C. Rodriguez-Barrueco (ed.), Fertilizers and Environment, 443–448.

Thallium concentration in soils and crops and critical values with respect to food chain

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Abstract

1. Thallium is known as an environment chemical, associated with dust from cement industry, sometimes used as K-fertilizer (30% K_2O).

2. In hydroponic experiments Tl was taken up by crops very easily, competing with potassium, and was accumulated in shoots. Toxicity levels (10% and 25% yield reduction) were 130 and 340 mg Tl for beans, however 800 and 1900 mg Tl/kg dry matter for rape.

3. Toxicity symptoms appeared as chlorosis along the leaf nervature.

4. In pot experiments cement dust was incorporated into soils (6.5 kg/pot) at pH 5.4, 6.5, 7.0 and an annual deposition of 125 g/m^2 The critical concentrations in plants (25% yield reduction) were 20 mg Tl for rye grass, 15 mg Tl for beans and 575 mg Tl/kg for rape on dry matter basis. Toxicity limits (25% yield reduction) in soils were: 8 mg Tl for rye grass, 11 mg Tl for beans and 10 mg Tl/kg soil for green rape.

5. Between thallium concentration in soils and plants there were positive correlations (rye grass r^2 =0.63, beans r^2 =0.78, rape r^2 =0.58).

6. CONCLUSIONS: Considering the tendency of green rape (as a fodder crop) to accumulating Tl in high concentrations the generally accepted limit of 2.5 mg Tl/kg dry matter seems too high with respect to great risks for food chain. Cement dust should be eliminated as K-fertilizer.

Introduction

The critical concentration of heavy metals in soil and in plant tissues has long been a subject of great interest for crop production and for public health. This regards the toxicity effects on plants and health hazards to human as well as to animal life and other forms of life (Allison and Dzialo, 1981; Page, 1981; Hall, 1972; Sauerbeck, 1982; Zitko *et al.*, 1975; Beckett and Davis, 1977).

Thallium is considered as toxic element for the environment and it is known that its presence is associated with dust from cement industry (Achenbach *et al.*, 1979; Heckt, 1982; Smith and Carson, 1977; Prinz *et al.*, 1979; Bambauer and Schaefer, 1981).

The use of dust from cement industry, rich in potassium, as fertilizer involves the hazardous effects of thallium on animals and human beings.

For this study the 2.5 mg Tl/kg dry matter in plant tissues, as a safe and general accepted limit with respect to food chain, was the reference point to determine the phytotoxic level of thallium concentration in soils and plants. At the same time the specific toxicity symptoms produced on different crops, were investigated, after the application of $TlCl_3 \cdot H_2O$ in nutrient solution.

Material and methods

Nutrient solution experiments

In plastic pots (4 L) which contain Hoagland solution, the plants of each crop that were previously sprouted in Blaehton were transplanted, four plants of bush beans (var. marona), six plants of green rape (var. akela), respectively. After eleven days for bush beans and sixteen days for the green rape the solution was changed with one that contained thallium in different concentrations of 0, 1, 2, 5, 10 and 20 mg Tl L^{-1} as $TlCl_3 \cdot H_2O$.

The plants were left to grow for 21 days for bush beans and 34 days for the green rape and then harvested for analysis. The nutrient solution was changed a few

Table 1. Characteristics of experimental soils

		Soil		
		I	II	III
Clay	%	18	17	13
Silt		55	55	60
Sand		27	28	27
pH		5.6	6.2	7.0
Organic matter	%	3.2	3.7	3.7
Thallium	mg/kg (d.m. soil)	0.42	0.37	0.67
CEC		12.9	14.9	12.8
Ex-Na		0.02	0.1	0.02
Ex-K	meq/100 g	0.5	0.9	0.3
Ex-Ca	soil	8.4	12.0	10.8
Ex-Mg	1.8	1.9	1.7	
Sum		10.7	14.9	12.8
Base saturation	%	82.9	100	100

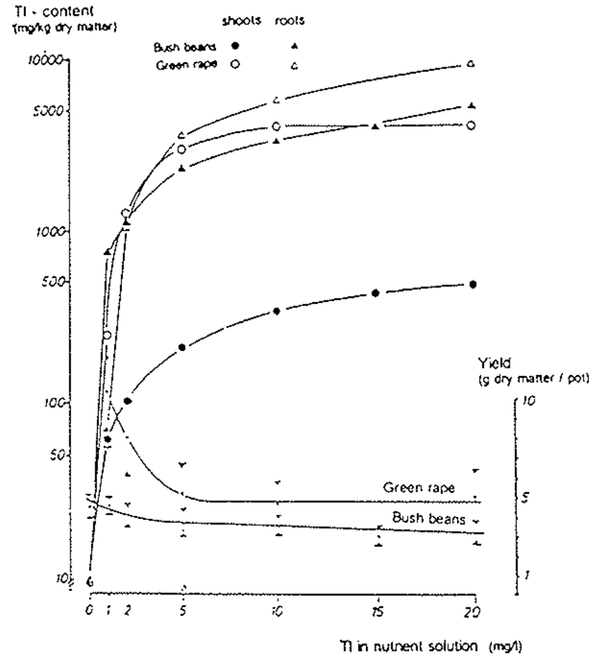

Fig. 1. Thallium contents and yield of bush beans and green rape as they are affected of thallium supply in nutrient solution.

times during the growing period in order to keep the concentration constant.

Soil experiments

The soil experiments involves the use of three different soils with pH 5.6, 6.2 and 7.0 (sandy-silty loam), as Table 1 shows. The dusts were mixed with soil 6.5 kg per pot corresponding to an annual deposition of 125 g/m^2 and the latter one was increased up to ninefold amount. Because the dust contains also calcium and potassium the corresponding amount of these elements was added to the control pots. Each crop was cultivated in the pots, in a greenhouse, and the next crop was planted in the same pots in a series, bush beans(var. marona) – green rape (var akela) – rye grass (var. perma). The plants were harvested at the beginning of flowering (bush bean), at the end of vegetative period (green rape) and at the 25 cm height (rye grass). The total thallium concentration was ranged between 0.4 to 13.1 mg Tl per kg of soil (Tl-soil+Tl-dust). The amount of Tl added as Tl-dust was ranged between 0.05 to 12.1 mg Tl per kg of soil. The crops received the common fertilization practice but concerning the estimated amount of nutrient added, the amount of nutrient the dust contained was taken into account.

Thallium was extracted from plant tissues by concentrated HNO_3 and from the soil by HNO_3 and H_2SO4 and determined photometrically with brilliant green (Scholl, 1981).

Results

Experiments with nutrient solution

Table 2 shows the results of nutrient culture. Yield reduction, statistically significant, was observed at 2 mg Tl/l. This reduction of bush beans was about 11% for shoots and 20% for roots. The corresponding reductions for the green rape were 22% and 23%.

Thallium was accumulated in high amounts in the plant tissues, Table 3, even at a concentration of 1 mg Tl/l and reached 62 ppm in the shoots and 742 in the roots of bush beans. The corresponding amounts for the green rape were 244 and 57 ppm.

After the manipulation of the available data, the concentration of Tl in the plant tissues of bush beans was 130 and 340 mg/l Tl when the corresponding yield reduction was 10% and 25%. The latter reduction was estimated for a growth period of 4 weeks from which the last ten days the plants were transplanted into the Tl

Table 2. Yield production of bush beans and green rape (After 10 days and 18 days influence of $TlCl_3 \cdot H_2O$ correspondingly)

Tl-conc. (mg/l in N.S.)	Yield (g dry matter per pot)			
	Bush beans		Green rape	
	shoots	roots	shoots	roots
Control	4.5	1.0	10.3 a*	1.3
1	4.5	0.9	11.0 a	1.2
2	4.0	0.8	8.0 b	1.0
5	3.7	0.7	5.2 c	0.7
10	3.5	0.6	4.7 c	0.7
20	3.2	0.6	5.1 c	0.7
p 5%	0.6	–	* Variance a > b > c	–

Table 3. Thallium concentration and uptake of bush beans and green rape from nutrient solution

Tl-conc. (mg/l in N.S.)	Thallium concentration in plant (mg Tl/kg dry matter)			
	Bush bean		Green rape	
	shoots	roots	shoots	roots
Control	< 1	3	1	8
1	62	742	244	57
2	104	1119	1134	991
5	212	2311	2983	3517
10	337	3336	4057	5822
20	487	5207	4163	6701

rich solution. With regard to green rape the concentration of Tl in the plant tissues was 800 and 1900 mg/l Tl when the corresponding yield reduction was 10% and 25%. The latter reduction was estimated for a growth period of 5 weeks from which the last eighteen days the plants were transplanted into the Tl rich solution.

If the Tl uptake (mg Tl per kg dry matter) is plotted against Tl concentration (mg Tl/l) in the nutrient solution (semilogarithmic scale), the concentration effect can be seen, Fig. 1.

From these plots one can see that the Tl uptake is a rapid one at the very low concentration of Tl in the nutrient solution and reaches already maximum concentration at about 1 mg Tl/l, whilst the plants seem not to be harmed by the presence of Tl, but at the same time is taking up large amounts of available Tl in solution.

From 2 mg Tl/l on, the plants continue to take up Tl, so that the Tl accumulation in plant tissues reaches the toxicity level and toxicity symptoms start appearing. The reduction of plant growth is very obvious and can be explained as "concentration effect".

In this figure one can see that in case of green rape at the concentration of 2 mg Tl/l the concentration of Tl in the shoot is higher than that in roots. The situation is reversed at the concentration of 5 mg Tl/l. If we look to the bush beans crop, even at the very low concentration of Tl in the nutrient solution, the concentration of Tl in the roots is always very much ahead to that of the shoots. Looking at the curves that show Tl concentration in shoots and roots for the two crops, the corresponding curves for the green rape go very close together while the curves for the bush beans are far away from each other.

(a)

(b)

Fig. 2. (a) Symptoms of thallium toxicity in bush beans at 10 mg Tl/l nutrient solution (b) Symptoms of thallium toxicity in green rape at 20 mg Tl/l nutrient solution

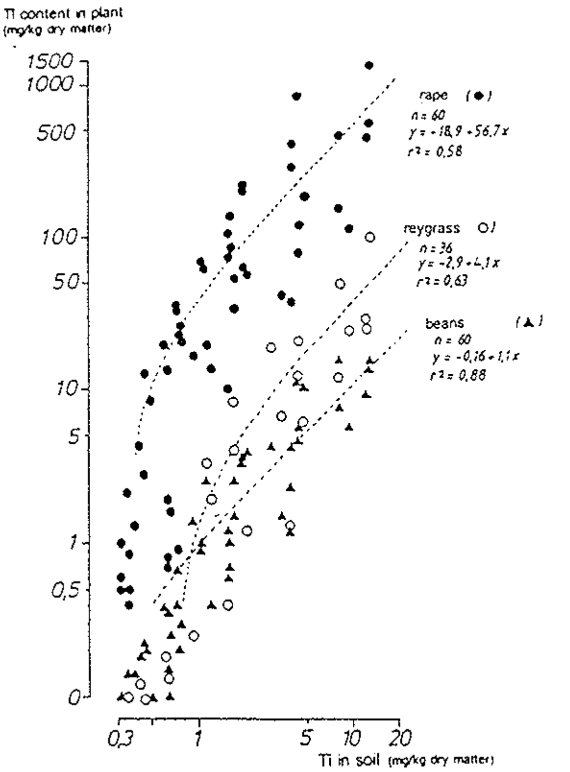

Fig. 3. Relation between thallium content in soils and crops.

This reveals as well a difficulty of Tl transport to shoots of bush beans as that there is a big difference with regard to Tl uptake between bush beans and green rape.

Figures 2a-b show the characteristic symptoms of Tl toxicity. For the bush beans the symptoms appear as chlorosis along the leaf nervature and for the green rape the symptoms are necrotic spots along the leaf nervature as well. These spots in severe situations are extended to the whole area between the leaf nervature.

With respect to phytotoxicity, beans proved to be very sensitive to Tl, compared with green rape which is very tolerant in spite of much high thallium uptake and concentration in leaves.

Experiments with soils

The pot experimental data (Fig. 3) revealed again a positive linear relationship between thallium supply to soil and thallium concentration in plants.

However a negative correlation exists between the thallium concentration in plant tissues and crop yield regardless the pH values. The differences in Tl uptake between the crops are distinguishable in the order of green rape > rye grass > bush beans with the regression coefficients $r^2 = 0.58$, $r^2 = 0.63$ and $r^2 = 0.78$.

From pot experiment it has been found that the addition even of 0.05 mg Tl/kg soil (total Tl content 0.47 mg Tl/kg soil) has significantly increased the Tl concentration in green rape. In contrast, 0.15 mg Tl/kg soil (total Tl content 0.56 mg Tl/kg soil) has to be added for the bush beans crop to produce a such significant increase. Tl availability is higher in acid soils and 18% of the added amount in dust was taken up by the plants.

A reduction of 25% in yield occurred at a concentration of 20 mg Tl/kg dry matter of plant tissues for rye grass, 15 mg/kg for beans and 575 mg/kg for rape.

The critical concentration of Tl in the soil at which a 25% reduction in yield occurred is: 8 mg Tl/kg dry soil for rye grass, 11 mg/kg for bush beans and 10 mg/kg for green rape.

Discussion

The experiments of the present study show a specific behaviour of the crops with regard to Tl. Green rape appeared to possess an ability to take up greater amounts of thallium than the rye grass and bush beans. These differences in uptake have been reported by Hoffmann *et al.*, 1982; Schweiger and Hoffmann, 1983.

Our experimental data from soil and nutrient solution show that Tl in green rape is more mobile than in bush beans. Differences in Tl mobility have also been mentioned by Hoffmann *et al.*, 1982; Kick *et al.*, 1981; Cataldo and Wildung, 1978.

The minimum concentration of an element that produces 10% yield reduction, is considered (Davis *et al.*, 1978) from the phytophysiological point of view, as "critical value" of plant toxicity. Such critical values, at which 25% of yield reduction is observed for the tested crops in nutrient solution culture, are 340, 1900 mg Tl/kg dry matter of plant tissues for bush beans and green rape respectively. However in soil culture experiments such reduction (25%) occurred when the Tl concentration in plant tissues is 15, 575 and 20 mg/kg dry matter for bush beans, green rape and rye grass correspondingly. The differences in the size of the "critical values" for toxicity, reported elsewhere, have their source from the level of yield reduction that has been adopted (10% or 25%).

Davis *et al.*, 1978 reported that the critical concentration for 10% yield reduction is 20 mg Tl/kg dry matter plant tissues for burley crop in sand culture experiments. Hoffmann *et al.*,1982 working with green rape and cabbage in soil culture, where the Tl was given as $TlNO_3$, mentioned 1000 and 30 mg Tl/kg dry matter as critical values.

In our experiments with bush beans and green rape, when the toxicity symptoms were observed, the corresponding concentration of Tl was 200 and 3000 mg Tl/kg of shoots.

The critical concentrations of Tl in our soil are 11, 10 and 8 mg Tl/kg for bush beans, green rape and rye grass. The latter ones are close to the ones reported for other crops (Hoffmann *et al.*,1982).

The concentration of Tl in soil at which the crops are severely contaminated must be investigated for each individual crop. The general accepted limit concerning the Tl content in soil is 1 mg Tl/kg. The limit for fodder crops and eatable crops is 0.25 mg Tl/kg fresh plant tissues and 2.5 mg Tl/kg dry matter.

It is an important result of our experiments with green rape that even a concentration of 1 mg Tl/kg soil was high enough to exceed the accepted limit of Tl content in plants. This limit is much more easier to be exceeded when the soil-thallium is brought high by using the dust from dust industry.

Conclusions

The use of dust from cement industry as K-fertilizer has to be considered very seriously. The contamination of soil and plants with high amounts of thallium can exceed often the general accepted limit of 1 mg Tl/kg soil and 2.5 mg Tl/kg plant dry matter for human or animal nutrition. Considering the great tendency of green rape (a fodder crop) to accumulate very high amounts of thallium without visible toxicity symptoms it is a great risk to food chain when this crop is fertilized with byproducts. Therefore cement dust should be eliminated as K-fertilizer.

References

Achenbach CO, Hauswurt C, Heidrichs R, Ziskoven F, Koehler J, Smend J and Kowalewski S (1979) Toxizitaet und Teratogenitaet von Thallium, Dt Aerztebl 48: 3189–3192.

Allinson DW and Dzialo C (1981) The influence of lead, cadmium and nickel on the growth of ryegras and oats, Plant and Soil 62: 81–89.

Cataldo DA and Wildung RE (1978) Soil and plant factors influencing the accumulation of heavy metals by plants, Environ Health Persp 27: 149–159.

Bambawer HV and Schaefer (1981) Der minerabestand eines Thallium-haltigen Reingasstaubes aus der Zementherstellung, Naturwiss 68: 571–572.

Beckett PHT and Davis RD (1977) Upper critical Levels of toxic elements in plants, New Phytol 79: 95–106.

Davis RD, Beckett PHT and Wollan E (1978) Critical levels of twenty potentially toxic elements in young spring barley, Plant Soil 49: 395–408.

Hall SK (1972) Pollution and Poisoning, Environ Sci Technol 6: 31–34.

Hoffmann G, Schweiger P and Scholl W (1982) Aufnahme von thallium durch landwirtschaftliche und gartnerische Nutzpflanzen, Landw Forsch 35: 45–54.

Heckt H (1982) Die verschiedenen Wege und Moeglichkeiten des Eintrags von Schwermetallen in die Futtermittel und die dabei ru beachtenden Belastungsgrenzen, Landw Forsch 39: 94–107.

Kick H, Buerger H and Sommer K (1981) Vegetationsversuche zur Aufnahme von Berillium und Thallium durch Sommergerste und Raps, Landw Forsch 34: 186–190.

Page AL (1981) Heavy metals in the Environment, Proceedings at an international conference in Amsterdam, CEP Consultant Ltd., Edinburgh, p 206.

Prinz B, Krause CjHM and Stratmann H (1979) Thallium schaeden in der Umgebung der Dyckerhoff-Zementwerke AG in Lengerich, Westfalen, Staub-Reinhalt Luft 39: 457–462.

Sauerbeek D (1982) Welche Schwermetallgehalte in Pflanzen duerfen nicht ueberschritten werden,um Wachstumsbeein traechtigungen zu vemeiden?, Landw Forsch 39: 108–129.

Scholl W (1981) Bestimmung von Thallium in verschiedenen anorganischen und organischen Matrizes–ein einfaches photometrisches Routineverfahren mit Brillant gruen, Landw Forsch 35: 216–223.

Schweiger P, und Hoffmann G (1983) Thallium-Aufnahme verschiedener Pflanzen in Hydrokultur, Kali Briefe 16: 391.

Smith IC and Carson BL (1977) Trace metals in the environment, Vol. 1, Thallium, Ann Arbor science Publ Inc, Michigan.

Zitko V, Carson MV and Carson WG (1975) Thallium occurence in the enviroment and toxicity to fish, Bull Environ Contam Toxical 13: 23.