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Chemical behavior of soil sulfur in the rhizosphere and its ecological significance

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Abstract

Sulfur naturally occurs in valences of –2 to +6. Various organic sulfur compounds can be found in soils. The rhizosphere is a key zone with view to the mechanisms of soil nutrient dynamics. This contribution summarizes the current knowledge about the chemical behavior of sulfur in the rhizosphere and its ecological impact and highlights future research needs.

Key words: arylsulfatase, elemental sulfur, soils, sulfur fertilization, rhizosphere

Introduction

Human activity highly influences the sulfur (S) cycle through anthropogenic emission from fossil fuel burning. Global SO_2 emissions from anthropogenic sources increased about 20-folds in 1985 compared to 1850 (Brimblecombe et al., 1989). This increase was strongest between 1940 and 1970 in Europe and North America, but then with the introduction of clean air acts coming into force the rend was reversed (Brimblecombe et al., 1989). However, SO_2 emissions are still increasing in Asia. Here the S emissions increased from 33.7 Tg in 1990 to 39.2 Tg in 1997, and peak values of 40-50 Tg are expected for the year 2020. China contributes with 66% of the total S emissions (David, et al., 2000).

Atmospheric S loads are closely linked to soil quality and an imbalanced S nutrition of plants (Hu, 2002a; McGrath et al., 1995; Schnug, et al., 1998). Atmospheric S depositions vary regionally in China and follow industrial activities (Wang et al., 2000). So, the hat total S deposition was 95 kg S/ha at the Experimental Station of Red Soil Ecology, Yingtan, Chinese Academy of Sciences in 1998/1999 (Hu et al., 2002b), and the soil pH value decreased by 0.6 units since 1992 (Xu et al., 2004). The excess of S may have a negative effect on the soil-plant system, for example on flooded paddy soils. Here, S will be reduced to H_2S, which obstructs plant growth (Hu et al., 2002a). In contrast, atmospheric S depositions are not sufficiently high in order to satisfy the demand in remote areas of China (Hu et al., 2002a). Yield responses to S fertilization of more than 20 different agricultural crops ranged from 4% to 81% (Cao et al., 1996).

The rhizosphere is a key zone with view to the mechanisms of soil nutrient dynamics (Darrah et al., 1993). Physico-chemical processes at the soil-root interface differ considerably from those in the non-rhizosphere soil. The effect of plant growth on soil nutrients in the rhizosphere was studied intensively for P (Gahoonia et al., 1992; Zoyza et al., 1997), N, K, Ca and Mg (Moritsuka et al., 2000). Only limited data is, however, available for the effect of plant growth on the chemical behavior of S in the rhizosphere, which is nevertheless required in order to assess agronomic and ecological impacts in relation to the local S cycle. This paper summarizes the present knowledge about the chemical behavior of soil S in the rhizosphere.

Chemical behavior of soil S in the rhizosphere

Oxidization of S^0 in the rhizosphere and non-rhizosphere

Elemental S (S^0) is used as a fertilizer to satisfy the S demand of cop plants. This reduced S needs to be oxidized to SO_4^{-2} before it becomes plant available. Oxidation of S^0 in soils is primarily a microbial process (Wainwright, 1984). The activity of *thiobacilli* is highly important for the oxidation of elemental S (McCaskill and Blair, 1987). Heterotrophic micro-organisms are other S^0 oxidizers in soils (Wainwright, 1984). Elemental S is oxidized by *thiobacilli* to sulfuric acid. The application of S^0 together with inoculation decreased soil pH rapidly from about 7.3 to 3.2 after 12 weeks of incubation. Adding *thiobacilli* together with S^0 to the rhizosphere yields a significantly faster oxidation than application of S^0 on its own (Fan et al., 2002). Grayston et al. (1991) isolated 273 bacterial phylas and 70 fungal species from the rhizosphere of canola (*Brassica napus*). From these 273 bacterial isolates, 245 (89.7%) oxidized S^0 to thisosulfate or tetrathionate, and 133 (48.7%) oxidized S^0 to SO_4^{-2}. All 70 fungal isolates oxidized S^0 to SO_4^{-2}. Bacterial isolates showed the highest S^0 oxidization rate (Table 1).

The rhizosphere is a key zone with view to the mechanism of soil nutrient dynamics. Physico-chemical processes in the soil-root interface differ considerably from those in the non-rhizosphere

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soil. A rhizobag culture experiment demonstrated that the oxidation of S^0 in the rhizosphere and non-rhizosphere varied in dependence on soil moisture content and soil type (unpublished data). The oxidation rate of S^0 was generally lower under waterlogged (1 cm water depth) than aerobic conditions (80% water holding capacity; Figure 2). On a paddy soil originating from lime rock, the oxidation rate of S^0 was higher in the rhizosphere of rice than in non-rhizosphere under waterlogged and aerobic conditions (Figure 2). However, these differences were not observed on the paddy soil originating from granite. The reason could possibly be different contents of plant available S and micobiological species.

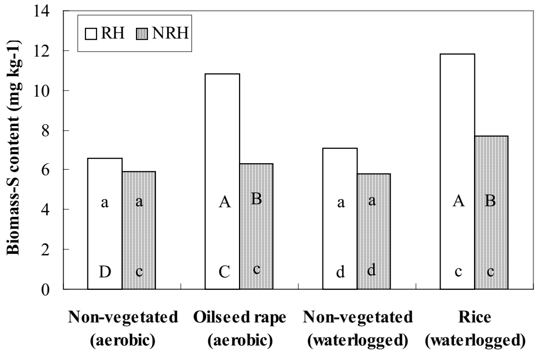

Figure 1:
Concentration of microbial biomass-S (MB-S) in the rhizosphere (RH) and non-rhizosphere (NRH). Different letters (a,b) and (A, B) indicate significant differences between RH and NRH at p<0.05 and p<0.01 level (student T-test).Different letters (c, d) and (C, D) indicate significant differences of MB-S in RH and NRH relative to no-vegetated soils at p<0.05, p<0.01 level(student T-test), respectively; source: Hu et al. (2003).

Soil microbial biomass S in the rhizosphere and non-rhizosphere

Soil microbial biomass is defined as the living part of soil organic matter (Chapmam, et al., 1987). The microbial biomass S in agricultural soils varied between 4.4% and 4.9% in non-vegetated soils and 5.2 and 8.8% in vegetated soils (Saggar et al., 1981; Chapmam, et al., 1987; Wu, et al., 1994). Despite its small size, the microbial bio-mass is a highly active fraction that acts as the driving force behind mineralization-immobilization and oxidation-reduction processes. A rhizobag culture experiment demonstrated that the S content of microbial mass was 6.3 mg S kg^{-1} in the non-rhizosphere soil and 11.8 mg S kg^{-1} in the rhizosphere soil of rice (Hu et al., 2003). The S content of microbial bio-mass was up to 72% higher in the rhizosphere of rice than in the non-rhizosphere (Figure 1). In non-vegetated soil samples the S content of microbial bio-mass was generally and significantly lower than in the vegetated treatments (Hu et al., 2003), because cropping increases the biological activity (Castellano et al., 1990).

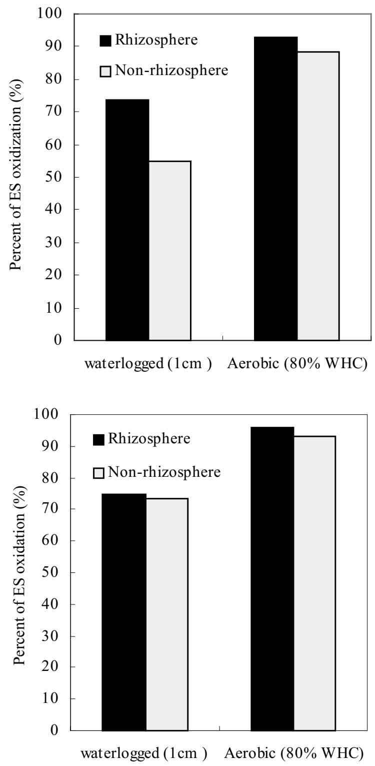

Figure 2:
Oxidization of elemental S (ES) in the rhizosphere of rice in dependence on water management and soil type (upper: paddy soil originated from lime rock; lower: paddy soil originated from granite; unpublished data).

Variations in the chemical behavior of S in the non-rhizosphere and rhizosphere

In a rhizobag experiment it was demonstrated that the distribution of S fractions in the rhizosphere and the non-rhizosphere soil varied in dependence on the crop type (Table 2). More total and inorganic SO_4^{2-}-S was found in the rhizosphere of oilseed rape and rice (Table 2), which supposedly relies on mass flow to the roots (Barber, et al., 1995). More organic S was found in the rhizosphere of oilseed rape, while inverse results were obtained for rice (Table 2). A possible explanation is that the turnover of organic matter was hampered under anaerobic conditions (Williams et al., 1967). Stanko-Golden (1991)

Table 1:
Number of S^0-oxidizing bacterial isolates from the rhizosphere and rhizoplane of canola grown in a growth chamber (source: Grayston et al., 1991).

Soil	Area of isolation	Total isolates	Number of isolates producing		
			$S_2O_3^{2-}/S_4O_6^{2-}$	SO_4^{2-}	$S_2O_3^{2-}/S_4O_6^{2-}$ and SO_4^{2-}
Haverhill	Rhizosphere	56	49 (87.5%)*	25 (44.6%)	25 (44.6%)
	Rhizoplane	43	42 (97.7%)	30 (69.8%)	30 (69.8%)
Carrot River	Rhizosphere	31	26 (83.9%)	15 (48.4%)	14 (45.2%)
	Rhizoplane	40	38 (95.0%)	20 (50.0%)	20 (50.0%)
Asquith	Rhizosphere	19	18 (94.7%)	7 (36.8%)	7 (36.8%)
	Rhizoplane	32	29 (90.6%)	13 (40.6%)	10 (31.2%)
Laird	Rhizosphere	15	11 (73.3%)	6 (40.0%)	5 (33.3%)
	Rhizoplane	37	32 (86.5%)	17 (45.9%)	13 (35.1%)
Total bacteria		273	245 (89.7%)	133 (48.7%)	124 (45.4%)

*Sulfur oxidizers as percentage of total isolates.

Table 2:
Contents of different S Fractions (mg S kg^{-1}) in the rhizosphere (RH), non-rhizosphere (NRH), and the RH to NRH ratio (mean; source: Hu et al., 2003).

Water management	Non-vegetated /cropping	RH/NRH	Total S	S fractions						
				Organic S fractions				Inorganic S fractions		
				Total organic	Ester bonded	Carbon bonded	Residual	Total inorganic	Soluble SO_4^{2-}	Adsorbed SO_4^{2-}
Aerobic condition	Non-vegetated	RH	141.9a	99.3a	20.4a	11.7a	67.2a	42.6a	33.0a	12.0a
		NRH	133.9a	91.4a	20.1a	13.8a	57.2a	42.5a	28.8a	13.7a
	Oilseed rape	RH	122.3a	99.6a	30.0b	14.6a	53.8A	44.0a	34.0a	10.0a
		NRH	120.4a	87.6a	44.5a	17.3a	25.8B	32.8b	23.0b	9.8a
		Ratio	1.02	1.13	0.67	0.84	2.08	1.34	1.48	1.02
Water-logged condition	Non-vegetated	RH	145.3a	96.0a	24.0a	15.7a	56.3a	49.3a	43.0 a	6.3 a
		NRH	133.0a	87.8a	27.0a	14.4a	46.4b	45.2a	40.4 a	4.8 b
	Rice	RH	155.2a	29.6B	6.0B	11.0a	12.6B	125.6A	110.3A	15.3A
		NRH	131.2a	91.2A	33.6A	10.7a	46.9A	40.0B	34.7B	5.3B
		Ratio	1.18	0.33	0.18	1.03	0.27	3.14	3.18	2.89

*Values followed by different letters (a, b), and (A, B) indicate significant differences between RH and NRH at $p < 0.05$, and $p < 0.01$ level (student T-test), respectively.

Table 3:
Concentrations (mean value ± SD, n=4) of different S fractions (mg S kg^{-1}) in the rhizosphere (RH) and non-rhizosphere (NRH) in dependence on soil and crop type (source: Hu et al., 2002c).

Soils	Treatment	RH/ NRH	Total S	Sulfur fractions							
				Total S in 0.01 M $CaCl_2$	Adsorbed SO_4^{2-}	Ester bonded	Carbon bonded	Residual	Total S in 0.01 M $Ca(H_2PO_4)_2$	SO_4^{2-} in 0.01 M $Ca(H_2PO_4)_2$	HI-reducible S
Haplic Acrisol	Fallow	RH	202±2	13.9 ± 1.3	13.8 ± 1.9	76.0 ± 5.1	19.7 ± 1.4	79.0 ± 8.6	39 ± 2	28 ± 2	104 ± 8
		NRH	182±14	14.8 ± 0.4	13.3 ± 0.9	75.3 ± 2.5	18.1 ± 2.1	69.4 ± 9.7	38 ± 1	28 ± 1	103 ±12
	Wheat	RH	193 ± 17	15.2 ± 1.8	10.8 ± 2.0	48.0 ± 3.1	19.2 ± 3.0	99.0 ± 7.8	36 ± 5	26 ± 3	74 ± 4
		NRH	175 ± 7	9.8 ± 0.7	14.0 ± 1.1	56.0 ± 4.1	22.3 ± 3.3	72.3 ± 9.3	33 ± 2	24 ± 1	80 ± 6
	Oilseed rape	RH	179 ± 5	8.8 ± 1.3	5.5 ± 1.4	58.6 ± 5.8	18.7 ± 2.0	87.4 ± 6.9	23 ± 2	14 ± 0	73 ± 6
		NRH	170 ± 9	5.5 ± 0.5	9.8 ± 1.3	60.8 ± 5.7	20.7 ± 2.4	72.9 ± 7.2	22 ± 1	15 ± 1	76 ± 6
	Radish	RH	194 ± 9	8.7 ± 1.4	5.4 ± 1.0	75.3 ± 1.5	19.5 ± 1.4	85.5 ± 9.9	24 ± 2	14 ± 1	89 ± 9
		NRH	174 ± 10	5.7 ± 0.9	9.0 ± 1.7	86.9 ± 1.7	21.2 ± 1.4	51.4 ± 6.3	22 ± 1	15 ± 2	102 ± 1
Hortic Anthrosol	Fallow	RH	141 ± 6	19.2 ± 2.7	4.9 ± 0.7	40.1 ± 3.1	1.3 ± 0.1	75.4 ± 4.1	32 ± 4	24 ± 3	64 ± 2
		NRH	130 ± 9	20.3 ± 3.1	3.9 ± 1.5	32.4 ± 2.8	0.1 ± 0.1	73.2 ± 8.3	38 ± 3	24 ± 3	57 ± 2
	Wheat	RH	131 ± 10	19.8 ± 2.0	5.0 ± 1.8	34.2 ± 2.9	1.6 ± 0.2	70.1 ± 7.6	33 ± 1	25 ± 2	59 ± 3
		NRH	131± 2	22.1 ± 4.0	1.8 ± 2.7	43.4 ± 2.5	<LLD	63.3 ± 3.7	38 ± 2	24 ± 3	67 ± 2
	Oilseed rape	RH	122 ± 5	13.2 ± 1.6	-0.4 ± 1.0	36.4 ± 1.2	1.8 ± 1.2	71.3 ± 4.5	20 ± 2	13 ± 1	49 ± 4
		NRH	130 ± 3	16.4 ± 4.0	1.3 ± 2.2	40.2 ± 1.9	0.1 ± 0.1	71.7 ± 2.7	30 ± 3	18 ± 3	58 ± 2
	Radish	RH	137 ± 5	13.8 ± 0.7	0.11 ± 0.6	40.7 ± 1.3	1.4 ± 0.2	80.7 ± 5.9	26 ± 4	14 ± 1	55 ± 1
		NRH	115 ± 6	10.8 ± 4.6	0.60 ± 3.3	51.1 ± 5.2	0.2 ± 0.1	52.5 ± 6.9	18 ± 2	11 ± 1	63 ± 4

note: <LLD < Lower Limit of Detection; RH rhizosphere; NRH non-rhizosphere (bare soil) reported that soil moisture was positively related with organic S. With view to rice the soil moisture is of minor relevance, because there are oxidizing conditions in the rhizosphere due to aeration tissues from the top to the roots which promote the activity of microbes and sulfatase (Han et al., 1982, Freney et al., 1966).

More ester-bonded S was found in the non-rhizosphere of oilseed rape and rice (Table 2). Hu et al. (2002c) observed similar results for oilseed rape, wheat and radish (Table 3). The reason could be a higher arylsulfatase activity in the rhizosphere as it is this enzyme, which catalyzes the decomposition of sulfate esters (Fitzgerald, 1978). Han et al. (1982) found, however, that the arylsulfatase activity was higher in the rhizosphere than in the non-rhizosphere of rice (Table 4). Additionally, the activity of microorganisms is higher in the rhizosphere as they use root exudates as an energy source (Yan et al., 1993). Thus, the rhizosphere soils had a higher organic C content than the non-rhizosphere soils (Hu et al., 2003).

Carbon-bonded S is not related to plant S uptake (Lee et al., 1979), though S may be mineralized from all organic S fractions (Li et al., 2001). Amino acids, such as cysteine and methionine are the major components of carbon-bonded S (Tabatabai et al., 1982; Freney et al., 1986). S-containing amino acids do not accumulate in free forms, because they are rapidly degraded in aerobic soils (Fitzgerald et al, 1978). Paul and Schmidt (1961) reported that the cysteine and methionine content was slightly higher in the rhizosphere than in the non-rhizosphere soil. Other experiments revealed no significant differences existed between the two compartments (Hu et al., 2002c; Table 2, 3). These results indicate that carbon-bonded S is of minor importance for the S nutrition of crops than for instance ester sulfate.

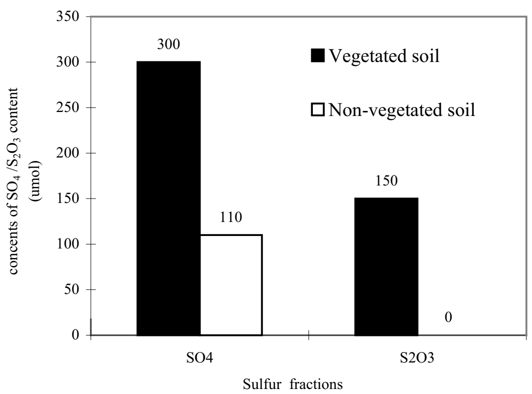

Figure 3:
SO_4^{2-} and $S_2O_3^{2-}$ content in the non-rhizosphere and rhizosphere of rice (Wind , 1995)

The amount of residual-S was significantly higher in the rhizosphere than in the non-rhizosphere of oilseed rape while opposite results were found for rice (Table 2). Other crops such as wheat and radish also showed higher levels of residual S in the rhizosphere (Table 3). Rice had a higher ability to utilize residual S from the soils which could be related to its aeration tissues.

In all treatments with plants, the content of soluble SO_4^{2-}-S and adsorbed SO_4^{2-}-S was higher in the rhizosphere than in the non-rhizosphere (Table 2). This can not be attributed generally to a higher mineralization in the rhizosphere, because the organic S content was higher in the rhizosphere of oilseed rape (Table 2). Enhanced mass flow of SO_4^{2-}-S to the rhizosphere after mineralization of organic S in the non-rhizosphere is supposedly the reason for this effect. Wind (1995) found that the concentrations of SO_4^{2-}, $S_2O_3^{2-}$ at the rhizosphere of rice were related to rice planting. The same author found more SO_4^{2-} in the rhizosphere (300 μmol kg^{-1}) of rice than in the non-vegetated (110 μmol kg^{-1}) treatment.

Ecological effects of soil S transformations in the rhizosphere

Grayston et al. (1991) selected eighteen isolated bacteria, which showed an increased efficacy of in vitro S oxidization for inoculating seeds, together with applications of elemental S. Results indicated that inoculation with 14 phyla increased canola leaf size, and root and pod dry weight at maturity was promoted by seven phyla. The shoot material had higher iron, sulfur, and magnesium contents after inocultion by two of the eighteen bacterial isolates (Table 5). In case of three isolates the treatment had a detrimental effect on the growth of the fungal pathogens, *Rhizoctonia solani* AG2-1, *R. solani* AG4, and *Leptosphaeria maculans* "Leroy". Besides a direct fungicidal effect of elemental S, the initiation of S induced resistance mechanisms through an enhanced oxidation of S^0 may explain the latter effect (Haneklaus et al., 2004).

Sulfur in nature occurs in valences from -2 to +6 (Hu et al., 2002a). Many types of organic S compounds were found (Morra et al., 1997, Hu et al., 2002a). Internal cycling reactions are responsible for maintaining a biologically available S supply through mineralization of organic substrates and redox transformation of inorganic species (Hu et al., 2002a). Speciation of S in natural organic matter could provide a clear understanding not only of bio-geochemical transformations of S, but also of the role of organic S in the complexation of toxic trace metals (Xia et al., 1998). Here, S-containing functional groups in humic substances may play an important role in complex formation with trace

Table 4:
Comparison of arylsulfatase activity in non-rhizosphere and rhizosphere soil of the different rice varieties grown on Pila clay loam and Maahas clay (source: Han et al., 1982).

Treatment	Weeks after transplanting				
	0	2	4	6	8
Pila clay loam soil*					
Non-rhizosphere soil	36	9.3	12.9	16.0	11.3
Rhizosphere soil of different rice varieties					
IR-8	36	25.5	31.3	45.1	54.6
IR-667	36	13.0	18.9	21.5	22.6
C-4	36	18.2	37.2	26.5	42.2
Maahas clay soil*					
Non-rhizosphere soil	7	5.8	5.4	4.4	5.8
Rhizosphere soil of different rice varieties					
IR-8	7	9.5	10.8	9.1	12.1
IR-667	7	8.2	8.7	9.1	11.2
C-4	7	10.4	10.4	8.1	10.4

* Cite from original text

Table 5:
Sulfur, iron, and magnesium content of canola shoots and pods after seed inoculation with sulfur-oxidizing rhizosphere (source: Grayston et al., 1991).

Treatment	Plant tissue	Mg (mg)	S (mg)	Fe (μg)
Control	Shoots	9.3 ± 1.6	21.6 ± 2.8	439 ± 64
Isolate No 13	Shoots	11.1 ± 1.1	23.2 ± 2.4	657 ± 155*
Isolate No. 14	Shoots	11.9 ± 1.2*	28.1 ± 1.2*	727 ± 118*

Note: Plants grown in 2 kg of soil amended with prilled S^0 fertilizer (50μg g^{-1}) in growth chamber. The control was inoculated with an autoclaved culture of isolate 10. Means of five replicates ± SD. *Significant increase above control ($p<0.05$).

metals such as Cd, Co, Ni, Pb, Zn, As, and Hg (Xia et al., 1998).

Conclusions

Only few studies about the chemical behavior of soil S in the rhizosphere were carried out (Hu, et al., 2002c, 2003, Wind , 1995; Grayston et al., 1991; Han, et al., 1982) so that information about factors influencing S transformation processes in the rhizosphere is still limited. In this context, the soil water regime, plant species, soil type, soil characteristics are parameters, which need to be paid more attention to.

A number of wetland plants, such as rice, have been shown to oxidize the rhizosphere, a process which may serve to protect against the entry of reduced phytotoxins, such as Mn^{2+}, Fe^{2+}, and S^{2-} (Armstrong et al., 1978). Iron plaque is commonly formed on the roots of aquatic plant species, such as *Oryza sativa,* and is mainly caused by the oxidation of ferrous to ferric compounds and the precipitation iron oxide on the root surface (Armstrong, 1967; Chen, et al., 1978). Results of Liu et al., (2004a) showed that P starvation can disturb formation of iron plaque onto the roots of rice plants grown under solution culture, but there is little information on the role of S in iron plaque development though S plays an important role for adjusting soil redox processes. Some reports have shown that iron plaque may be a barrier to the uptake of heavy metals, such as Cu, Ni, Mn, As, Cd (Taylor and Crowder, 1983; Greipsson, 1994; Liu et al., 2004a, b). Effect of chemical behaviors of soil S in the rhizosphere and iron plaque induced by S transformation is therefore of particular interest.

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