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CRITICAL LEVELS OF TWENTY POTENTIALLY TOXIC ELEMENTS IN YOUNG SPRING BARLEY

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SUMMARY

The *upper critical level* of a potentially toxic element is its minimum concentration in actively growing tissues of a plant at which yield is reduced.

The following values for upper critical levels in the leaves and shoots of spring barley at the five-leaf stage were determined by means of sand culture experiments in the glasshouse: Ag 4; As 20; B 80; Ba 500; Be 0.6; Cd 15; Co 6; Cr 10; Cu 20; Hg 3; Li 4; Mo 135; Ni 26; Pb 35; Se 30; Sn 63; Tl 20; V 2; Zn 290; Zr 15ppm of dry matter. They are presented as the basis of a simple procedure for monitoring harmful accumulations of these elements in the soil environment. We also present the concentrations of simple solutions of these elements which induced toxicity under the conditions of the experiments. There was little uptake of Bi, Sb and Te even from solutions that reduced the yield of young barley. It is believed that these elements may have reduced the availability or translocation of other nutrient elements.

INTRODUCTION

Toxic elements in sewage sludge[5] are likely to accumulate in soils onto which the sludge is disposed[2]. Good current practice therefore monitors sludges or sludge-treated soils for Zn, Cu, Ni, Cr and Pb, and for Cd and Hg which are particularly toxic[21]. However, there are some 20–30 more elements which have shown to be toxic to some organisms in certain circumstances (*e.g.* Bowen[8]). For some of these it is largely unknown whether sludges contain enough of them to give rise to significant accumulations in sludge-treated soils, or whether their toxic forms persist in the soil. Furthermore, there are no established tests whereby the hazards presented by accumulations of many of these elements in soil can be assessed.

In view of these uncertainties we have attempted, in collabora-

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tion with the former West Hertfordshire Main Drainage Authority, to develop simple tests using indicator plants to serve as interim monitoring procedures.

Choice of procedures

Numerous studies (*e.g.* Epstein,[14]) have shown that for any particular set of growing conditions, the dry matter yield of a plant varies with the concentration of an essential element in its actively growing tissues according to the diagram of Fig. 1. The height of the

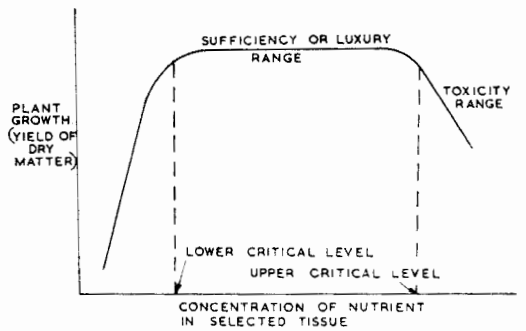


Fig. 1. Generalised plot of the yield of plant dry matter as a function of the concentration of a nutrient element in it (after[30])

plateau of sufficiency depends on the growing conditions. Essential elements show a 'lower critical level' indicative of deficiency and usually an 'upper critical level' indicative of toxicity. Both of these are employed in advisory work: diagnostic tissue analyses for trace element deficiencies are interpreted in the light of the appropriate deficiency thresholds,[30] and Harrod[16] has employed leaf analyses to confirm Mn toxicity.

It has already been demonstrated[4] that the upper critical level of Cu, Ni and Zn in young spring barley is remarkably independent of variations in growing conditions, and of the levels of other nutrients, sufficient to cause a threefold variation in the plateau yield. We have suggested therefore that it would be possible to assess the hazards of accumulations of these elements in soil by growing a test plant on the suspect sites, or on soil from them, and comparing the concentrations of these elements in the plant tissue with the corresponding upper critical levels. Barley is more widely grown than

any other crop, is easy to grow and sample, and has already been used in related experiments (*e.g.*[3 12 25 32]). We have therefore proposed spring barley, harvested at the five-leaf stage, as the test plant.

It seemed likely that once in the toxic range, the yield of a plant would depend more closely on the concentrations of toxic elements in its actively growing tissues than on how they got there, or on their forms and concentrations in the soil or in culture media (*e.g.* Bould, Bradfield and Clarke,[7]). The constancy of the upper critical levels for Cu, Ni and Zn was consistent with this assumption. We assume provisionally that the upper critical level of any other toxic element that shows a yield curve like that of Fig. 1 is also effectively constant and therefore provides a basis for simple monitoring procedures. Unfortunately, though there have been considerable efforts (see Chapman,[11]) to determiine the deficiency thresholds of many elements in many plant species, their upper critical levels are less well known. This paper presents the results of experiments to determine preliminary values for the upper critical levels of 20 elements in young spring barley.

MATERIALS AND METHODS

Selected undressed seed of spring barley (*Hordeum vulgare* L. cv Julia) was pregerminated in demineralised water for 48 h, and 8–15 seeds planted in 20 cm pots of washed silver sand (7.5 kg) in the glasshouse. Each pot was percolated with 1.5 l of the appropriate solution before sowing and, after emergence, flushed through daily by top-watering with the solution, and weekly with 1.5 l of demineralised water, followed by 500 ml solution, to wash out accumulated salts.

The *basic nutrient solution* (170 ppm N as nitrate; 41 P; 156 K; 36 Mg; 48 S; 160 Ca; .27 Mn; .032 Cu; .032 Zn; .27 B; .024 Mo; 1.4 Fe as sodium ferric EDTA; after Hewitt[17]) contained N, P and K and essential elements in the proportions that preliminary experiments had shown to produce maximum dry matter yields. To this were added graded concentrations (Table 1) of a soluble salt of each potentially toxic element in the hope that they would produce a set of barley plants in which the tissue concentrations would range from the benign to the toxic. There were two control pots for each set of treated pots. In a few cases (Table 2) these received basic nutrient solution alone, but in most cases sodium or potassium salts were added to match the anion concentration of the most concentrated of the corresponding treatment solution. Nine elements (* in Table 1) formed insoluble precipitates with the basic nutrient solution. In these cases the basic nutrient solution and simple solu-

TABLE 1

Concentrations of potentially toxic elements in the nutrient solutions

Element	Salt used		Levels (ppm of element)				
Ag	$AgNO_3$*		0.5	5	50	200	
As	Na_2HAsO_4*		5	10	20	50	
B	H_3BO_3		1	5	10	20	
Ba	$BaCl_2$*		20	50	100	200	
Be	$BeSO_4$		0.05	0.5	5	50	
Bi	$Bi(NO_3)_3$*		0.5	5	50	200	
Cd	$CdSO_4$		0.05	0.5	1	5	
Co	$CoCl_2$	*a*	10	20	50	100	
		b	0.05	0.5	2.5	5.0	
Cr	$KCr(SO_4)_2$		20	50	100	200	
Cu	$CuSO_4$		5	10	20	50	100
Hg	$HgCl_2$*		10	20	50	100	
Li	LiCl	*a*	0.5	5	50	200	
		b	0.1	1	10	100	
Mo	Na_2MoO_3		0.5	5	50	200	
Ni	$NiCl_2$	*a*	5	10	20	50	100
		b	0.05	0.5	1.0	5.0	
		c	0.05	0.5	2.5	5.0	
Pb	$Pb(NO_3)_2$*		10	20	50	100	
Sb	$Sb_2(SO_4)_3$*		10	20	50	100	
Se	SeO_2	*a*	10	20	50	100	
		b	0.05	0.5	2.5	5.0	
Sn	$SnCl_2$*		20	50	100	200	
Te	$TeCl_4$*		0.5	5.0	50	200	
Tl	TlCl		0.5	5.0	50	200	
V	VCl_3		0.5	5.0	50	200	
Zn	$ZnSO_4$		10	20	50	100	200
			0.05	0.5	5.0	10.0	
Zr	$Zr(NO_3)_4$*		20	50	100	200	

* alternate solutions

tions of soluble salts of the elements were applied to the pots in alternate days ('alternate solutions'); their controls received basic nutrient solution and NaCl or $NaNO_3$ solution on alternate days as above.

The position of all pots was randomized on days 0 and 14 and the plant tops harvested when the corresponding control plants had reached the five-leaf stage at the onset of tillering. Distinctive toxicity symptoms were noted (Table 3).

The harvested parts were dried at 90°C, and weighed. Dried and ground material from the As, Ba, Hg, Se, Tl, V and Zr treatments was pelleted with pure cellulose for analysis by X-ray fluorescence. Material from the remaining treatments was digested with concentrated HNO_3 and then (except for the Pb-treated plants) with a tri-acid mixture (67% conc. HNO_3, 27% $HClO_4$ (60%), 6% conc. H_2SO_4). Cd, Co, Cr, Cu, Li, Ni, Pb, Te and Zn were determined by

atomic absorption spectrophotometry and Be and Sn by emission spectrography. The remaining elements were determined by colorimetric methods (Ag[28]; B[13]; Bi[29]; Mo[19]; Sb[33]). If, in the first trial, the tissue concentrations of an element all lay below or all above its upper critical level, the trial was repeated with different concentrations until it produced values that bracketed the upper critical level.

RESULTS

The dry matter yields of the control pots, and the time taken to reach the five-leaf stage, varied considerably with the weather and season (Table 2), so the weights for all treatments in each trial are expressed as percentages of the mean weight of their two controls, and plotted against the logarithm of the tissue concentration of the element (Fig. 2). Barley yields were depressed by high concentrations of Bi, Sb and Te in the nutrient solutions but these elements could

TABLE 2

Control solutions, growth periods and weights of control plants

	Control solution	Dates	Age (days)	Mean dry weight per plant (mg)
Ag, Bi	BN + $NaNO_3$ 2.89*	12.7–8.8	27	284
As, Hg, Sn	BN + NaCl 3.76	22.5–13.6	22	147
B	BN	7.5–29.5	22	239
Be	BN + Na_2SO_4 20.76	17.7–13.8	27	582
Cd	BN + Na_2SO_4 0.06	19.8–11.9	23	239
Co *a*, Ba	BN + NaCl 3.76	22.5–13.6	22	274
Co *b*, Se *b*	BN + NaCl 0.17	9.8–28.8	19	171
Cr	BN + K_2SO_4 8.27	22.5–13.6	22	295
Cu, Zn *a*	BN + Na_2SO_4 3.94	7.5–29.5	22	214
Li *a*, V	BN + NaCl 28.7	17.7–13.8	27	393
Li *b*	BN + NaCl 1.44	5.9–2.10	27	189
Mo	BN	17.7–13.8	27	465
Ni *a*	BN + NaCl 2.05	7.5–29.5	22	237
Ni *b*	BN + NaCl 0.17	19.8–11.9	23	159
Ni *c*	BN + NaCl 2.05	11.6–5.7	24	141
Pb, Zr	BN + $NaNO_3$ 8.8	22.5–13.6	22	217
Sb	BN + $MgSO_4$ 1.23	22.5–13.6	22	189
Se *a*	BN	22.5–13.6	22	210
Te, Tl	BN + NaCl 6.67	12.7–8.8	27	199
Zn *b*	BN + Na_2SO_4 0.26	9.8–28.8	19	159

* $M \times 10^{-3}$

BN Basic nutrient solution

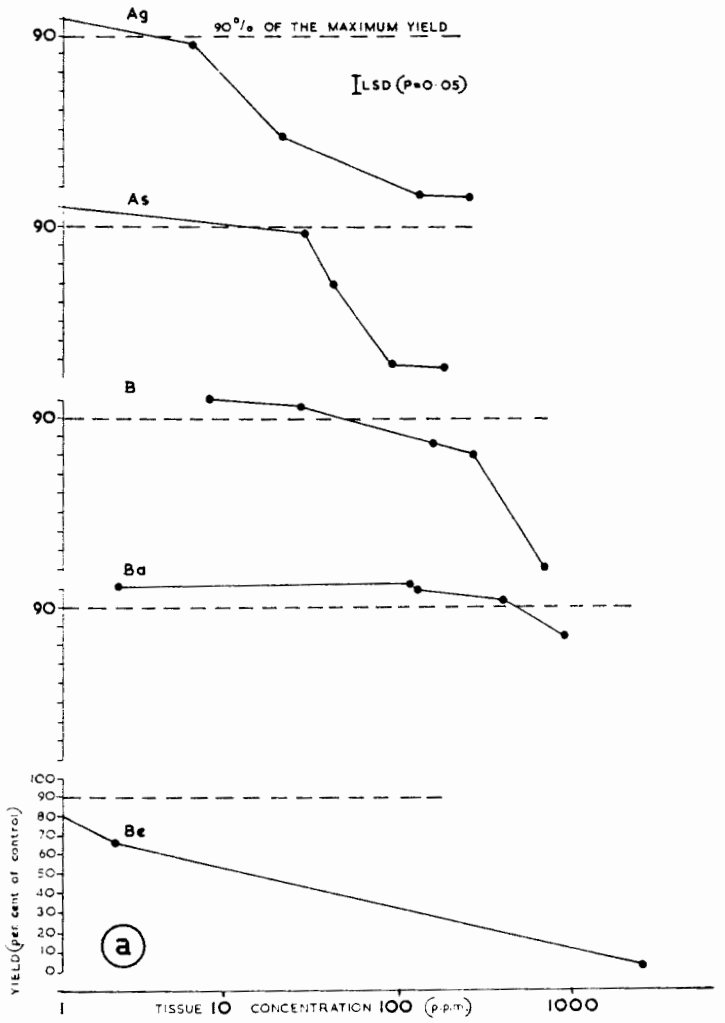
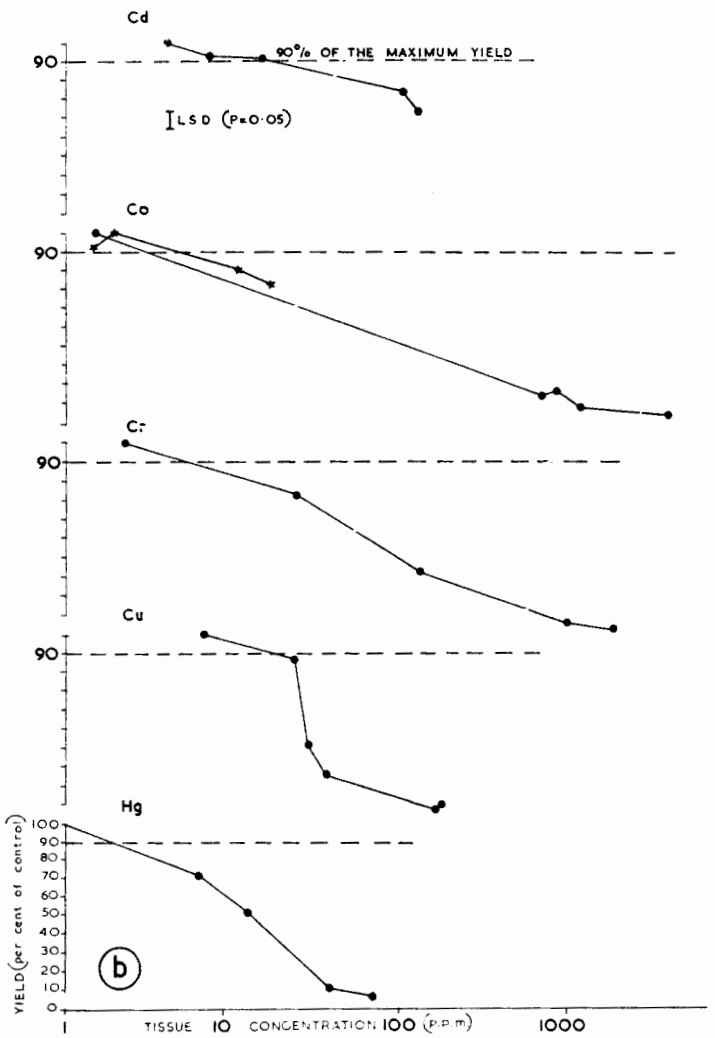


Fig. 2. Dry matter yield (per cent of control) against log tissue concentration (ppm), for 20 elements in young spring barley. *See also following pages.*

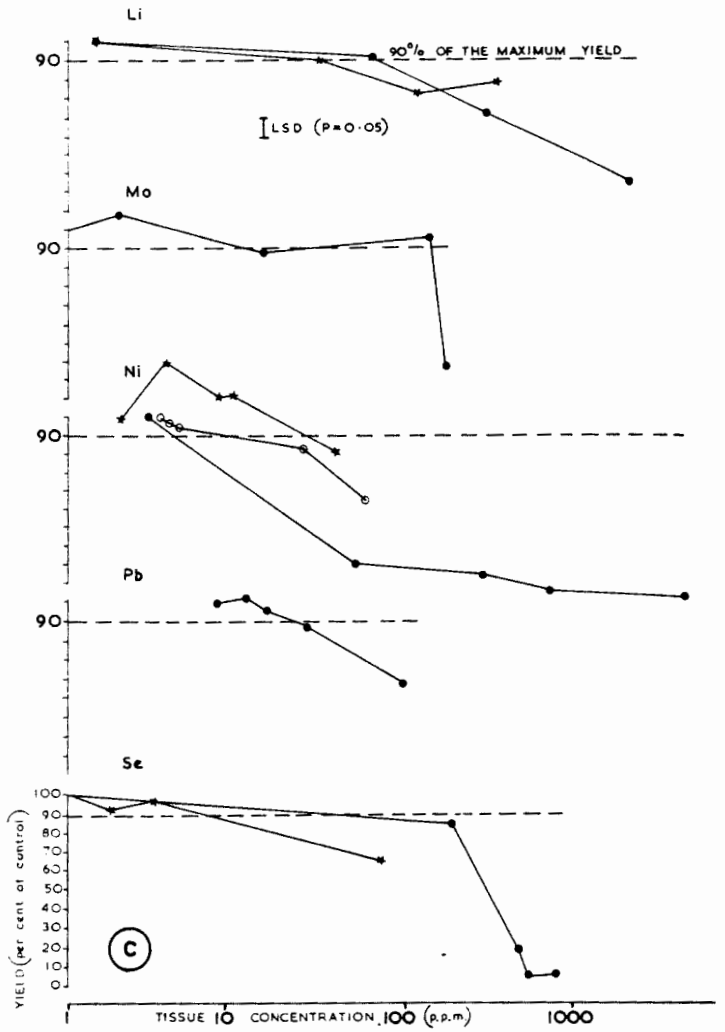
not be detected in the plant tops (<2 ppm). For the remainder the results are consistent with Fig. 1.

For most elements visual toxicity symptoms (Table 3) became apparently only in severely poisoned plants and in general, agreed with previous observations[18]. In some trials the barley showed non-specific symptoms of toxicity which were clearly distingiushable



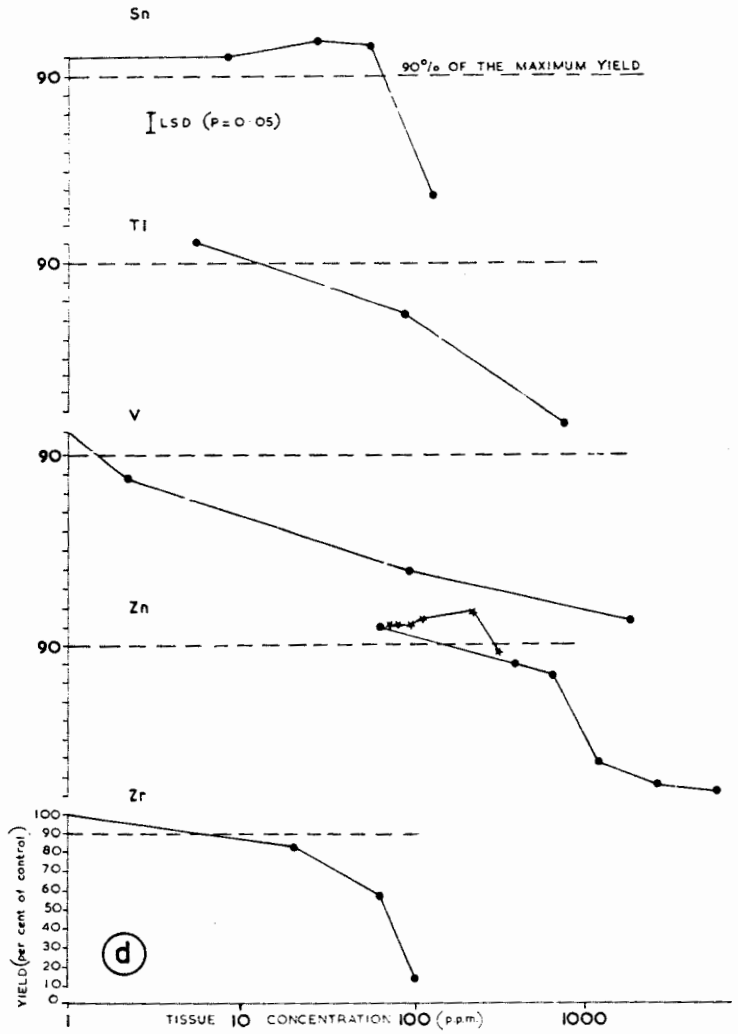
from those for macro-nutrient deficiencies. The Te-treated plants appeared to display symptoms of P deficiency.

Strictly the upper critical level of an element is its tissue concentration at the point of inflexion (*i.e.* x on Fig. 3a), and elsewhere[4] we have presented a procedure for locating this point without employing subjective judgement. In the present trials, with relatively sparse data, it was easier to recognise the concentration y (Fig. 3a) corresponding to a 10% reduction in the yield of dry matter. Table 3 pre-



sents the results. However even this may present problems of interpretation. Consider Fig. 3b, where X———X is the true plot but X— — —X is the line that joins the measured points; q corresponds to y above but p is the value that would be read from the graph. Hence, some of the levels prented (Table 3) are likely to be lower than the true values: however errors in this sense will not invalidate the test procedure proposed.

Barium proved to be the least hazardous of the elements tested. It



is likely that solutions of barium chloride will give rise to harmful osmotic effects or to chloride toxicity before they are concentrated enough for a specific Ba toxicity.

Bi, Sb and Te may have depressed barley yields by reducing the availability or translocation of other nutrients, perhaps phosphate.

Table 3 also presents very approximate estimates of the critical levels of these elements in herbage for animals. The toxicity of an ingested element depends on many factors including the amount

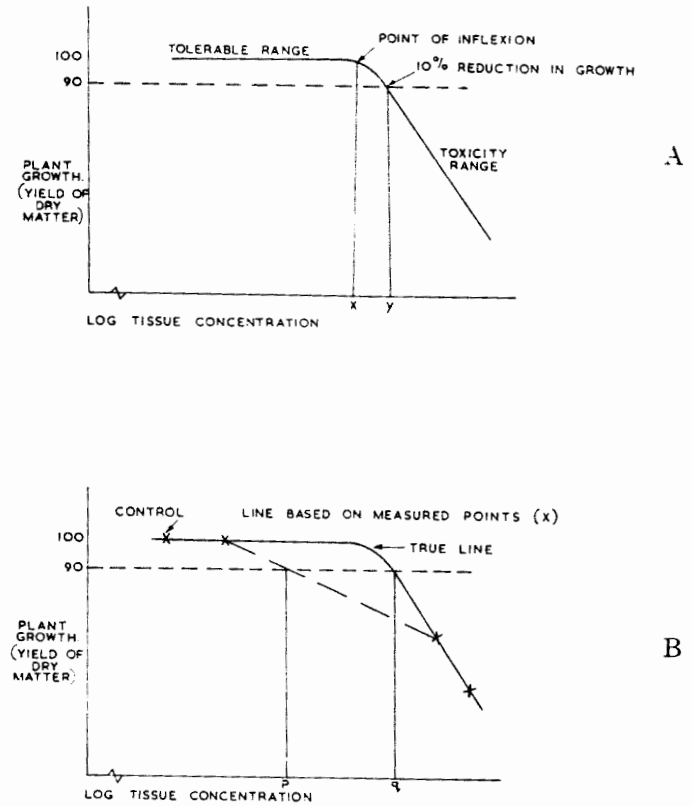


Fig. 3. Generalised plot of yield as a function of the concentration of a toxic element in plant tissue, showing the upper critical level.

eaten, the age and health of the animal, and the balance of other elements in the diet[31], and it is particularly difficult to assign threshold figures for Cd, Hg and Pb, which are cumulative poisons[8]. Note however that the critidal levels for animals of Cd, Hg, Mo, Pb and Se in herbage appear to be lower than those for the barley plant itself, so animals may be poisoned by apparently healthy plants.

Table 3 also records the minimum concentrations of potentially toxic elements in the nutrient solution that, under our conditions, reduced the yield of five-leaf barley. The critical solution concentrations for the elements that had to be applied in 'alternate solutions' are bracketed, and are probably higher than the concentrations experienced by the barley roots.

TABLE 3

Upper critical levels

Critical levels for barley			Approximate critical levels for livestock (ppm total diet)***	Visual symptoms of toxicity
In tissue (ppm dry wt.	Other values* (with Ref.)	In solution**(ppm)		
4 (4–5)		(0.5) as Ag^{+}		Red-brown patches on leaves, red stems.
20 (11–26)		(4) as $HAsO_4^{2-}$		Yellow leaves, red stems.
80 (40–130)	200[9]; 150[24]	2 as BO_3^{3-}		Brown specks on leaves, yellow leaves
500 (400–800)		(160) as Ba^{2+}		—
0.6		0.6 as Be^{2+}		Yellow leaves, stunted stems.
15 (14–16)	8[4]	0.5 as Cd^{2+}	3	Red-brown patches on leaves, stunted stems
6 (3–9)		1 as Co^{2+}	50	Pale green leaves with pale longitudinal stripes.
10 (5–20)		8 as Cr^{3+}	50	Yellow leaves, pale green longitudinal stripes on leaves.
20 (18–21)	20[1]; 20[26]; 20–30[20]; 30[22]; 20[4];	4 as Cu^{2+}	50	Bluish leaves.
3 (2–5) . .	6[23]	(4) as Hg^{2+}	1	Yellow leaves, red stems.
40 (22–60)		1 as Li^{+}		Narrow curled and twisted leaves.
135 (130–140)		70 as MoO_3^{2-}	10	
26 (4–26)	50[18]; 147[6]; 25–30[15 22 27] 11[4]	1.5 as Ni^{2+}	50	Longitudinal white stripes and brown patches on leaves.
35 (20–35)		(25) as Pb^{2+}	3	
30 (7–90)		5 as Se_3^{2-}	5	
63		(110) as Sn^{2+}		Red stems.
			25	Red stems, premature senescence of leaves.
20 (11–45)		0.5 as Tl^{+}		Yellow leaves.
2 (1–2)		1	25	Pale green longitudinal stripes on leaves.
290 (160–320)	400[10]; 300[24]; 200[4].	9 as Zn^{2+}	500	Yellow leaves, brown patches and pale green stripes on leaves.
15 (5–18)		(40) as Zr^{4+}		Red stems.

ral species. ** bracketed figures for alternate solutions. *** tentative figures, generalized mainly wood[31]

DISCUSSION

The critical levels derived from Fig. 2 are no more precise than the exploratory experiments from which they are derived or the logarithmic form in which they are plotted. Nevertheless they are of the same order of magnitude as our more precise values for Cu, Ni, Zn and Cd,[4] and such values as may be extracted from the literature, also presented on Table 3. We present them therefore as the basis for preliminary assessments of harmful accumulations of potentially toxic elements until such time as more exact tests have been developed.

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