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Influence of Fulvic and Humic Acids on Cu- and V-Toxicity to *Zea mays* (L.)

By S. M. Ullah and M. H. Gerzabek

(With 8 figures)

1. Introduction

Copper in excess is the most detrimental micronutrient and there is a great concern about Cu-toxicity in agriculture (Tiller and Merry 1981).

In recent years, Cu-toxicity to plants and animals due to its accumulation in the environment as a result of the continual use of Cu-containing fungicides, domestic and industrial sludges, pig and poultry slurries has developed a serious problem (Purves 1977, Rousos and Harrison 1987). Phytotoxic limit values of copper in soils (Walsh et al. 1972, Mathur and Levesque 1983, Scholl and Enkelmann 1984, Davis and Carlton-Smith 1984, Adriano 1986, Tyler et al. 1989), in nutrient solution culture (Rahimi and Bussler 1973, Vogel 1973, Rousos and Harrison 1987), in plant tissue (Davis et al. 1978, Adriano 1986) and sheep (Adriano 1986) have been reported.

Humic substances being one of the most reactive parts of the soil play an important role in regulating heavy metal availability to plants. They have polyfunctionality and chelating characteristics, which are outstandingly vital for environmental protection through complexing toxic metals and compounds (Stevenson and Ardakani 1972, Vaughan and Malcolm 1985, Hargitai 1989). The divalent Cu-ions form strongly bound stable complexes with humic and fulvic acids (Stevenson and Fitch 1981, Adriano 1986). Fulvic acid, being more reactive than humic acid, has been proven to be effective in reducing Zn- and Ni-toxicity in corn plants (Gerzabek and Ullah 1988, 1990).

Vanadium is not essential for higher plants and its phytotoxicity under field conditions is also non-existent. Recent interest in V is due to its release in large amounts to the environment from the combustion of fossil-fuels, from factories manufacturing steel for high speed tools, ceramics, dyeing and printing.

Vanadium at low concentrations (0.5 mg/L or more) in nutrient solution culture has been demonstrated phytotoxic for a number of plants (Warington 1954, Cannon 1963, Hara et al. 1976, Wallace et al. 1977, Davis et al. 1978). Reduction in yield was obtained with concentration as low as 0.5 ppm. Little is known on the complex formation between vanadium and humic substances, since the information on V in terrestrial system is generally sparse.

The present study was undertaken to investigate the ability of humic and fulvic acids in reducing the phytotoxicity of copper and vanadium to corn plants grown in nutrient solution culture.

2. Materials and Methods

A series of four experiments with nutrient solution culture was carried out. The solutions (Gerzabek and Edelbauer 1986) contained mmol/L: N: 4.0, P: 0.5, S: 1.3, K: 2.5, Ca: 1.3 and Mg: 0.8. The pH of the nutrient solution culture was adjusted to 6.0. Micronutrient solutions A, B, C, D, and E after Steineck (1951) were used. The total concentration of the nutrient solution was 0.866 ‰. The corn seedlings (*Zea mays* L., variety LG 3) were transplanted three days after germination into plastic pots containing 1.3 L nutrient solution. One week after transplantation the corn plants were exposed to the treatments with heavy metals, fulvic and humic acids. Fulvic acid (FA) concentrations were 27 and 54 OD/pot (OD = Optical density at 400 nm) and humic acid (HA) concentrations were 90 and 180 OD/pot. Two levels of heavy metals — Cu (1.0 and 2.0 mg/L) and V (0.5 and 1.0 mg/L) — were added to the nutrient solution. The heavy metals (Cu and V) were mixed to humic or fulvic acids extracted from sewage sludge compost (Mohamad 1984) one day before changing the nutrient solution in order to allow them to form stable complexes. The design of the four experiments was a randomized complete block with 9 different treatments (control, 2 heavy metals, 2 fulvic or humic acid treatments and their combinations) and 4 replications. The nutrient solutions were renewed twice a week. *Zea mays* was harvested four weeks after transplantation and separated into roots and shoots, which were then dried at 80° C for a week and powdered. Heavy metal concentrations were measured by Plasma Emission Spectrometry after wet digestion of the samples.

3. Results and Discussion

Humic acids in heavy metal-free nutrient solution stimulated both root and shoot growth of corn plants (fig. 1, 2, 3, 4; tables 1, 2). Humic acid at concentration of 180 OD/pot enhanced dry matter (DW) production of corn shoot up to 25 % and root up to 21 % compared to the control in both Cu- and V-experiments. The positive influence of humic substances is a well known phenomenon (Aso and Takenaga 1979) and a similar increase in dry matter yield was also reported in nutrient solution culture (Mylonas and McCants 1980, 1980 a, Tan and Nopamornbodi 1979, Gerzabek and Ullah 1988, 1990). Fulvic acids on the other hand increased dry matter production only up to 9 % in roots (Cu experiment) and 11 % in shoots (V experiment) compared to the control. Fulvic acid has thus only a minor effect on corn tissue production in comparison to humic acid (Gerzabek and Ullah 1988, 1990). This better yield has been attributed to the participation of humic substances in the biochemical and physiological processes of plants. They promote plant growth by their effects on ion transfer at the root level (Blanchet 1957, Levesque 1970) by activating the oxidation-reduction state of the growth medium and hence increase the absorption of micronutrients by preventing precipitation in the nutrient solution (Kononova and D'yakonova 1960). Humic substances enhance cell permeability, which results in rapid entry of plant nutrients into the root cells (Pagel 1960, Mylonas and McCants 1980 a). The main physiological function of humic acids is the reduction of oxygen deficiency in plants resulting in the utilization of larger amount of nitrogen and a more intensive synthesis of proteins and nucleic acids (Khristeva and Luk'yanenko 1962, Schnitzer and Kahn 1978, Vaughan and Malcolm 1985).

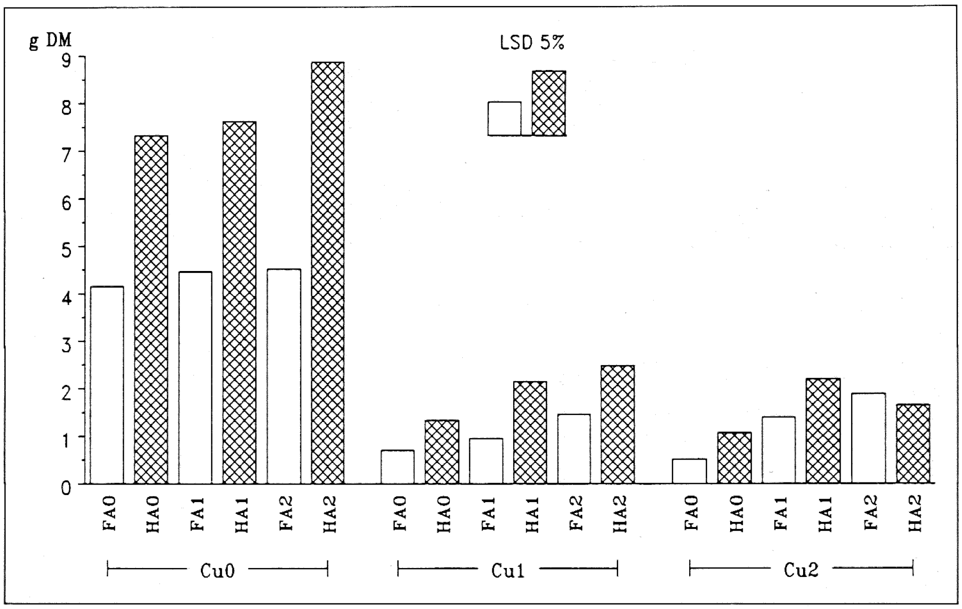

Fig. 1: Influence of fulvic acid, humic acid and Cu on the shoot growth of Zea mays L. (dry matter)

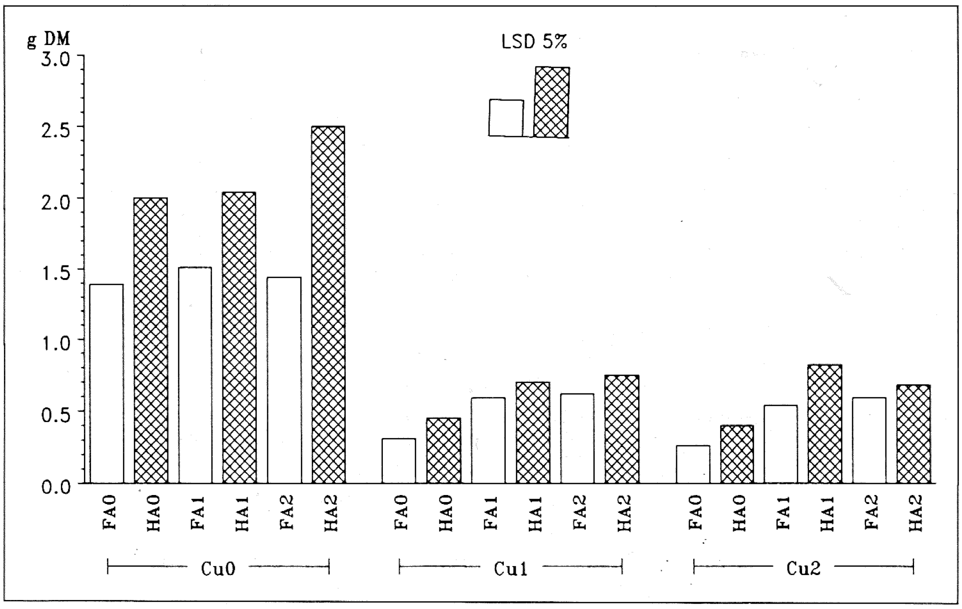

Fig. 2: Influence of fulvic acid, humic acid and Cu on the root growth of Zea mays L. (dry matter)

Both Cu and V reduced yields (fig. 1, 2, 3, 4; tables 1, 2). Depression in yield was much pronounced in Cu-enriched nutrient solution (without humic or fulvic acid). 1.0 and 2.0 mg Cu/L nutrient solution decreased the shoot growth up to 80 % and 85 % respectively compared to the control. Root growth was also severely affected by copper treatments (fig. 2). The reduction of root dry matter production compared to the control was 75 % and 76 % at 1.0 and 2.0 mg Cu/L nutrient solution respectively. A similar growth reduction was reported by many authors (PATEL et al. 1976, LEXMOND and VORM 1981). Copper supply beyond allowable limit values effects root growth before shoot growth, causing reduced shoot vigour, stunted and discoloured root systems, leaf chlorosis (DANIELS et al. 1973, ROBSON and REUTER 1981), which may be due to Cu-induced iron deficiency (ROBSON and REUTER 1981) and may also be due to a direct lipid oxidation by excess Cu and thus destruction of thylakoid membranes (SANDMANN and BÖGER 1983).

Table 1

Analysis of variance procedure (Cu experiments); DF2 = 27

treatment	variable	source	DF1	F value (SS error)	P
FA	DM shoot	CU	2	202.63	0.0001
		FA	2	1.33	0.2816
		CU*FA	4	0.13	0.9718
				(6.3653)	
	DM root	CU	2	169.30	0.0001
		FA	2	1.08	0.3530
		CU*FA	4	0.06	0.9926
				(0.7791)	
	Cu conc. shoot	CU	2	58.62	0.0001
		FA	2	7.33	0.0029
		CU*FA	4	2.55	0.0621
				(312.8347)	
	Cu conc. root	CU	2	265.93	0.0001
		FA	2	18.32	0.0001
		CU*FA	4	8.89	0.0001
				(6229690.7)	
HA	DM shoot	CU	2	158.41	0.0001
		HA	2	1.22	0.3124
		CU*HA	4	1.28	0.3015
				(23.6484)	
	DM root	CU	2	77.64	0.0001
		HA	2	0.64	0.5364
		CU*HA	4	1.44	0.2479
				(3.1199)	
	Cu conc. shoot	CU	2	31.15	0.0001
		HA	2	2.36	0.1141
		CU*HA	4	1.66	0.1871
				(397.7287)	
	Cu conc. root	CU	2	72.71	0.0001
		HA	2	4.10	0.0280
		CU*HA	4	2.81	0.0454
				(11292914.6)	

DF = degrees of freedom; P = probability; DM = dry matter
FA = fulvic acid; HA = humic acid; SS = sum of squares

Vanadium phytotoxicity was less pronounced than that of copper (fig. 3, 4; table 2). Shoot growth dropped to 15 % (0.5 mg V/L) and 35 % (1.0 mg V/L); while root dry matter production decreased up to 19 % (0.5 mg V/L) and 32 % (1.0 mg V/L) compared to the control. Vanadium phytotoxicity has also been demonstrated for a number of plants (WARINGTON 1954, CANNON 1963, WALLACE et al. 1977, ADRIANO 1986). Older leaves exhibited chlorosis in V-enriched nutrient solution culture.

Table 2

Analysis of variance procedure (V experiments); DF2 = 27

treatment	variable	source	DF1	F value (SS error)	P
FA	DM shoot	V	2	0.39	0.6804
		FA	2	12.85	0.0001
		V*FA	4	2.59	0.0595
				(90.5811)	
	DM root	V	2	6.92	0.0037
		FA	2	13.48	0.0001
		V*FA	4	4.63	0.0056
				(4.1030)	
	V conc. shoot	V	2	35.13	0.0001
		FA	2	12.52	0.0001
		V*FA	4	1.87	0.1449
				(1.0634)	
	V conc. root	V	2	452.03	0.0001
		FA	2	139.58	0.0001
		V*FA	4	50.66	0.0001
				(43695.8)	
HA	DM shoot	V	2	1.70	0.2022
		HA	2	49.66	0.0001
		V*HA	4	8.63	0.0001
				(44.2342)	
	DM root	V	2	3.51	0.0443
		HA	2	44.46	0.0001
		V*HA	4	6.52	0.0008
				(3.1608)	
	V conc. shoot	V	2	1.85	0.1769
		HA	2	29.57	0.0001
		V*HA	4	4.27	0.0083
				(0.4010)	
	V conc. root	V	2	650.69	0.0001
		HA	2	119.27	0.0001
		V*HA	4	49.30	0.0001
				(24379.8)	

DF = degrees of freedom   P = probability   DM = dry matter
FA = fulvic acid   HA = humic acid   SS = sum of squares

Both humic and fulvic acids had a tendency to increase the growth of roots and shoots of maize plants compared to the treatments where Cu alone was applied. Divalent Cu-ions are reported to be strongly bound to humic and fulvic acids forming Cu-humic and Cu-fulvic acid complexes (STEVENSON and FITCH 1981, ADRIANO 1986). However, fulvic acid- and humic acid-Cu-interactions were not significant in the case of dry matter production. In the present study the humic substances had therefore no positive influence on Cu-toxicity.

Fulvic and humic acids enhanced the dry matter production of maize significantly in V-treated nutrient solution culture. The dry matter yield significantly exceeded the V-enriched treatments as well as in some cases the control and V-free humic or fulvic acid treatments (fig. 3, 4; table 2). Shoot growth was increased up to 28 % (V1HA2) and root growth up to 53 % (V1HA2) compared to the control, while in V-fulvic acid treatments the dry matter production in roots increased up to 63 % (V2FA2) and in shoots up to 31 % (V2FA2) in comparison to the control. Thus humic and fulvic acids not only eliminated the detrimental effects of vanadium in V-enriched nutrient solutions but also stimulated and enhanced the growth of maize roots and shoots. This might be due to the uptake of free V-ions, which were left in a non-toxic concentration after complex formation in the nutrient solution or due to the uptake of V-humic of V-fulvic acid complexes, which may be at low concentrations stimulatory to root and shoot growth

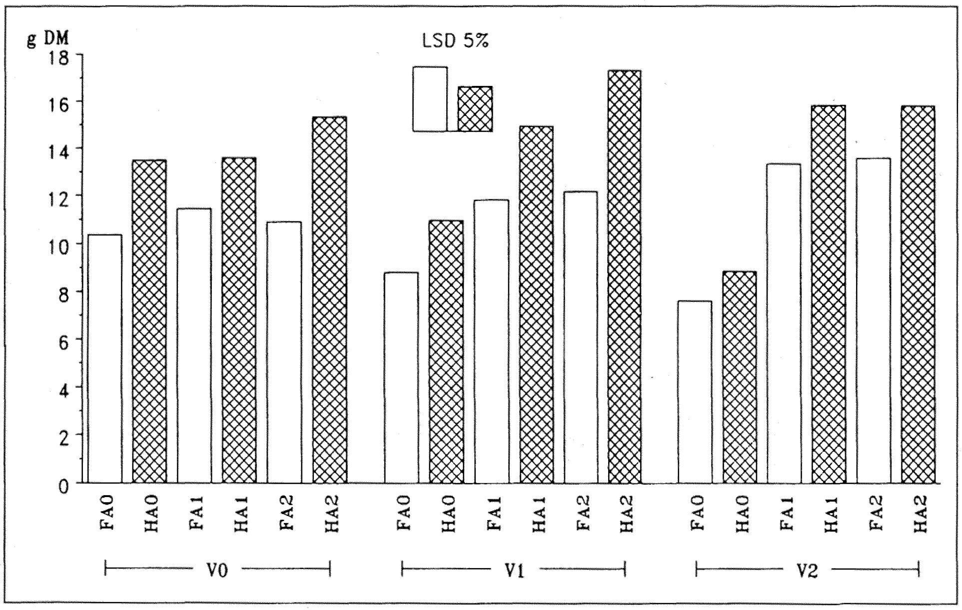

Fig. 3: Influence of fulvic acid, humic acid and V on the shoot growth of Zea mays L. (dry matter)

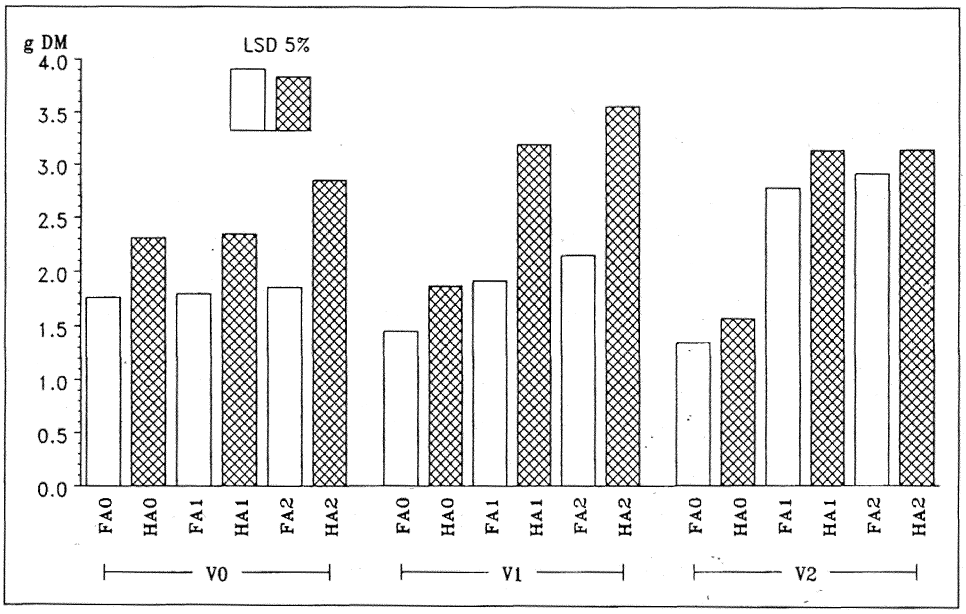

Fig. 4: Influence of fulvic acid, humic acid and V on the root growth of Zea mays L. (dry matter)

of corn plants. Vanadium as vandate ion can stimulate plant growth (BERGMANN 1988). SINGH (1971) observed a growth stimulation by vanadium at a concentration up to 0.25 mg/L in the nutrient solution. WALLACE et al. (1977) showed an

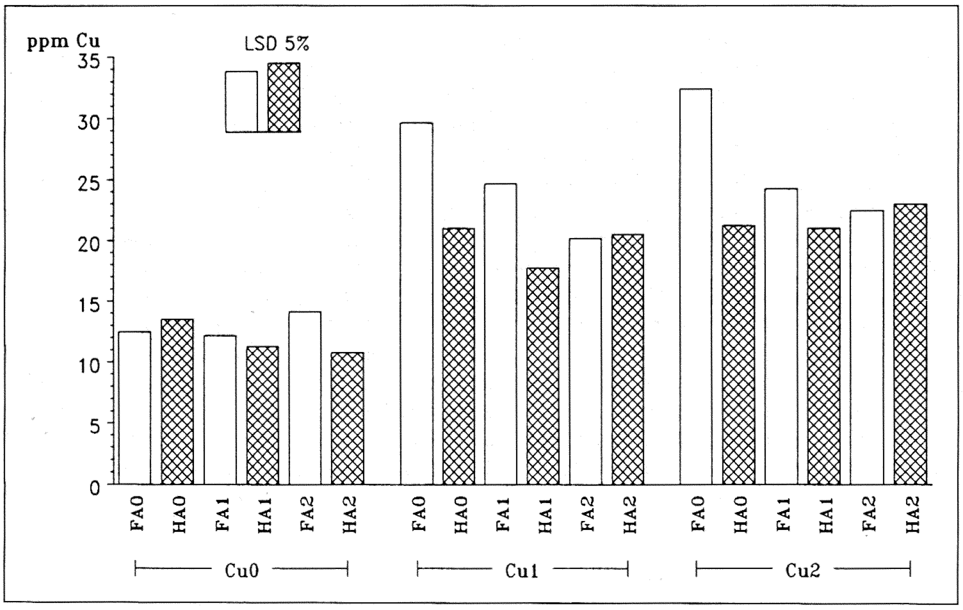

Fig. 5: Influence of fulvic acid, humic acid and Cu on the Cu concentrations in shoots of Zea mays L. (mg Cu/kg DM)

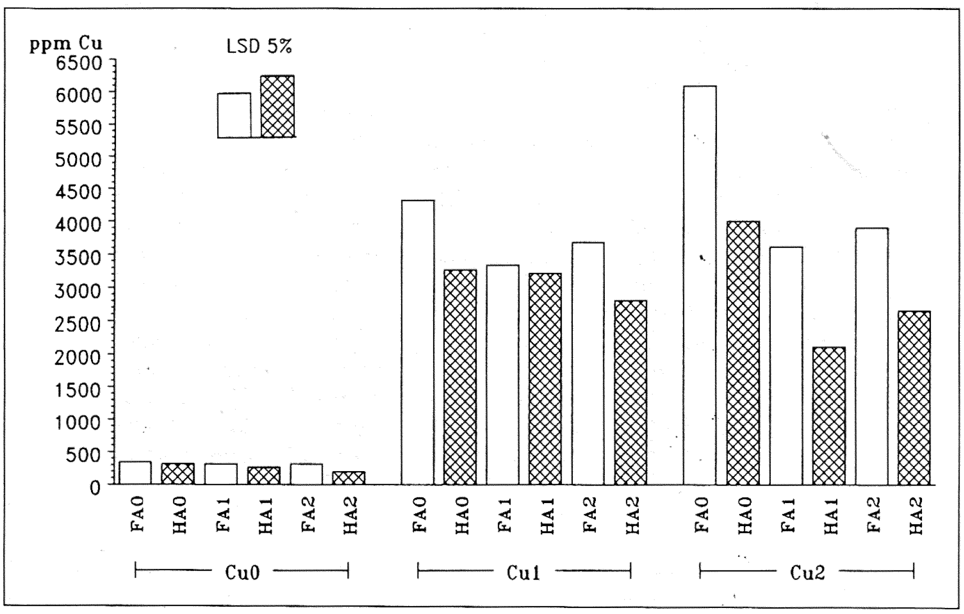

Fig. 6: Influence of fulvic acid, humic acid and Cu on the Cu concentrations in roots of Zea mays L. (mg Cu/kg DM)

increase in bean yield of 7% at 0.05 mg V/L in the nutrient solution. In the present experiment, the root and shoot dry matter showed significant V-HA and V-FA interactions, which were more pronounced in case of V-humic acids (table 2).

The contents of Cu and V were enhanced both in roots and shoots, where these heavy metals were applied, their accumulation being considerably higher in roots than in shoots (fig. 5, 6, 7, 8). Copper concentration in shoots (DM) ranged from 10.75 mg Cu/kg (Cu0HA2) to 32.44 mg Cu/kg (Cu2FA0), while root contents varied from 190 mg/kg (Cu0HA2) to 6095 mg/kg (Cu2FA0). The preferential Cu accumulation in roots, when its external supply is large and its restriction of root to shoot transport has been reported (Marschner 1989).

Humic acid had only minor effects on reducing Cu-concentration in shoots. Fulvic acid on the contrary significantly suppressed Cu concentrations in shoots (fig. 5). Probably Cu-fulvic acid complexes absorbed by roots did not behave like free Cu-ions and their translocation from roots to shoots was restricted. Although humic acid had little effect on diminishing Cu contents in shoots, its contents in roots were significantly reduced by HA compared to the heavy metal enriched nutrient solution (fig. 6). The root to shoot translocation of Cu was hardly affected by humic acid. Cu-HA interactions in roots were statistically significant (table 1). Fulvic acid treatments decreased Cu concentration in root and its translocation from root to shoot was influenced as well. Cu-FA interactions were highly significant especially in case of roots (table 1). In fulvic acid experiments, the shoot to root copper concentration ratio dropped from 0.0069 (Cu1FA0) to 0.0047 (Cu1FA2) and 0.0053 (Cu2FA0) to 0.0037 (Cu2FA2). A similar decrease in shoot to root concentration ratio of Ni due to fulvic acid treatments was reported earlier (Gerzabek and Ullah 1990).

Vanadium contents in maize shoots were between 0.0745 (V1HA2) and 0.6328 mg/kg dry matter (V2HA0) to 680 mg/kg dry matter (V2HA0) in the humic acid experiment. In the fulvic acid experiment shoot V-contents varied between 0.42 (V0FA1) and 1.44 mg/kg DM (V2FA0), in roots its concentration ranged from 1.53 (V0FA2) to 815 mg/kg DM (V2FA0). Plants exposed to excess vanadium have been reported to contain only 1.0 to 2.0 mg V/kg in their shoots, while exhibiting much higher concentrations in their roots (Cannon 1963, Davis et al. 1978, Adriano 1986). Just like in the case of Cu, root to shoot translocation of V was also restricted, but its overall translocation was much lower.

Although both humic and fulvic acids were found to reduce significantly V concentration in roots and shoots compared to the treatments, where only V was applied, humic acids were shown to be more effective in diminishing V-uptake in plants than fulvic acids (fig. 7, 8). V-HA interactions on V concentrations in corn plants were statistically significant (table 2). V-FA interactions were significant only in the case of root concentration of vanadium (table 2).

Both humic and fulvic acids reduced the absorption of V by roots and also restricted its translocation from roots to shoots, thereby alleviating its phytotoxic effects on corn plants. V shoot to root concentration ratio decreased from 0.004 (V1HA0) to 0.0002 (V1HA2) and from 0.0009 (V2HA0) to 0.0001 (V2HA2), while in FA-experiments shoot to root concentration ratio dropped from 0.0028 (V1FA0) to 0.0018 (V1FA2) and from 0.0018 (V2FA0) to 0.0010 (V2FA1). V shoot to root concentration ratio was nearly 10 times higher in V-fulvic acid than in V-humic acid treatments.

The reduction of vanadium by humic substances (Goodman and Cheshire 1975, Cheshire et al. 1977, McBride 1980, 1980 a, Thurman 1985) and its complex formation with humic substances (Templeton and Chasteen 1980) may be the reasons of eliminating V-phytotoxicity in corn plants.

nating phytotoxicity caused by most of the heavy metals. On the contrary, humic acids were very efficient in removing only toxic effects due to vanadium. V-HA interactions also stimulated corn growth. However, neither fulvic nor humic acids had any influence in ameliorating Cd- and Cu-toxicity in corn plants.

Table 3

Influence of fulvic and humic acids on phytotoxicity of various heavy metals to maize

heavy metal	fulvic acid	humic acid
Cd*	–	–
Cu	–	–
Ni*	+	–
V	+	+
Zn**	+	–

\+ positive significant influence
– not significant

* GERZABEK and ULLAH (1990)
** GERZABEK and ULLAH (1988)

Summary

Zea mays (L.) was grown in a nutrient solution to investigate and evaluate the influence of humic (90 and 180 OD/pot) and fulvic acids (27 and 54 OD/pot) on phytotoxicity due to excess Cu (1.0 and 2.0 mg/L) and V (0.5 and 1.0 mg/L). In most cases fulvic and humic acids improved corn tissue production markedly in heavy metal free nutrient solution probably by facilitating the uptake of cations as chelates and affecting metabolic processes. All heavy metal treatments caused a pronounced depression in yields. Both root and shoot growth of maize plants were more severely effected by Cu than V treatments. Fulvic and humic acids moderately increased the corn growth in copper enriched nutrient solution, but none of them could prevent typical Cu-excess chlorosis. Humic and fulvic acids enhanced the growth of corn plants in V-treated nutrient solution. They not only eliminated the toxic effects due to excess V but also stimulated the growth of roots and shoots in V-enriched nutrient solution. This is probably due to the uptake of V-FA or V-HA complexes, which obviously have no toxic effects in corn tissue and the ameliorating influence of the available vanadium at low concentrations to plant growth. Humic acids were found to be more capable of stimulating corn growth than fulvic acids in V-enriched nutrient solution.

Einfluß von Fulvo- und Huminsäuren auf Cu- und V-Toxizität bei Mais *Zea mays* (L.)

Zusammenfassung

Vier Nährlösungsexperimente mit Mais wurden angelegt, um den Einfluß von Fulvosäuren (27 und 54 OD/Gefäß) und Huminsäuren (90 und 180 OD/Gefäß) auf die Pflanzentoxizität von hohen Cu- (1,0 und 2,0 mg/l) und V-Konzentrationen (0,5 und 1,0 mg/l) zu testen. Fulvo- und Huminsäuren konnten das Pflanzenwachstum in schwermetallfreier Nährlösung in den meisten Fällen verbessern. Dies ist wahrscheinlich auf eine höhere Nährstoffverfügbarkeit durch Komplexbildung zurückzuführen. Alle Schwermetallvarianten verminderten die Substanzproduktion drastisch, wobei Kupfer (Sproß bis 85 %) eine deutlich höhere Toxizität als Vanadium (Sproß bis 35 %) zeigte. Fulvo- und Huminsäuren verbesserten das Maiswachstum der Cu-Belastungsvarianten geringfügig, die Cu-Überschußchlorose wurde nicht verhindert. Im Falle des Vanadiums konnten die Huminstoffe der Ausprägung von

Toxizitätssymptomen vorbeugen. Darüber hinaus führte die Kombination von Huminstoffen und Vanadium zu teilweise höheren Erträgen als die der Kontrolle. Dies wurde einerseits mit der Aufnahme von V-Fulvosäure- bzw. -Huminsäurekomplexen, die keine Toxizität zeigen, andererseits mit der fördernden Wirkung von geringen verfügbaren Vanadiumkonzentrationen in der Nährlösung erklärt. Die Kombination von Vanadium und Huminsäuren führte zu stärkeren Wachstumssteigerungen als die V-Fulvosäurevarianten.

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