# Transfer of trace elements with low soil mobility into plants

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#### **ABSTRACT**

Trace elements with a low mobility and with a low transfer are Cu, As, Be, V, Cr, Hg. Copper has at low mobility an increased transfer quotient (content plant/soil). The lowest mobility and transfer show Cr and Hg. Only at the very high contents or increased mobilities of trace elements, which accompany the anthropogenic contamination, soil critical loading for crops can be attained. Because of the amount of the examined extremes, it was not possible to derive the proper critical values. Therefore we were able to assess only critical protective values. They represent minimum total contents of trace elements or their mobile forms, which eliminate risks.

Keywords: Cu; As, Be, Cr, V, Hg; critical transfer into plants; protective critical values

This paper turns attention to trace elements (TEs) characterized by low mobility (Hornburg and Brümmer 1993, Němeček et al. 1998, Podlešáková et al. 1999, Němeček and Podlešáková 2001a, Podlešáková et al. 2001a) in soils (As, Cu, Be, V and especially Cr, Hg) and low transfer (Podlešáková et al. 2001a, b) quotient (except of Cu). But some of them are zootoxic and humanotoxic – Hg, As, Be and in a lesser degree phytotoxic. Cu is an important biogenic element with a higher plant uptake. Some of them, especially As, Cu, Cr, Be, V can occur in soils in very high concentrations due to geogenic origin (Koch and Gruppe 1993, Němeček et al. 1996), in mafic and ultramafic rocks and their weathering products (Cr, V, Cu – from other TEs Ni, Co) or in ore zones of acid rocks (especially As, Cu – from the others TEs Pb, Zn).

Even when these TEs are characterized by a low mobility, appropriate attention must be paid to their extreme values (Němeček and Podlešáková 2001a). They are more affected by factors that increase their solubility (especially pH) than those TEs, the mobility of which is due to anthropogenic inputs (Koch and Gruppe 1993).

Moustakas et al. (1997) found in ore zones total contents of Cu up to 3000 mg.kg<sup>-1</sup>. The content of Cu in wheat growing on soils with extreme geogenic soil contents increased from 12 mg.kg<sup>-1</sup> d.w. up to 42 mg.kg<sup>-1</sup> d.w. in comparison with soils with high enough Cu contents (140 mg.kg<sup>-1</sup> d.w.). There appeared additional symptoms of phytotoxicity, indicated not only by crop growth, but also by chlorophyll content and photosynthetic activities. Phytotoxic effects were observed on serpentinites due to the high Ni and Cr content. The tolerance of some plants (*Alyssum* sp., *Thlaspi* sp.) to extreme Ni, Co, Mn, Cu, Cr contents in soils with extreme geogenic loads is caused by their ability to accumulate these TEs in roots.

## MATERIAL AND METHODS

The methodology is described in four previous papers (Němeček and Podlešáková 2001b, Němeček et al. 2001, Podlešáková and Němeček 2001, Podlešáková et al. 2001b). This paper aims at the demonstration of possibilities how to deduce critical soil values concerning the pathway soil-plant for TEs with a low mobility in soils.

## RESULTS AND DISCUSSION

## Arsenic

Arsenic belongs to trace elements (TEs) with a low positively pH-dependent mobility unlike Cd, Zn, Mn, Co, Pb. This TEs is characterized by low transfer quotients, but mainly by zoo- and humanotoxicity.

We used for the calculation of critical soil loads the strictest critical loading of crops 2 mg.kg $^{-1}$  d.w. The following critical soil loadings were found out: total content (TO) 350 mg.kg $^{-1}$  and content of the mobile soil species (MN) 4 mg.kg $^{-1}$  for triticale and TO 720-760 mg.kg $^{-1}$  for radish. The mentioned values were derived from the following relationships (\* significance at 95%):

| Triticale | $\ln T = 0.776 \ln TO^* - 3.854^*$ |
|-----------|------------------------------------|
|           | $\ln T = 0.830 \ln TO^* - 4.172^*$ |
| Radish    | $\ln R = 0.847 \ln TO^* - 4.843^*$ |
|           | $\ln R = 0.875 \ln TO^* - 5.109^*$ |

The first row is for the whole set (n = 97), the second one for the set lacking geogenic extremes (n = 81).

In the examined set the following mean and maximum (in parentheses) contents (including geogenic extremes) were found out (in mg.kg<sup>-1</sup> d.w.).

Table 1. Transfers of trace elements into plants from soils characterized by increased up to extreme contents of elements (mg.kg-1 d.w.)

| Element Kind of extremes |     |      | ED    | O MN  | ED/TO<br>× 100% | MN/TO<br>× 100% | pН  | pH Radish | Triticale | Critical referent values |   |
|--------------------------|-----|------|-------|-------|-----------------|-----------------|-----|-----------|-----------|--------------------------|---|
|                          |     |      |       |       |                 |                 |     |           |           |                          |   |
| Cu                       | Gb  | 83   | 9     | 0.04  | 11              | 0.050           | 6.8 | 2.0       | 7.5       | 10-30                    | _ |
|                          | Ga  | 108  | 20    | 0.29  | 18              | 0.270           | 4.5 | 6.9       | 4.9       |                          | _ |
|                          | Ga  | 110  | 55    | 0.64  | 50              | 0.580           | 6.0 | 4.0       | 9.4       |                          | _ |
|                          | An  | 115  | 86    | 0.14  | 75              | 0.120           | 5.5 | 36.2      | 28.1      |                          | + |
|                          | F   | 408  | 370   | 1.52  | 91              | 0.370           | 6.4 | 26.1      | 34.5      |                          | + |
| Cr                       | Gb  | 1846 | 0.87  | 0.018 | 0.047           | 0.0010          | 6.2 | 2.9       | 1.8       | 5                        | _ |
|                          | Gb  | 670  | 0.40  | 0.010 | 0.059           | 0.0015          | 6.9 | 4.8       | 1.2       |                          | _ |
|                          | GAc | 207  | 0.31  | 0.012 | 0.149           | 0.0058          | 4.5 | 0.9       | 1.0       |                          | _ |
|                          | F   | 539  | 6.50  | 0.03  | 1.200           | 0.0056          | 6.7 | 0.7       | 0.6       |                          | _ |
|                          | F   | 372  | 18.20 | 0.01  | 4.890           | 0.0027          | 6.3 | 0.2       | 0.6       |                          | _ |
| As                       | Ga  | 2789 | 13.10 | 1.02  | 0.470           | 0.0360          | 4.8 | 13.0      | 8.0       | 2-4                      | + |
|                          | Ga  | 1200 | 4.00  | 0.02  | 0.330           | 0.0017          | 4.8 | 1.7       | 0.3       |                          | _ |
|                          | Ga  | 319  | 9.70  | 0.17  | 3.040           | 0.053           | 3.9 | 3.0       | 2.2       |                          | + |
|                          | An  | 68   | 41    | 0.12  | 60              | 0.176           | 5.0 | 3.8       | 5.3       |                          | + |
|                          | F   | 448  | 348   | 0.59  | 78              | 0.132           | 5.5 | 5.8       | 4.8       |                          | + |

Ac = very acid soils, An = anthropogenic loads, F = fluvial loads, G = geogenic extremes, AcG = very acid soils with geogenic loads, AnF = anthropogenic and fluvial loads, Ga = of acid rocks, Gb = of mafic rocks bold numeric data = exceeding of critical plants loading

| Crops         | Soils |       |    |      |        |
|---------------|-------|-------|----|------|--------|
| Triticale     | 0.32  | (8.8) | TO | 33.2 | (3025) |
| Radish        | 0.38  | (9.9) | ED | 1.5  | (69)   |
| Fodder plants | 0.13  | (1.9) | MN | 0.05 | (1.7)  |

Figure 1 indicates that only the high content of the mobile species (MN) or high total content (TO) of As can cause a critical crop loading. Besides this fact, it is evident from the Figure 2a, b that the high solubility (ED/  $TO \times 100$ ) contributes at low and medium As total contents to the transfer hazards in accordance to the mobile (MN) species content. Very high total contents are of geogenic origin.

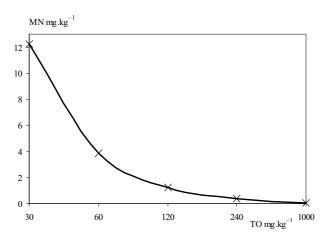


Figure 1. Dependence of critical transfer values of As into triticale upon the total content (TO) and mobile species (MN) of As in soils

Figure 3 displays the increasing content of the mobile species (MN) of As from the strong acid to neutral soils in dependence upon the increasing of the total As content.

All mentioned facts are confirmed by the examination of extreme values (Table 1). Critical crop values are exceeded in the range 2–5 mg.kg<sup>-1</sup> d.w.:

- Either at extreme geogenic loads if the total As content exceeds 2000 mg.kg<sup>-1</sup> (contents 300–1000 mg.kg<sup>-1</sup> do not satisfy this need) even at low solubility (< 10%) and also at strong acidity (pH 3.9–4.8)
- Or at increased As contents 70–300 mg.kg<sup>-1</sup> at a high solubility (> 50% ED/TO x 100) in soils with anthropogenic airborne or fluvial pollution (often at slightly acid conditions)

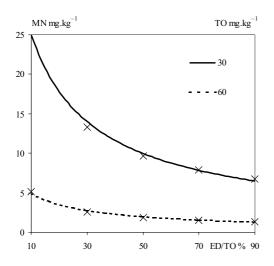
## Copper

Copper belongs to the biogenic TEs with a low mobility, but with increased transfer into plants. Excessive uptake can bring about zootoxicity.

The critical loads 10, 20 and 30 mg.kg<sup>-1</sup> d.w. were examined. Thereafter we are dealing only with values deduced from the strictest limit 10 mg.kg<sup>-1</sup> d.w.

Critical values were derived from the following equations:

Triticale  $\ln T = 0.092 \ln MN^* + 2.326^*$  (lacking geogenic extremes, n = 81)  $\ln T = 0.126 \ln MN^* + 1.675^*$  (the whole set, n = 97)



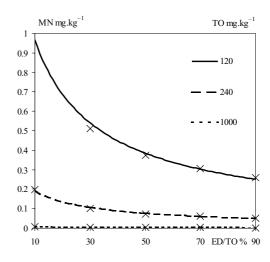


Figure 2. Dependence of critical transfer values of As into triticale upon the As solubility (ED/TO × 100) and mobile species of As in soils

| Radish       | $\ln R = 0.163 \ln TO^* + 0.551^*$ |
|--------------|------------------------------------|
|              | (the whole set)                    |
|              | $\ln R = 0.119 \ln ED^* + 0.862^*$ |
|              | (the whole set)                    |
| Fodder plant | $\ln F = 0.141 \ln MN^* + 2.501^*$ |
|              | (the whole set)                    |

The following soil critical values were derived:

- For triticale: total content 100–150 mg.kg<sup>-1</sup>, content of the mobile (MN) species 0.8 mg.kg<sup>-1</sup>, pH < 3
- For fodder plants: mobile species (MN) 0.2–0.3 mg.kg<sup>-1</sup>, pH < 3.5

The mentioned values can be compared (mean, maximum) with Cu contents in tested plants and Cu contents and mobilities in the investigated set.

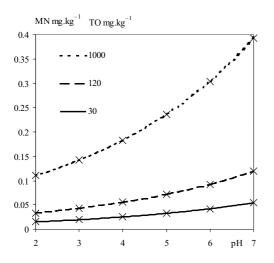


Figure 3. Dependence of the content of mobile species (MN) of As upon the total content of As and pH in soils

| Crops         |     |      | Soils |      |       |  |
|---------------|-----|------|-------|------|-------|--|
| Triticale     | 8.3 | (17) | TO    | 34   | (433) |  |
| Radish        | 3.2 | (42) | ED    | 7.6  | (402) |  |
| Fodder plants | 8.1 | (34) | MN    | 0.09 | (2.1) |  |

Figure 4 shows the dependence of the critical content of the mobile species (MN) upon the total Cu content and Figure 5 on soil pH. The both relations are integrally displayed in Figure 6. Critical Cu transfer decreased in general with increasing pH values, but the growth of the limiting value of the mobile species (MN) is mitigating if the total content increased. The general limit of the mobile species 800 μg.kg<sup>-1</sup> applies e.g. at 15 mg.kg<sup>-1</sup> TO if the pH is 5.5 and at 35 mg.kg<sup>-1</sup> TO (mean content) at pH 6 and at 120 mg.kg<sup>-1</sup> in the neutral pH range, limit 300 μg.kg<sup>-1</sup> at the mean content at pH 4.7.

It seems profitable to compare the critical transfer values with the dependence of the mobile species content (MN) on pH, total content (TO) and the Cu solubility (ED/TO  $\times$  100). Figures 7 and 8 show the fact that at common values of the total content of Cu and its solubility the content of the mobile species does not exceed 100–200  $\mu g.kg^{-1}.$  The value 800  $\mu g$  – general (generic) critical value of the mobile species (MN) – can be surpassed at high total Cu contents only at high solubility rates. The Cu mobility increased in neutral conditions in dependence on rising the potentially mobilizable species.

Investigations of extreme Cu contents in soils support all above described facts. These values show (Table 1) that critical contents both in triticale and radish can be exceeded only at total contents above  $100 \text{ mg.kg}^{-1}$  accompanied by a high relative solubility (>  $50\% \text{ ED/TO} \times 100$ ).

## Beryllium

Beryllium is an element with an inversely pH-dependent mobility, but with both a low content, low mobility in soil

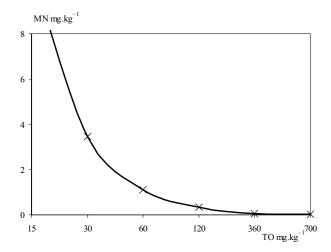


Figure 4. Dependence of critical transfer values of Cu into triticale upon the total content (TO) and the content of mobile species (MN) of Cu in soils

MN mg.kg<sup>-1</sup>

1.2

1

0.8

0.6

0.4

0.2

2

3

4

5

6

pH

7

Figure 5. Dependence of critical transfer values of Cu into triticale and fodder plants upon the mobile species (MN) of Cu and pH in soils

and a low transfer quotient. Crop critical loadings are mostly lacking.

From simple prediction equations, based on crop contents close above the plant base values – 0.1 mg.kg<sup>-1</sup> d.w. we derive soil critical value of the total contents 10–15 mg.kg<sup>-1</sup>. In the examined set, the following concentrations were found (mean, maximum in parentheses):

| Crops (mg.kg <sup>-1</sup> d.w.) |       |        | Soils (mg.kg <sup>-1</sup> ) |       |        |  |
|----------------------------------|-------|--------|------------------------------|-------|--------|--|
| Triticale                        | 0.006 | (0.05) | TO                           | 2.54  | (7.8)  |  |
| Radish                           | 0.021 | (0.48) | ED                           | 0.02  | (0.13) |  |
| Fodder plants                    | 0.011 | (0.09) | MN                           | 0.001 | (0.08) |  |

This comparison shows that the selected critical crop values were not attained in the investigated set. Even the

value 50 μg.kg<sup>-1</sup> proposed by Prüeß (1992) is rarely exceeded. Figure 9 testifies that this value can be exceeded only at very low pH, especially at low total contents.

### Chromium

Chromium ( $Cr^{III}$ ) is an element with the lowest solubility and transfer into crops. The low mobility of the trivalent phytotoxic Cr manifests itself in the limitations which unable us to derive prediction equations of the Cr transfer into crops.

Neither from simple nor from more complicated relations could have been derived satisfying critical soil loadings. In the investigated set following values were found out (mean, maximum in parentheses):

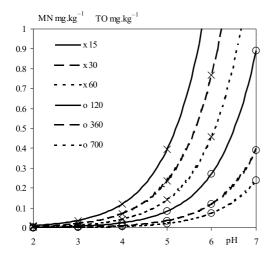


Figure 6. Dependence of critical transfer values of Cu into triticale upon the mobile species (MN) of Cu and pH at different levels of the total content (TO) of Cu in soils

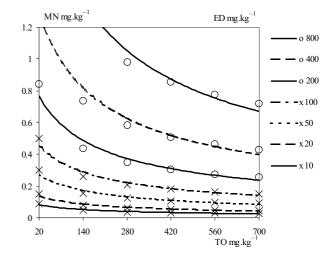


Figure 7. Dependence of the content of the mobile species (MN) of Cu upon the total content (TO) of Cu at different levels of the potentially mobilizable species (ED) in soils

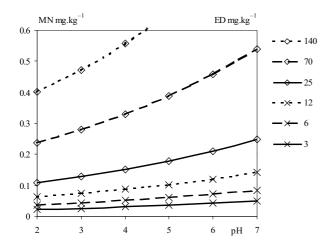


Figure 8. Dependence of the content of the mobile species (MN) of Cu upon the potentially mobilizable content (ED) and pH

| Crops         |     |        | Soils | Soils |        |  |  |
|---------------|-----|--------|-------|-------|--------|--|--|
| Triticale     | 0.7 | (1.8)  | TO    | 85    | (184)  |  |  |
| Radish        | 0.6 | (12.9) | ED    | 0.4   | (26)   |  |  |
| Fodder plants | 1.0 | (5.7)  | MN    | 0.01  | (0.04) |  |  |

The investigation of extreme soil contents testify the fact that in the whole set critical crop loads were not surpassed. Extremes involve (Table 1):

- a) Soils from geogenic extremes reaching 1800 mg.kg $^{-1}$  with a very low solubility (ED/TO  $\times$  100 < 1%)
- b) Soils with increased contents 350–1000 mg.kg<sup>-1</sup>, mostly Fluvisols, with slightly increased solubility 1–4%

## Vanadium

Vanadium represents a trace element the critical values of which are only rarely noticed in crop loading stan-

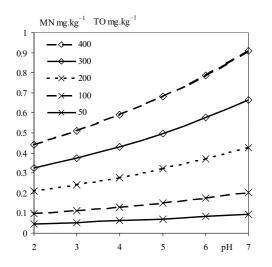


Figure 10. Dependence of the mobile species (MN) of V upon the total content (TO) of V and pH in soils

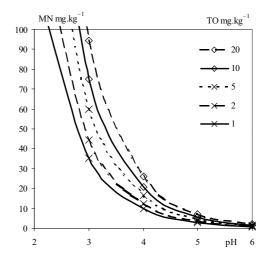


Figure 9. Dependence of the mobile species (MN) of Be upon pH in soils

dards. From the noticed values 5 and 10 mg.kg<sup>-1</sup> d.w. the value 5 mg.kg<sup>-1</sup> was taken.

The following mean and maximum values were determined in the set (mg.kg<sup>-1</sup> d.w.):

| Crops         | Soils |        |    |      |        |
|---------------|-------|--------|----|------|--------|
| Triticale     | 1.06  | (2.7)  | TO | 89   | (391)  |
| Radish        | 1.83  | (18.1) | ED | 2.3  | (15.4) |
| Fodder plants | 0.75  | (8.5)  | MN | 0.14 | (1.08) |

Critical transfer values in relation to the total content and pH are not reached in the investigated set. The content of the mobile species in soils depends directly on pH (Figure 10). Critical transfer values resulting from the investigated set are at pH 5 100  $\mu g.kg^{-1}$  at pH 6 300  $\mu g.kg^{-1}$  and they arise at pH 7 to the value 900  $\mu g.kg^{-1}$ . They can be exceeded at pH 6 when the content of V in soil exceeds 150 mg.kg $^{-1}$  and at pH 7 400 mg.kg $^{-1}$ .

## Mercury

Mercury is an element with the higher toxicity, but with an extremely low mobility and low transfer quotient. The conclusions about the behaviour of Hg were made from a set that comprises not only the total content, but also the share of mobilizable and mobile fraction.

Only if the total content of Hg exceeds  $0.4 \, \text{mg.kg}^{-1}$  the potentially mobilizable species (ED) has values over  $3 \, \mu \text{g.kg}^{-1}$ . But the share of the mobile species does not exceed values over  $0.2 \, \mu \text{g.kg}^{-1}$  even in soils with distinctly increased total and potentially mobilizable contents. These data testify the very low Hg mobility.

The critical value of the crop loading by Hg is considered to be 0.1 mg.kg $^{-1}$  d.w. But even at the contents 0.5 mg.kg $^{-1}$  Hg in soils the mentioned critical crop loading was not surpassed. Only the content 1.7 mg.kg $^{-1}$  in a Fluvisol caused the crop concentration of Hg 0.27  $\mu$ g.kg $^{-1}$ . The critical soil load is approximately total Hg content 1.0 mg.kg $^{-1}$ .

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## **ABSTRAKT**

#### Transfer stopových prvků s nízkou mobilitou v půdě do rostlin

Stopovými prvky s nízkou mobilitou a s nízkým transferem do rostlin jsou As, Be, V, Cr, Hg. Cu má při nízké mobilitě v půdě zvýšený transferový kvocient (obsah rostlina : půda). Nejnižší mobilitu a transfer vykazují Cr a Hg. Pouze při extrémním obsahu uvedených prvků a při zvýšené mobilitě, doprovázející vysokou antropogenní kontaminaci, může být dosaženo kritických hodnot pro rostlinu. U všech těchto prvků nebylo možné vzhledem k počtu zkoumaných extrémů odvodit vlastní kritické hodnoty. Byly odvozeny pouze kritické ochranné hodnoty. Představují minimální celkové obsahy stopových prvků nebo minimální obsahy jejich mobilních specií, zajišťujících bezrizikovost.

Klíčová slova: Cu; As, Be, Cr, V, Hg; kritický transfer do rostlin; ochranné kritické hodnoty

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