1995).

In this contribution I will elaborate on the potential of higher plants to phyto-extract sulfur from soils enriched with sulfur with or without the co-occurrence of other elements in excess.

Sulfur sources for higher plants

Realization of an effective phyto-extraction demands a good knowledge of the physiology of the plant species which are used for the process. Sulfur is a major, essential nutrient for all living organisms. The effectiveness of phyto-extraction for remediation of sulfur-enriched soils is highly dependent on the availability of sulfur for the plant. The most important source of sulfur for higher plants is sulfate which can be taken up by roots (Marschner 1995). On the contrary, reduced sulfur in the rhizosphere is phytotoxic. As far as sulfur is bound to organic compounds in the soil, it has to be mineralized by microorganisms (Cooper 1972) to become available as sulfate to higher plants.

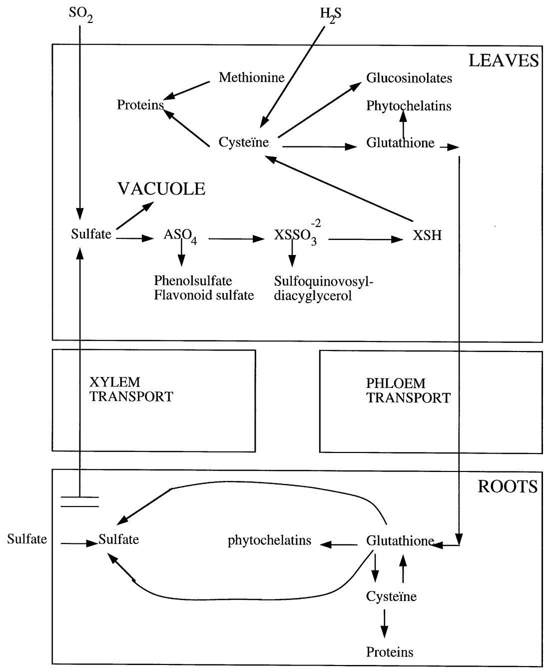

Figure 1. Sulfur uptake and metabolism in higher plants; not all plants can realize all secondary sulfur compounds. Based on Rennenberg & Herschbach (1995), Kleppinger-Sparace et al. (1990) and Schnug (1993).

To a lesser degree volatile sulfur compounds such as carbondisulfide (CS_2), carbonylsulfide (COS), hydrogen sulfide (H_2S), methylmercaptan (CH_3SH), and sulfur dioxide (SO_2) can be taken up by leaves (Goldan et al. 1988, Bosma et al. 1990, Van der Kooij et al. 1997); the magnitude of the flux of gaseous sulfur compounds into plant leaves has been ranked in the following order: $SO_2 > H_2S > COS > CH_3SH > CS_2$ (Taylor et al. 1983).

Sulfur metabolism in higher plants

Sulfate is actively taken up by root cells. In barley roots the uptake rate (V_{max}) of sulfate is the lowest one (Vange et al. 1974) of all other macronutrients and micronutrients (Table 1). Sulfate is passed through the root epidermis and cortex up to the xylem and translocated into the shoot and the leaves (Figure 1). In the leaves, sulfate is (1) activated in the cell, (2) the activated sulfate is transfered to a not-yet identified carrier (Schiff et al. 1993), and (3) finally is reduced to the level of sulfide, i.e. the assimilatory sulfate reduction (Brunold 1990). Reduced sulfate is necessary for the synthesis of the sulfur-containing amino acids cysteine and methionine, the important biological tripeptide glutathione, and finally of proteins; it is also necessary for the biosynthesis of sulfolipids, which are important components of biomembranes (Kleppinger-Sparace et al. 1990). The concentration of all these primary sulfur-compounds in the plant is not able to rise essentially with an increase of external sulfur supply.

Enrichment of the sulfur content of plants can be achieved in another way. As soon as there is a surplus of activated sulfate in the cell it can be translocated into the vacuole where it accumulates as sulfate (Ernst 1997), flavonoid sulfate (Barron et al. 1988) and phenol sulfate (Sheahan 1996) with increasing leaf age (Ernst 1997) because in contrast to accumulated nitrate (Janiesch 1973) sulfate can not be remobilized from the vacuole. Therefore this type of sulfate accumulation can play an important role in phyto-extraction of sulfur (Ernst 1997). Another option of increasing the sulfur content of plants is the synthesis of sulfur-containing secondary metabolites which are, however, restricted to a few plant families and taxa (Schnug 1993).

The general pattern of sulfur metabolism of higher plants is modified by the sulfur supply of the environment and by the biodiversity of the sulfur demands among plants. During the evolution of higher plants the sulfur requirement by plants has resulted in species-specific and sometimes even family-specific demands. Plants with a sulfur content in their leaves ranging from 2.5 to 8.2% in dry matter have been classified as thiophores (Duvigneaud & Denayer-De Smet 1968). Herbs, not belonging to the family Brassicaceae and Liliaceae, may extract per annuum from the soil less than 10 kg S ha^{-1}, cereals and wild grasses 10 – 15 kg S ha^{-1}, legumes and cruciferous crops 20 – 45 kg S ha^{-1} (Jolivet 1993, Schachtschabel et al. 1992). Members of the family Brassicaceae (Brussels sprout, cabbage, cauliflower, radish, rape seed, turnip) and of the taxon Allium (onion, garlic, leek) are the most sulfur-demanding plants and therefore excellent candidates for phyto-extraction. The enhanced sulfur demand of the members of the Brassicaceae is due to the occurrence of glucosinolates which have an array of function in plants (Ernst 1990, Schnug 1993) and play an important role in the economic use of these plants (Schnug 1997). Glucosinolates are accumulated in the vacuoles of the cell and have been detected in all plant parts, from roots to seeds (Halkier & Du, 1997). The sulfur demand of the genus Allium, e.g. onion (Allium cepa), leek (Allium porrum), scallion (Allium fistulosum), garlic (Allium ampeloprasum), shallot (Allium ascalonicum), chive (Allium schoenoprasum) and Chinese chive (Allium tuberosum) is related to the synthesis of thiosulfinates (Block et al. 1992). In the case of onions the content of thiosulfinates increased linearly with the sulfur supply (Randle et al. 1994) which makes this species a good candidate for desulfurization of a sulfur-enriched soil.

Higher plants do not only take up sulfur from the environment, but can also release sulfur compounds into the atmosphere, not only the above-mentioned volatile sulfur compounds (Schröder 1993), but also methanethiol (Saini et al. 1995) and in coastal salt marshes dimethyl sulfide accounting for the greatest part of the biogenic sulfur flux to the atmosphere (Dacey et al. 1987). At a phytoremediation site with a surplus of sulfur such emissions may cause local air pollution and have to be considered in designing phyto-extraction procedures.

Sulfur-enriched soils and substrates

Sulfur-enriched soils may be the result of natural processes like soils in the vicinity of volcanoes, S/CO_2 vents and lignite burns, saline soils, heavy metal soils (cf. Ernst 1997) and acid sulfate soils (Palko & Weppling 1994; Bronswijk et al. 1993; Ahmed & Dent 1997) or the result of man-made processes like soils in areas with high sulfur deposition as a result from SO_2-emission, tailings of coal and ore mines, and piles of flue gas desulfurization (FGD) by-products. In addition to high sulfur concentrations, these soils and substrates may be enriched with elements which are more hazardous to plant growth than sulfur itself and thus hamper phytoremediation.

In the natural situation sulfate does not accumulate in soils of the humid climatic zones. Due to leaching the annual loss of sulfate is estimated between 20 and 120 kg S ha^{-1} yr^{-1} (Schachtschabel et al. 1992). Under arid conditions, however, sulfate can accumulate in the surface soil and finally precipitate as *gypsum.* In the case of gypsiferous soils which cover 100 million ha in the world (Verheye & Boyadgiev 1997) two major nutrients, i.e. calcium and sulfate occur simultaneously in excess which is demonstrated by the element concentration in plants (Table 2). A

Table 2. Element concentration in leaves of plants on sulfur-enriched soils. Data are from (1) Heinze et al. (1982), (2) Duvigneaud & Denayer-De Smet (1968), (3) Denayer et al. (1968), (4) Ernst (1978), and (5) Rodin (1975)

Site	Plant species	K	Na	Ca	Mg	S	Cl
				(mmol kg^{-1})			
Gypsum soils							
Rottleben/D[1]	Gypsophila fastigiata	338	n.d.	1437	218	150	n.d.
Bujaraloz/E[2]	Gypsophila hispanica	255	26	1949	781	372	<1
Saragossa/E[2]	Gypsophila hispanica	176	17	2071	617	1684	<1
Saragossa/E[2]	Salicornia herbacea	460	418	157	535	343	3640
Saline soils							
Yser/B[3]	Salicornia herbacea	358	6870	132	366	225	8870
Schiermon-	Salicornia brachystachya	399	3260	175	339	254	3500
nikoog/NL[4]	Suaeda maritima	610	4350	63	310	185	4320
Gobi desert[5]	Anabasis salsa	261	3850	422	275	80	838
	Haloxylon ammonchin	1360	2690	818	847	87	195

high calcium concentration in the plant may be nicely regulated either by precipitation in cell walls or by accumulation in vacuoles as organic compounds such as Ca-oxalates, but never as Ca-sulfates (Kinzel 1982) whereas sulfates are often accumulated as flavone sulfates (for a review: Ernst 1990). Nevertheless the very specific vegetation of gypsum-bearing soils indicates that there is a physiological problem to cope simultaneously with a surplus of calcium and sulfate which demands specific adaptations. Those plants which can survive on gypsiferous soils under semi-arid conditions accumulate to more than 30 g S kg^{-1}, more than 50% of the sulfur as sulfate (Al-Ani et al. 1971, Boukhris & Lossaint 1972). Plants on gypsiferous soils under humid conditions have sulfur contents not surpassing 11 g S kg^{-1} dry mass, more than 60% is present as sulfate (Heinze et al. 1982).

In *saline soils* the major problem is not the surplus of sulfur, but that of sodium which is only a minor nutrient in several, but not all higher plants (Marschner 1995). Plants growing on saline soils primarily have to cope with the imbalance between potassium and sodium in the soil solution and consequently in their metabolisms (Table 2). Wild plants of these soils have a high sodium tolerance by a preference of potassium uptake compared to the K/Na ratio in the soil solution over sodium uptake compared to the K/Na ratio in the soil solution and by storage of Na in the vacuole (Albert 1982), whereas the surplus of sulfur can be regulated by storage in the vacuole or by volatilization (Albert 1982). Some of these halophytic plant species regulate a surplus of elements by excretion of salts via salt glands; during rains the salt containing a variety of chemical elements (Ernst 1974) is washed from the leaves and returns to the soil. Therefore, such plant species are not very useful for a desulfurization of soils. To overcome the salinity problem in agriculture, crops are nowadays selected by breeders for salt tolerance taking advantage from the genome of wild plants (Munns et al., 1995; Dubcovsky et al. 1996) and may be helpful in soil amelioration, but only marginally in desulfurization.

Plants on *heavy metal soils* have evolved very metal-specific resistance mechanisms (Ernst 1997) which enable them not only to survive on these soils but to accumulate or even hyperaccumulate some of these metals (Ernst 1974, Baker & Brooks 1989, Krämer et al. 1997). The heavy metal content in the soil is often more decisive for the success of phytoremediation than the sulfur content. Therefore the limits of phyto-extraction of sulfur from heavy metal soils will mostly be set by the metal resistance of the plants. Metal resistance is based on a rapid detoxification of the metal in the cytosol and its compartmentation into the vacuoles. To this rule is only one exception: On copper mine tailings in Chile the sulfate content of the soil is so high that the two tested woody species suffered more from the excess of sulfate than the excess of copper (Ginocchio 1996).

Acid sulfate soils estimated to 12 million ha in the world (Bronswijk et al. 1993) are not only rich in sulfate, but more important is the high content of aluminium, iron, manganese and zinc (Palko & Weppling 1994; Quang et al. 1995). Therefore in acidic soils not the soil pH *per se*, but the surplus of micronutrients and aluminium and the imbalance in action/anion uptake is deregulating the excretion of H^+ and $HCO^-{}_3$ by plant roots, and thus hampering plant growth (Marschner 1995).

Anthropogenic sulfate soils occur in the vicinity of industrial SO_2 emission sources; most plants, however, suffer more from the high sulfur dioxide concentration in the atmosphere (Rennenberg & Polle 1994) than from the increased sulfate of the soil, although the latter may also exceed critical concentrations (Mikula 1995). On the other hand, in highly industrialised countries crop plants have relied for their sulfur supply on atmospheric sulfur for decennia (Thomas et al. 1950) because this sulfur was free of charge for farmers as long as the gaseous SO_2 did not injure the crop. Not only crops, but other very sulfur-demanding higher plants and their associated herbivores were stimulated by additional atmospheric sulfur supply in growth and extension of the population size (Ernst 1993) because they could make profit from the increased ambient SO_2 due to their SO_2-resistance (Van der Kooij et al. 1997). In addition, the increased SO_2 concentration has stimulated the selection of SO_2 resistance in plants (Taylor & Murdy 1975, Ernst et al. 1985). Such a resistance protects the leaves of a plant from the direct impact of SO_2 on biomembranes and enzymes, and enhances the metabolic incorporation of SO_2 into cellular compounds (Taylor & Tingey 1983) and the storage of sulfate in the vacuoles. Due to the signal function of the sulfur status in the leaves as feed back for the sulfate uptake by roots, sulfur uptake from the soil is diminished. Clean air legislation from 1968 onwards has resulted in a strong decrease of wet and dry sulfur deposition, by over 30% in the United Kingdom from 1970 to 1982 (Roberts & Fisher 1985) and by over 70% in The Netherlands from 1968 to 1994 (Ernst 1993; Somhorst & Stolk 1996). As a consequence of a half-life of 24 to 38 year for sulfur in soils and the increased use of non-S-containing fertilizers (Kirchmann et al. 1996), sulfur deficiency has started to arise in very sulfur-demanding crops like rape seed (Brassica napus) in England and Germany (Schnug 1997). Therefore, in western European countries it is not the problem of sulfur surplus, but sulfur deficiency which has to be ameliorated by sulfur fertilizing.

Clean air legislation has a further consequence, i.e. the production of sulfur-enriched substrates, the FGD by-products, which have to be handled either by storage or by re-use as substitute for agricultural limestone or as a general sulfur fertilizer (Zaifnejad et al. 1996). In the latter case some minor nutrients such as B and Mo may be concentrated in such amounts in the FDG by-products that they may adversely affect the growth of crop plants (Stehouwer et al. 1996; Zaifnejad et al. 1996). Therefore, the surplus of B and Mo has to be phyto-extracted from these FDG by-products prior to application in agriculture. This additional processing makes FDG less attractive for agriculture.

Phytoremediation of sulfur-enriched sites

The potential of sulfur extraction from the soil by plants is quite high in comparison to that of the accompanying elements like aluminum and heavy metals (Ebbs et al. 1997) due to the role of sulfur as major nutrient. In areas with high atmospheric sulfur dioxide, however, the uptake of sulfate by roots is diminished upon exposure of the shoot to SO_2 (Rennenberg & Polle 1994) due to a leaf-guided feed-back mechanism (Figure 1). In the case of *gypsiferous soils*, sulfur contents of extractor plants can easily exceed 1% sulfur in the dry matter: *Gypsophila* species are well adapted to gypsiferous soils and may be good sulfur extractors (Duvigneaud & Denaeyer-De Smet 1968), but their low biomass (Fiedler et al. 1987) will demand a similar transfer of genes to higher reproductive plants as proposed for metal-hyperaccumulators (Ebbs et al. 1997). The low nitrogen content of most soils with an increased sulfur content, however, may hamper the growth rate of plants so that the annually harvestable biomass remains low. Without improvement of the plant species or application of nitrogen and phosphate fertilizers, desulfurization of gypsiferous soils will be difficult. Prior to any considerations on desulfurization of gypsum soil, a balance has to be made between gypsum precipitation rate from evaporating groundwater and sulfur removal rates by plants; up to now the available data are not consistent enough for such balances. Further problems may arise. The high calcium content together with a high pH of gypsum soils may diminish the iron supply to plants. Therefore, plants have to improve the iron uptake efficiency by exudation of protons and organic acids by roots of dicotyledonous plants and siderophores by grass roots (Römheld & Marschner 1990).

Salinized soils hamper the plant growth in many arid and semi-arid regions of the world (Bresler et al. 1982). Desalinization of these saline soils will greatly enhance the area of agricultural land in the world. Saline soils, independent of the sulfur content, diminish the productivity of plants by an imbalance between the high concentration of sodium versus a low one of potassium, and a surplus of boron. Therefore, prior to desulfurization of such soils the sodium and boron content of the soils have to be diminished or the selection of boron-resistant crops has to be stimulated (Bagheri et al. 1996). Phyto-extraction of boron has already been realized in practice (Banuelos et al. 1993). Desulfurization of saline soils is a posteriority compared to the annual increase in salt by evapotranspiration.

The toxicity of enhanced concentrations of most heavy metals in *metalliferous soils* restricts at present the phytoremediation to a phyto-stabilization of these soils. Only in the case of iron mines the combination of a high iron content and a high sulfur content of the drainage water (Salminen & Sipilä 1996) gives a possibility for phytoremediation by phyto-extraction.

In contrast to the above mentioned soils, phytoremediation of *acid sulfate soils* is at least partly possible by liming which is very effective because it can increase the pH and the availability of Ca to plants and decrease the availability of Fe^{2+} (Moore et al. 1990) and other chemical elements. A reduction of the bioavailability of aluminium, manganese and zinc makes the soils suitable for crops as long as the concentration of heavy metals and aluminium can be kept below the limits for animal and/or human food (Palko & Weppling 1994).

Conclusion

Higher plant species have a high biodiversity with regard to the sulfur metabolism and the handling of a surplus of sulfur. In western European countries the effective reduction of SO_2 emission has diminished the enrichment of sulfur in the soils to such a degree that sulfur-demanding crops suffer from sulfur deficiency if not fertilized. In eastern European countries the implementation of clean-up technologies for SO_2 emission will diminish SO_2 damage to crops, sulfur deposition on soils and sulfur accumulation in crops so that the present problems (Mikula 1995) can be solved; if sulfur fertilizer is not supplied in time, subsequently similar problems may arise concerning the sulfur supply to agricultural crops as nowadays experienced in western Europe. Phytoremediation of sulfur-enriched soils may only be effective in gypsiferous and acid sulfate soils due to the millions of hectares involved. Prior to phytoremediation a balance has to be made between sulfurization of the soil by evapotranspiration and desulfurization by plants. Unfortunately, up to now the research on the chemical dynamics of these sulfur-enriched soils and on the uptake of sulfur by plants at such sites is not sufficiently consistent (Konsten et al. 1994; Carvalho & Van Raij 1997; Pearce & Sumner 1997) to establish such a balance which should have first priority. The implementation of desulfurization of sulfur-enriched soils by plants is mostly not hampered by the sulfur content of the soil, but by the surplus of other chemical elements which affect plant growth more than sulfur. In acid sulfate soils liming can diminish the bio-availability of the accompanying elements; liming will increase the pH to around 5 so that the formation of gypsum will be unlikely. Generally, phytoremediation is still in statu nascendi; a lot of scientific and processing problems have to be solved prior to bring phytoremediation of sulfur-enriched soils except of acid sulfate soils in practice.

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