Verteilung und Biotransfer von Schwermetallen bei ausgewählten ägyptischen Böden

Distribution and bio-transfer of heavy metals in selected Egyptian soils



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#### ENGLISH TRANSLATION OF SELECTED PARTS

# Contents of the thesis "Distribution and bio-transfer of heavy metals in selected Egyptian soils" (1.-11. in German / E. selected parts in English<sup>1</sup>)

		Page
	Abbreviation list	VIII
1.	INTRODUCTION	1
2.	SURVEY OF LITERATURE	2
2.1.	Essentiality and toxicity of heavy metals	2
2.1.1.	Plants	2
2.1.2.	Agricultural domestic animals	4
2.1.3.	Human beings	5
2.2.	Heavy metals in the earth's crust	8
2.3.	Heavy metals in soils	8
2.4.	Soil factors affecting the availability of heavy metals	10
2.4.1.	pH-value	10
2.4.2.	Adsorption and release reactions	12
2.4.2.1.	Clay and metal oxides	14
2.4.2.2.	Organic matter	15
2.4.2.3.	Effects of the rhizosphere	16
2.5.	Heavy metal transfer coefficients	17
2.5.1.	Transfer coefficient	17
2.5.2.	Relative transfer coefficient	18
2.6.	Heavy metal problems in African developing countries	18

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<sup>&</sup>lt;sup>1</sup> EL KASABI, M. N. (2001): Distribution and bio-transfer of heavy metals in selected Egyptian soils. Thesis. Friedrich Schiller University of Jena, Faculty of Biology and Pharmacy, Institute of Ecology, Department of Environmental Science, Jena, Germany: V-VII, 1-2, 5, 9, 17-18, 22, 28, 33-34, 53-57, 117-120

3.	SETTING TASKS	22
4.	MATERIAL AND METHODS	23
4.1.	Description of the investigation area	23
4.2.	Description of taking soil and plant samples	23
4.2.1.	Sampling of the soil	23
4.2.2.	Sampling of the plants	24
4.3.	Conducting the pot trial	24
4.4.	Methods of analysis	25
4.4.1.	Soil sample preparation	26
4.4.2.	Determination of the pH-value of the soil samples	26
4.4.3.	Determination of the carbonate content, respectively CaCO <sub>3</sub> of the soil samples.	26
4.4.4.	Particle size analysis of soil samples	26
4.4.5.	Determination of fine parts content (< 0,0063 mm) of the soil samples	26
4.4.6.	Determination of the organic carbon content of the soil samples	26
4.4.7.	Determination of the raw soil density (g/cm <sup>3</sup> )	27
4.4.8.	Determination of the maximum water retaining capacity, respectively field capacity of the soil samples	27
4.4.9.	Determination of the element content	27
4.4.9.1.	Extraction of the soil samples with aqua regia for the determination of the content of Cd, Pb, Cr, Ni, Cu, Zn, Mn and Fe	27
4.4.9.2.	Extraction of the plant samples with hydrochloric acid for the determination of the content of Cd, Pb, Ni, Cu, Zn, Mn and Fe	28
4.4.9.3.	Microwave wet digestion of the plant samples for the determination of P, K, Mg, S, Ca, Na and Se	28
4.4.9.4.	Determination of the P-content of the soil samples	28
4.4.9.5.	Computer programs and statistic analysis	28
5.	RESULTS AND DISCUSSION	29
5.1.	Soil characteristics in the Egyptian investigation area	29
5.2.	Heavy metal contents in the soil of the Egyptian investigation area	29
5.2.1.	Heavy metal contents in 030 cm depth	29

5.2.2.	Heavy metal contents in 5560 cm depth in comparison with the upper soil profile (030 cm)
5.2.3.	Influence of the irrigation method on the heavy metal contents in the soil
5.2.4.	Influence of the street traffic on the heavy metal contents in the soil
5.2.5.	Lateral distribution of the heavy metal contents in the soil of the investigation area.
5.2.5.1.	Lateral distribution of Pb.
5.2.5.2.	Lateral distribution of Zn
5.3.	Comparison of heavy metal contents in the Egyptian soil with contents in soils of other areas and countries
5.4.	Element contents of plants of the Egyptian investigation area
5.5.	Investigations on the transfer
5.5.1.	Calculation of the transfer coefficients
5.5.2.	Transfer coefficients of the plants in the investigation area and comparison with literature data
5.5.2.1.	List of a sequence of the heavy metal accumulation at the same site with regard to the different plant species
5.5.2.2.	Comparison of the transfer coefficients of different parts (organs) of the plant
5.5.3.	Study of the correlation between transfer coefficients and heavy metal soil contents in the investigation area (correlation analysis)
5.6.	Pot trial
5.6.1.	Relative transfer coefficients of the pot trial
6.	GENERAL OVERVIEW AND CONCLUSIONS
7.	SUMMARY
8.	REFERENCES
9.	APPENDIX
10.	LIST OF FIGURES
10.1.	Figures in the text
10.2.	Figures in the appendix
11.	LIST OF TABLES

11.1.	Tables in the text	118
11.2.	Tables in the appendix	120
<b>E.</b>	ENGLISH TRANSLATION OF SELECTED PARTS	124
E.1.	INTRODUCTION	128
E.2.5.	Heavy metal transfer coefficients	130
E.2.5.1.	Transfer coefficient	130
E.2.5.2.	Relative transfer coefficient	130
E.3.	SETTING TASKS	131
E.4.4.9.5.	Computer programs and statistic analysis	131
E.5.2.5.1.	Lateral distribution of Pb	132
E.5.2.5.1.	Lateral distribution of Zn	133
E.6.	GENERAL OVERVIEW AND CONCLUSIONS	134
E.7.	SUMMARY	136
E.10.	LIST OF FIGURES	139
E.10.1.	Figures in the text	139
E.10.2.	Figures in the appendix	139
E.10.3.	Figures in the English translation	139
E.11.	LIST OF TABLES	140
E.11.1.	Tables in the text	140
E.11.2.	Tables in the appendix	141
E 11 3	Tables in the English translation	142

#### E.1. INTRODUCTION

Up to now, 55 heavy metals are well-known in the ecological sphere, made by the Creator as a part of the Universe.

Most rocks and soils, which are generated from them, contain often only traces of those heavy metals. The living beings are adapted to the natural heavy metal concentrations in the lithosphere and some of the heavy metals are even of vital importance for living beings.

But heavy metals have a poisonous effect already in relatively low concentrations which exceed the tolerance concentration.

In consequence of human-caused activities, as mining, processing of minerals, industrial production and its waste, street-traffic, processes of combustion and use of refuse products (e.g. sludge), heavy metals come into the environment and eventually have been brought increasingly into the soils.

As the heavy metals are not decomposed in the environment, it comes to an accumulation, namely in upper-soils in particular. That is the consequence of natural and technological cycles. From the quantity, nature and dispersion of the heavy metals in a soil-profile may be concluded the occurrence of primary and secondary accumulations. The primary, geogenic heavy metals are found in approximately equal element relations throughout the soil profile. On the other hand pedogenetical processes can cause secondary redistributions specific to soil layers in consequence of accumulations and reverse accumulations [42].

Heavy metals introduced by man into the soils ought to be considered with more criticism than heavy metals naturally present in the soils, since they are easier absorbed by the plants and thus enter considerably into the food chain. As a result of the accumulation by way of food chains, their action upon ecological systems and human beings may have toxicologically dangerous effects [170].

The heavy metal contamination is a global problem and concerns many countries in different continents, especially after the second World War, due to the fast increase of industrialization. The consequences are increased cases of chronic diseases owing to permanent heavy metal contamination and acute poisoning symptoms through excessive ingestion of heavy metals. Considering that the food chain frequently starts with the soil as substratum [129], laws

Considering that the food chain frequently starts with the soil as substratum [129], laws and directives have been issued in many countries in order to protect the soil and consequently avoid harm to human beings and other creatures. In Germany for example there are, among others, the federal law for soil protection, the federal directive on soil protection and dangerous waste residues and the directive on sludge (see table 68 {German tab. 11}), as well as the regulations of the law on fertilizers and plant protection, furthermore rules of the

federal law on air pollution protection and the appropriate legal directives. In addition, there is the directive on fodder and a definition of maximum contents of heavy metals in food.

STAIGER & MACHELETT (1984) as well as HELAL et al. (1995) have pointed out that irrigation water can have adverse effects on cultivated farmland by the input of heavy metals, especially when communal or industrial waste water reach the agricultural irrigation system [109, 123]. MESHREF & FAWZI (1987) as well as RABIE et al. (1996) have proved heavy metal accumulations in the soil owing to contaminated irrigation water [109, 123].

Cultivated farmland is also menaced by immissions of heavy metals within the precincts of traffic routes [81]. Decreasing contents of the heavy metals Cd, Ni, Pb and Zn were found in soils at increasing distances from traffic routes [10, 49, 65, 76, 122].

In general, it is possible to prove the negative influence of streets by increased heavy metal contents on the soil surface as far as up to 50...100 m distance  $\square$  [71].

Table 68 (German tab. 11): Soil protection levels from land administrative regulations, federal directives and guide data in Germany

	Total element content in dry substance of soil in ppm (mg/kg)							
	Background value - total content * for	Contin- gency value	Test value - total content farmland for	(B W I) <sup>c</sup> Multifunc- tional possibilities of use	Maximum permissible value in soil	(B W II) <sup>c</sup> Tolerance value	(B W III) <sup>c</sup> toxitiy value	
	soil with clay quota 0 - 8% <sup>a</sup>	•	soil with clay quota 0 - 8% <sup>a</sup>		according to directive on sludge (AbfKlärV)		ultivation of fruit getables	
Cd	0,2	0,4	1	1	(1) <sup>d</sup> 1,5	2	5	
Cr	20	30	100	50	100	200	500	
Cu	10	20	60	50	60	50	200	
Ni	15	15	50	40	50	100	200	
Pb	25	40	100	100	100	500	1000	
Zn	35	60	150	150	$(150)^d$ 200	300	600	
references	30	18	30	32	79	32	32	

Extraction method: aqua regia

<sup>\*:</sup> Background value - total content = top limit of the natural content in soil

<sup>&</sup>lt;sup>a</sup>: 3. Administrative regulation of the Ministry of Environment Bad.-Württ. for the soil protection law

b: Federal directive for soil protection and dangerous waste residues (BBodSchV)

<sup>()</sup> c: Rule-of-thumb values relative to beneficial and protected goods for (damaging) matter in soil

### **E.2.5. Heavy metal transfer coefficients**

#### **E.2.5.1.** Transfer coefficient

Transfer coefficients are calculated according to the following formula:

transfer coefficient =  $\frac{\text{heavy metal content in the plant}}{\text{heavy metal content of the soil}}$ 

The transfer coefficient of heavy metals determines the effect of a unit of the heavy metal soil content on the heavy metal content of a plant growing in the soil and is therefore a particularly suitable parameter for the evaluation of the accumulation and/or inverse accumulation of heavy metals in the plant tissue. Since it describes the heavy metal uptake independently of the concentration, it can be used even for comparisons between different elements. It depends on the influencing factors of the plant's heavy metal uptake, therefore it varies within relatively large ranges, which are specified in table 69 {German tab. 15} for selected heavy metals.

Table 69 (German tab. 15): Transfer coefficients according to different references

Cd	Cu	Fe	Ni	Pb	Zn	references
0,0310,00	0,012,00		0,012,00	< 0,50	0,0310,00	133
1,0010,00	0,101,00		0,101,00	0,010,10	1,0010,00	134
0,08 5,55	0,060,33		0,051,18	0,010,13	0,16 6,04	99
		0,010,05				111

#### **E.2.5.2.** Relative transfer coefficient

The relative transfer coefficient is a helpful parameter for the evaluation of the effectiveness of the soil as a sink for heavy metals (ability in fixing heavy metals), whereby it offers also a better comparability for different soils. It determines the influence of the increase of one unit of the heavy metal soil content on the increase of the heavy metal (HM) content in the plant and is calculated as follows:

relative transfer coefficient =

(HM content of the plant with HM soil addition) - (HM content of the plant without HM soil addition heavy metal (HM) soil addition

#### **E.3. SETTING TASKS**

On account of the imminent dangers which exist or may arise in the developing countries as a result of heavy metal contaminations the soil, water, air and victuals ought to be intensively examined and constantly controlled, in order to find out the real causes of threat.

Numerous investigations have shown that the heavy metal inputs into soil increase near roads [49, 65, 71, 76, 81, 122], owing to street-traffic.

Heavy metal contents also raise in the soil in consequence of contaminated irrigation water  $\square$  [109, 123]. That can have adverse effects on the ecological system  $\square$  [70] and especially the quality of victuals and fodder plants  $\square$  [4].

For these reasons investigations are prosecuted, within the scope of his thesis, relating to the distribution of heavy metals in a newly cultivated Egyptian soil<sup>1</sup> of a former desert region, adjoining a country road and irrigated by two irrigation systems. While doing so there is put a special emphasis on investigating the influences of the country road traffic and the different irrigation systems on the heavy metal content of the former desert soil, which is regarded as uncontaminated.

As in desert soils with little fine parts high heavy metal transfer coefficients are expected, the transfer of heavy metals from the soil to the plant is examined in the investigation area. Then the statistical relation between heavy metal contents in the Egyptian soil and the bio-transfer into the plants growing there is analysed.

The relative transfer coefficients of heavy metals of the Egyptian soil and German soils are compared in pot trials, in order to find out in which way the soil in the survey area acts as a sink for heavy metals (ability in fixing heavy metals).

#### **E.4.4.9.5.** Computer programs and statistic evaluation

The following computer programs were used:

Canoco version 4, CanoDraw version 3.1, Excel 95 and 97, Word 6,0 and 97.

For the statistic analysis see appendix to 4.4.9.5. (page 73).

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<sup>&</sup>lt;sup>1</sup> The first cultivation was in in the year 1987.

#### **E.5.2.5.1.** Lateral distribution of Pb

The soil contents of Pb in 0...30 cm depth in the survey area are normal distributed with a coefficient of variation of 27.8. In figure 2 we can see, that the Pb-contents of the sample sites are distributed relatively regular in the range of a quadrangle with higher contents of Pb. On the other hand outside the quadrangle lower Pb-contents occur in an irregular distribution. The results of chapter 5.2.3. and 5.2.4. are also recognizable in figure 2, because in general the values in the northern part are lower than in the southern part (possible influence of irrigation method), and because the occurrence of the highest Pb-contents is not restricted to the most western row besides the street (no influence of street traffic).

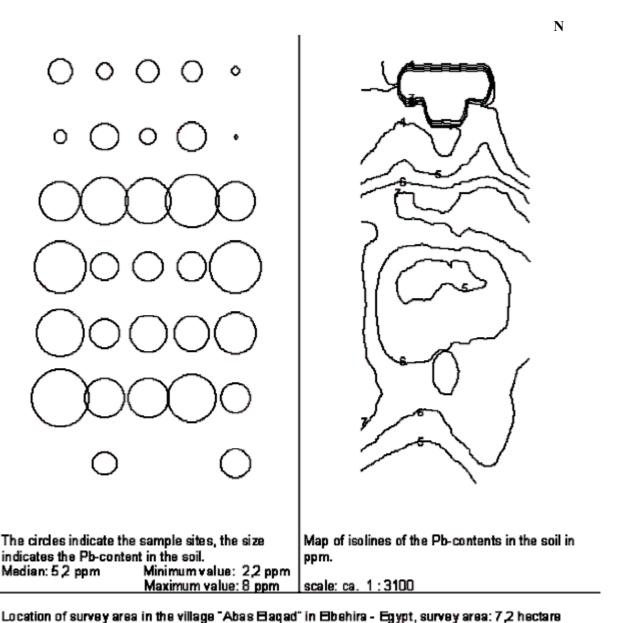


Figure 19 (German fig. 2): Distribution of the Pb-contents in the Egyptian investigation area (produced with Canoco version 4 and CanoDraw version 3.1 programs)

depth of samples: 0..30 cm, number of samples: 32, date of sampling: January 1998

extracted in aqua regia

#### E.5.2.5.2. Lateral distribution of Zn

Figure 3 shows the lateral distribution of Zn of the survey area in 0...30 cm depth with relatively high deviations of the normal distributed measured values (coefficient of variation: 33,6). High and low values are scattered over the whole area, which again confirms the results of chapter 5.2.3. and 5.2.4., showing that the soil contents of Zn are neither influenced significantly by the street traffic nor by the irrigation method.

We can see from the isolines, that the highest values are concentrated in three areas, namely in the centre of the northern part, in the the east of the southern part and in the west of the southern part.

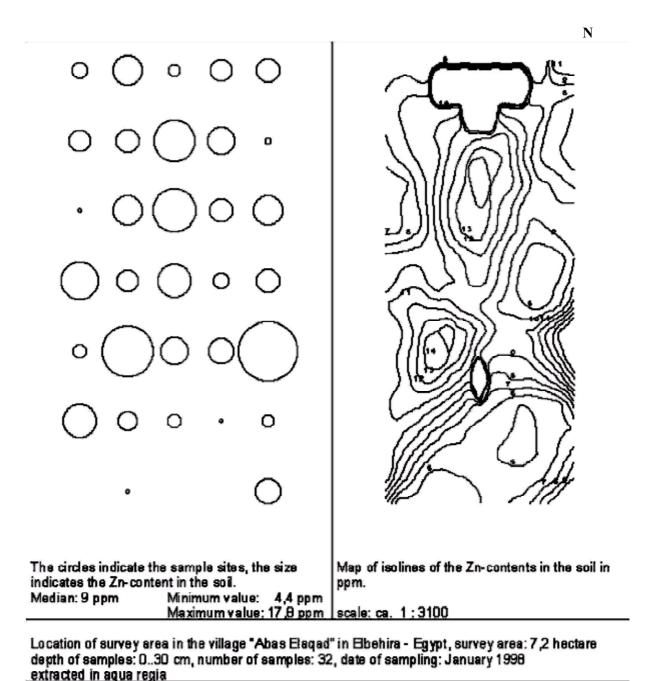


Figure 20 {German fig. 3}: Distribution of the Zn-contents in the Egyptian investigation area (produced with Canoco version 4 and CanoDraw version 3.1 programs)

#### E.6. GENERAL OVERVIEW AND CONCLUSIONS

All heavy metals are normal distributed in the alkaline sandy soil of the survey area, in the depth of 0...30 cm. There is no significant difference between the soil layer in 0...30 cm depth and in 55...60 cm depth. This result corresponds to the statements of BERGMANN (1998) that shiftings of heavy metals into deeper layers of soil happen more likely in acid wet soils [8].

The **Cd** contents in soil and plants of the investigation area are below the determination limit (0,2 and respectively 0,05 mg/kg). In the pot trial with oat sprout in Egyptian sandy soil of the survey area (addition of 1 mg Cd/kg), Cd shows common transfer coefficients for Cd in sandy soil (between 0,5 and 1,025).

The Cu transfer coefficients show in the survey area with quite low Cu contents in the soil an exceptionally high accumulation (up to transfer coefficient 7,78), as a result of Cu deficiency of the plants. In case of a higher Cu content in the soil of the survey area, equally in the pot trial, with Egyptian soil (addition of 7 mg Cu/kg), Cu shows common transfer coefficients (< 2).

In the Egyptian soil, there can result a danger threatening the ecological system with **Ni** because of its high mobility, when Ni introduced by man (e.g. by sludge and refuse composts) spreads in the soil, as the relative transfer coefficients come up to 9,185 in the pot trial with Egyptian soil (addition of 5 mg Ni/kg).

In the soil of the survey area with a relatively low Ni content (4,3 mg Ni/kg), irrigated by the dripping system, lucerne shows a considerably increased Ni content in the sprout (35 mg/kg). The Ni transfer coefficient is very high there (8,13) owing to possible low pH-values in the rhizosphere, combined with a very low clay mineral content, as well as low contents of Feand Mn-oxides<sup>1</sup> in the soil.

In the pot trial with the soil 1A, which had also been irrigated by the dripping system in the survey area, containing 9,8 mg Ni/kg (from it 5 mg/kg were added in the form of Ni-sulphate x 7 H<sub>2</sub>O), oat shows a considerably increased Ni content (52,3 mg/kg) in the sprout with a very high Ni transfer coefficient. That is due to the fact that Ni, brought into these soils by man, is widely available to the plants, combined with a very low clay mineral content, as well as low contents of Fe- and Mn-oxides in the soil.

The German maximum permissible values for Ni (table 68 {German tab. 11}) are not suitable for the investigated Egyptian soil, because with the above mentioned values in the pot trial the soil content comes up to about 65 % of the contingency value for sandy soils, only 19,6 % of the maximum permissible value, according to the directive on sludge, however the Ni plant

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<sup>&</sup>lt;sup>1</sup> The term "oxides" includes all forms of including hydrous oxides and oxyhydroxides.

content is considerably approached to the maximum permissible value of the directive on fodder (table 70 {German tab. 4}), reaching 92 % of that value. After all Ni has already shown a significant positive correlation between Ni soil content and Ni transfer coefficients in the investigation area with the family *Gramineae*.

These results with the Egyptain sand soil reinforce the investigation of HEIN et al. (1995), who proved that the maximum permissible value of 50 mg/kg with sandy and acid German soils ought to be even reduced by any possible means, because Ni, brought into these soils by man, is widely available to the plants  $\square$  [54].

Table 70 {German tab. 4}: Selected proposed threshold values of beginning heavy metal (HM) toxicity for fodder [3] and maximum permissible concentration of harmful substances in the plant material according to the directive on fodder (FMVO) for grassland [82]

mg / kg air dried matter	Cd	Cu	Fe	Mn	Ni	Pb	Zn	references
proposed threshold of beginning HM toxicity		15	500	1000	100	25	500	3
FMVO-values for grassland	1,14	40			57	45	284	82

The **Pb** contents in the soil and plants of the survey area are relatively low, but the Pb transfer coefficients are high, though there is no accumulation yet (the highest transfer coefficient is 0,95 with leaves of the Egyptian small lime). The reason may be that the soil contents of clay minerals as well as Fe- and Mn-oxides are relatively low and at the same time the plants are subject to a deficiency in micronutrients.

There is a significant difference of Pb soil content with different methods of irrigation (sprinkling and dripping system), but there is no significant influence of street traffic emissions on Pb soil contents. That shows that up to the time of taking the samples the input of Pb into the soil is more influenced by irrigation water and other factors than by street traffic. For that reason the quality of irrigation water and fertilizers ought to be particularly examined.

The **Zn** transfer coefficients are within the common range in the investigation area and also in the pot trials of Egyptian soil (addition of 25 mg Zn/kg).

Heavy metals introduced by man into the survey area can easily come into victuals, as in the prevailing sandy soil with little fine parts, in spite of high pH-values, comparatively high (relative) transfer coefficients were ascertained.

For that reason in the event of human-caused heavy metal soil contamination man is exposed to a special danger.

#### E.7. SUMMARY

The dispersion of heavy metals and its bio-transfer to plants have been investigated in a lately cultivated land of a region westward of the Nile delta, on the border of the Western Sahara, in the village "Abas Elaquad" of the region El Bustan, district Elbehira in Egypt.

Both the lateral distribution and the distribution in two different soil layers were examined. As the survey area is situated beside a country road and has two different irrigation systems, the influence of the street traffic and the different irrigation systems on the heavy metal content was investigated. Furthermore the bio-transfer of heavy metals was examined in 10 plant species and additionally the correlation of the transfer coefficient with the soil content was analysed for the family *Gramineae* on the site. Besides comparative studies on the heavy metal accumulation at the same site were conducted with regard to the different plant species and also with regard to different parts of the plant.

In addition, by means of a pot trial (according to Neubauer), the uptake of heavy metals introduced by man (in the form of Cd-acetate, Cu-, Ni- and Zn-sulfate) by plants was compared with German soils, by calculation of the relative transfer coefficients. That was done in order to find out the capacity of the soil in the survey area as a sink for heavy metals (in fixing heavy metals).

The result showed the presence of alkaline lithosole sandy soil in the investigation area with a Cd content in the soil and plants generally below the determination limit (0,2 mg/kg for soil and respectively 0,05 mg/kg for plants). The soil contents of all examined heavy metals were low, respectively normal for sandy soil.

A normal distribution of the Cr-, Cu-, Fe-, Mn-, Ni-, Pb- and Zn-soil contents was proved by the Chi-square-test in the soil (depth 0...30 cm).

By means of the t-test it was shown that there exists no significant difference between the heavy metal soil content of Cr, Cu, Fe, Mn, Ni, Pb and Zn in the soil depth 0...30 cm and 55...60 cm.

With the different irrigation methods (sprinkling and dripping system) resulted no significant difference in the Cu-, Cr-, Fe-, Mn-, Ni- and Zn-soil content.

A significant difference was ascertained by t-test only with Pb, in which case the average values of the Pb soil contents were 24 % higher in the southern part of the area, irrigated by sprinkling, than in the northern part, irrigated by the dripping system. The main reason for this may be an increased Pb content in the irrigation water. There is the imminent danger of a future human-caused Pb contamination of the soil as a result of the proved tendency of Pb accumulation in the survey area.

The application of the t-test showed that the emissions of the street traffic had no significant effect on the Cd-, Ni-, Pb- and Zn-soil contents. However, unwashed leaves of a she-oak tree in a hegde-row growing directly at the country road showed a higher content of Ni, Pb and Zn in case they grew in the direction of the road than in case they grew in the direction of the survey area (Ni  $\sim$  25 % higher, Pb  $\sim$  58 % higher and Zn  $\sim$  25 % higher.) Therefore it may be supposed that the hedge of she-oak trees acts as a filter for the traffic immissions.

In general the Cu-, Fe-, Mn-, Pb- and Zn-contents in the plants of the survey area are relatively low, but the Ni contents in the plants are, on principle, in the normal range, respectively a little increased, however in the individual case of lucerne sprouts considerably increased, with a very high transfer coefficient (8,13).

The Pb transfer coefficients of the survey area are considerably increased, owing to the low soil contents of clay minerals as well as Fe- and Mn-oxides, even though there was not yet any accumulation. The transfer coefficient 0,95 in Egyptian small lime leaves was the highest. The Cu transfer coefficients show extraordinary high accumulations (the highest Cu transfer coefficient with 7,78 was found in leaves of the date palm) with very low Cu soil content, by reason of Cu deficiency of the plants. On the other hand, reverse accumulations occurred in the same plant species (Napier grass and date palm) when the Cu soil contents were comparably higher.

The Fe, Mn and Zn transfer coefficients in the survey area were within the common ranges.

The investigation of the correlation between soil contents of heavy metals and their transfer coefficients in *Gramineae* plants at the site, by means of Pearson's coefficients of correlation and degrees of certainty showed that the correlation was significantly positive for Ni (B = 0,771), for Cu, Mn, Pb and Zn significantly negative (B = 0,801; 0,935; 0,778 and 0,732) and for Fe not significant. Deficiency of micro elements is considered as the cause of the significantly negative correlation. In order to obtain sufficient contents of micro elements, the plants react with root exudates, whereby the transfer coefficients decrease with rising soil contents.

In the pot trial the soil 1A and 4C of the examined Egyptian soils and the soil from Großbeeren of the compared German soils showed similar relative transfer coefficients of Cd, namely the highest of all compared soils, though their pH-values (7,8/7,9 and 6,2) and clay mineral contents (< 1 and 7 %) are different. The relative transfer coefficients of the soil 7E\* of the investigated Egyptian soils and the soil from Kösnitz of the compared German soils were also similar. They were at about half of the above mentioned, whereby their pH-values (7,9 and 7,3) and clay mineral contents (< 1 and 37 %) didn't take any increased significance,

as the organic matter and to some extend the Fe- and Mn-oxides in all soils of the pot trial were decisive for the reaction of the soils in fixing Cd.

Therefore, the soil from Fehrbellin showed a remarkably low relative transfer coefficient of Cd, as well as of Ni and Cu, owing to its high content of organic matter (orgC-content 28,1%), though its soil reaction was more acid (pH 5,4). Also for Zn it showed a great ability in fixing heavy metals, however, compared to Cd, Cu and Ni, Zn was least stronlgy fixed.

Soils with high pH-values (7,8/7,9), combined with low clay mineral contents (< 1 %), as well as low Fe- and Mn-oxides, don't have a high capacity to absorb Cu and Zn and particularly Ni. They cause rather, to different degrees, a mobilization of those heavy metals, by formation of soluble and plant-available organic heavy metal complexes. Consequently, the Egyptian soils 1A, 4C and 7E\* had the highest relative transfer coefficients of Cu, Ni and Zn and were fixing Cu and Zn, and especially Ni, to a smaller extent than the examined German soils.

On the whole Cd, Cu, Zn and especially Ni, which have been introduced by man, and for example may come into the examined Egyptian soil through sewage sludge and refuse-compost, ought to be considered critically.

They may represent a danger to human beings and also to animals. That stands also for similar soils in the same region El Bustan in Egypt, where the newly cultivated area is intended to reach the size of 62250 ha by the year 2017.

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<sup>:</sup> C content of organic matter; it varies strongly within individual classes of substances, but on average it is usually around 50 % [137]. For the calculation the following formula is usually used: "% org. substance = 1,67 \* (%orgC)"

## **E.10. LIST OF FIGURES**

## **E.10.1.** Figures in the text

		Page
Figure 1:	Comparison of the maximum permissible values in soil after the sewage sludge order with medium heavy metal contents of selected Egyptian soils at El-Saff and Helwan (data in mg/kg dry matter)	19
Figure 2:	Lateral distribution of Pb	33
Figure 3:	Lateral distribution of Zn	34
Figure 4:	Transfer coefficients of the different plant species at the site 7E of the Egyptian investigation area	44
Figure 5:	Relative transfer coefficients of heavy metals for oat shoots of the Egyptian soils (1A, 4C, 7E *) and the German soils (Großbeeren, Kösnitz, Fehrbellin)	48
E.10.2.	Figures in the appendix	
Figure 6:	Location of the investigation area "Abas Elaqad" in the district Elbehira in Egypt, layout plan on a scale 1: 1,560,000	75
Figure 7:	Location of the soil samples in the investigation area	76
Figure 8:	Photo of the location of the investigation area	77
Figure 9:	Photo of the northern part of the investigation area	77
Figure 10:	Photo of the southern part of the investigation area	78
Figure 11:	Photo of the western edge of the investigation area with a dense row of she-oak trees, which separates the area from a country road	78
Figure 12:	Situation of the plant samples in the investigation area	79
Figure 13:	Lateral distribution of Cr	80
Figure 14:	Lateral distribution of Cu	81
Figure 15:	Lateral distribution of Fe	82
Figure 16:	Lateral distribution of Mn	83
Figure 17:	Lateral distribution of Ni	84
Figure 18:	Influencing factors for the uptake of heavy metals by plants adapted from Altmann (1996) and expanded	85
E.10.3	Figures in the English translation	
Figure 19 {	German fig. 2}: Lateral distribution of Pb	132
Figure 20 {	German fig. 3}: Lateral distribution of Zn	133

## **E.11. LIST OF TABLES**

## **E.11.1.** Tables in the text

		Pag
Table 1:	Important biological functions of selected heavy metals for plants	3
Table 2:	Sufficient Cu -, Mn -, Zn-contents for selected plants	4
Table 3:	Heavy metal contents in leaves, respectively in shoots of plants representing lack, yield limit, optimal range, normal content, tolerable content for agronomic crops as well as surplus or toxicity	4
Table 4:	Selected proposed threshold values of beginning heavy metal (HM) toxicity for fodder and maximum permissible concentrations of harmful substances in the plant material according to the directive on fodder for grassland	5
Table 5:	Biological functions of selected heavy metals for human beings	5
Table 6:	Different characteristic figures of heavy metals with regard to human beings	6
Table 7:	Guideline values, respectively maximum permissible contents for some heavy metals in selected vegetable food in the GDR and the FRG, data in mg/kg related to fresh substance, respectively related to the form, it is offered in the market	7
Table 8:	Medium total contents of heavy metals (mg/kg dry matter after HF digestion) in the earth's crust	8
Table 9:	Normal and frequent ranges of heavy metal contents in soil (mg/kg dry matter) according to different references	8
Table 10:	Medians of soil heavy metal contents (mg/kg dry matter after HF digestion) of agricultural lands in East Germany dependent on the geological soil parent material	9
Table 11:	Soil protection levels from land administrative regulations, federal directives and guide data in Germany	9
Table 12:	Medium Cd- and Pb-contents in fertilizers (mg/kg dry matter)	10
Table 13:	Threshold-pH-values, below which heavy metal mobilization begins	12
Table 14:	Description of the bonding energy of main soil components with heavy metals according to BLUME & Bruemmer (1987)	13
Table 15:	Transfer coefficients according to different references	18
Table 16:	Contents of heavy metals in streams (global) and water of the Nile, respectively waste water in Egypt, as well as the quality demands by the international river-side communities (LAWA) for maximum contents of heavy metals in irrigation water of agricultural lands	20

Table 17:	Average heavy metal concentrations in the blood (µg/100 ml) of children and adults in Egypt and not contaminated areas in Germany as well as recommendations by the WHO for limiting values	21
Table 18:	Location of the investigation area	23
Table 19:	Experimental arrangement and conditions of the pot trial	25
Table 20:	Soil characteristics of the examined soil of "Abas Elaqad" in the district Elbehira in Egypt (average values)	29
Table 21:	Median, minimum, maximum, mean, standard deviation and coefficient of variation of the heavy metal contents of the Egyptian soil of "Abas Elaqad" in the district Elbehira (after tab. 33)	30
Table 22:	Comparison of mean heavy metal contents of 7 sample sites in the Egyptian investigation area "Abas Elaqad" depending on the depth	30
Table 23:	Comparison of the means of the heavy metal contents of selected parts (northern part, irrigated by dripping system and southern part, irrigated by sprinkling system) of the investigation area "Abas Elaqad" in Egypt.	31
Table 24:	Comparison of the means of selected parts (western edge and remaining part) of the investigation area "Abas Elaqad" in the district Elbehira in Egypt	32
Table 25:	Factors for the conversion of values after HF digestion, respectively HNO <sub>3</sub> -extraction into values after aqua regia extraction	35
Table 26:	Average Cd -, Cr -, Cu -, Ni -, Pb -, Zn -, Fe -, Mn-contents (mg/kg dry matter) of soils of different lands/ areas, which were found by the aqua regia extraction method, respectively which could be determined by use of aqua regia digestion	36
Table 27:	(Mean) element contents of the plants of the investigation area "Abas Elaqad" in the district Elbehira in Egypt	39
Table 28:	Element contents in the soil and plants and transfer coefficients, respectively mean transfer coefficients in "Abas Elaqad" in the district Elbehira, Egypt	41
Table 29:	Transfer coefficients for uncontaminated soil of the investigation area	42
E.11.2.	Tables in the appendix	
Table 30:	Climate of the climatic station of Tahrir, which is the nearest to the investigation area	86
Table 31:	Description of the plant samples and sample sites	86
Table 32:	Components (salts) of the Hoaglands A-Z-solution (mg/l water)	86
Table 33:	Mean heavy metal contents in the aqua regia extract of the soil samples of "Abas Elaqad" in the district Elbehira in Egypt	87

Table 34:	Mean elemer	nt contents of the plants at the site	88					
Table 35:	Sufficient ma	Sufficient macro-nutrient content for selected plants						
Table 36:		Normal, excess or toxic contents of Se in plants and proposed hreshold values for fodder as well as range of Se transfer coefficients						
Table 37:	the statistic a	efficients of correlation (r) and degree of certainty (B) for inalysis of the correlation between transfer coefficients ents	89					
Table 38:	Measured va	lues of the soils of the pot trial	89					
Table 39:	Transfer coef	fficients and relative transfer coefficients of the pot trial	89					
Table 40:	Measured va	lues of the soils of the Egyptian investigation area	90					
Table 41:		um water retaining capacity (WHKmax) in the area	91					
Table 42:	whole soil as	he soil particle size proportions from the weight of the well as % weight of the organic substance from the different soil particle size proportions	91					
Tables 43-45		on of the measured heavy metal values in soil for the fthe program Canoco	92-94					
Tables 46-67	:Laboratory ta	ıbles	95-116					
E.11.3	Tables in the	English translation						
Table 68 {Ge	rman tab. 11}	Soil protection levels from land administrative regulations, federal directives and guide data in Germany.	129					
Table 69 {Ge	rman tab. 15}:	Transfer coefficients according to different references	130					
Table 70 {Ge	rman tab. 4}:	Selected proposed threshold values of beginning heavy metal (HM) toxicity for fodder and maximum permissible concentrations of harmful substances in the plant material according to the directive on fodder for grassland.	135					