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Uptake of heavy metals by food crops from highly-polluted Chernozem-like soils in an irrigation district south of Tbilisi, eastern Georgia

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Abstract. In the middle and lower reaches of the Mashavera valley in SE Georgia, most of the irrigated soils under different agricultural land use display a strong enrichment of heavy metals (HM) that can be traced back to irrigation with water polluted by mining wastes contributed over a period of several decades. The concentrations of total amounts of Cu, Zn and Cd increase with intensity of land use and amount of irrigation in the following sequence: arable fields < occasionally submerged meadows < vegetable gardens < wine gardens and orchards with mixed cropping of vegetables. A high proportion of HM belongs to the supply fraction, which displays the (un-)specifically adsorbed HM, dissolvable in ethylenediamine tetra-acetic acid (EDTA). The narrow correlation of this fraction with the mobile and plant-available fraction of HM indicates a high long-term risk potential for the food chain. Due to the recent high adsorption capacity of the soils for HM, only a small amount of HM in the mobile fraction was found with proportions less than 1 % of the total amounts for Cu and Zn, and a maximum of 1.5 % for Cd. On the other hand, initial investigations of cereals and vegetable species indicate a high uptake of Cu, Zn and Cd, which for Cu and Cd causes concentrations in plants exceeding the tolerance thresholds for plants, animals and human beings. A field experiment established the strong uptake of heavy metals by spinach, which was unexpected due to the weakly alkaline pH as well as the high contents of clay and organic matter of the soils. This result indicates the high risk of soil pollution by heavy metals for the food chain and consumers.

Key words: heavy metals, pollution, irrigation, contaminated waste, soil

INTRODUCTION

Because agriculture is the main economic sector of Georgia, long-term conservation of the high yield potential of the fertile soils under irrigation in SE

Georgia is of great concern. Decades of mining of copper and precious metals in the mountain ranges have caused severe environmental problems. Near Kazreti, at the middle reaches of the Mashavera valley, mining wastes were deposited on the mountain slopes around the opencast mine. The use of the Mashavera waters for irrigation led to pollution of the fertile Chernozem and Kastanozem soils by suspended fines, rich in heavy metals.

In the framework of a research project, generously funded by the German Volkswagen Foundation, irrigated soils of the Mashavera valley were investigated for the amount and spatial distribution of heavy metals resulting from the deposition of mining wastes (Narimanidze et al. 2005, Felix-Henningsen et al. 2007 a,b). The soils, rich in clay, organic matter and calcium carbonate display a high adsorption capacity for heavy metals. This is indicated by rather low amounts of soluble and weakly adsorbed HM, which dissolve in NH_4NO_3 soil extracts.

In this paper we investigate the risk of contamination of the food chain by the uptake of heavy metals (HM) from soils in the Mashavera valley. In order to prove a possible uptake of heavy metals by crops, field and pot experiments were carried out using spinach (*Spinacia oleracea* L. cv. Calata) and summer wheat (*Triticum aestivum* L. cv. Thasos).

MATERIALS AND METHODS

Georgia is situated at the northern boundary of the northern subtropics with a gradient of decreasing humidity and increasing continental character from west to east. The natural steppe vegetation formations (Nakhutsrishvili, 2000) of the Mashavera valley were changed by agriculture. Due to the continental type of climate the typical main soil orders belong to Kastanozems and Chernozems (Javakhishvili & Gvelesiani,1962).

The study area is situated in SE Georgia, about 60 km SW of the capital Tbilisi, in the administrative district Bolnisi, and contains the middle and lower reaches of the Mashavera valley. South of Bolnisi, the Mashavera valley is bordered by the volcanic high plateau of Javakheti, which passes into the Armenian highlands in the south and is the source area of the Mashavera river (Javakhishvili & Gvelesiani, 1962). The open mine pit is situated 10 km SW of Bolnisi village and covers an area of about 350 ha in the summit area of a mountain range between the Mashavera valley to the west and the Poladauri valley to the east. Surface and subsurface waters from the mine and the mine spoils, which cover the slopes adjacent to the pit, form acid mine drainage (AMD) with pH values < 3 and high dissolved HM concentrations. AMD is collected in sedimentation basins by a channel and pump systems, but a lack of financial and technical possibilities in the past prevented further processing of the AMD by neutralization with lime and extraction of the dissolved copper by binding agents. Therefore in most years considerable amounts of untreated AMD were dumped into the adjacent rivers. Especially after strong rains and power blackouts, the pump system of the mine is unable to take up the drainage water thus leading to uncontrolled runoff.

In addition, highly contaminated wastewater from the Madneuli flotation plant contributes to the pollution of the Mashavera river (MSPM, 2000). Violations against existing security regulations caused a temporarily closure of mining in the past. Fine grained flotation wastes are deposited on two heaps situated about 2–3.5 km NW of the open mine pit, covering a total area of 240 ha. The sulphidic rock material is subject to intensive biochemical oxidation, which causes a release of large amounts of AMD and dissolved HM. The steep slopes of the large heaps are bare and unfixed by vegetation, thus causing sheet and rill erosion and the transport of fines to the Mashavera and Kazretula rivers, while AMD runoff directly contaminates the rivers with HM. Furthermore, the physical state of the deposits was not taken into account and resulted in slope failures (MSPM, 2000). During the dry summer months the heaps of flotation waste are the source of dust, which amounts to about 30 Mg a^{-1} (Burnod-Requia, 2003), and pollutes large areas in the surroundings with HM. Thus the non-irrigated arable soils and uncultivated soils of the mountain regions also display relatively high "natural" background concentrations of HM.

Table 1 displays the ranges of analytical data of topsoils (n = 112), which were subject to the investigation, derived from different land use plots. The humus content decreases with increasing intensity of soil cultivation in the sequence grape fields and wine gardens, orchards, house gardens, and arable fields. As a further reason for the high humus contents in topsoils of wine gardens, a lower mineralization rate can be assumed resulting from an accumulation of Cu due to strong irrigation (see below) as well as from the use of copper bearing fungicides. Arable fields, on the other hand, are subject to soil erosion during periods of rotation fallow, which diminishes the humus content in slope positions and leads to the formation of colluvium in depressions and on the flat valley floor. On slopes with severe erosion, the calcic horizon is exposed at the surface and causes the formation of Calcisols.

Table 1. Characteristics of topsoils (Ap horizons, n = 112) under different land use.

Soil Characteristics		Land use		
		Arable Fields	House Gardens	Wine Gardens, Orchards
Organic substance	(mass-%)	1.90–3.80	2.00–4.80	2.80–4.60
Calcium carbonate [1]	(mass-%)	4.43	4.46	2.05
pH (CaCl2)		7.20–7.50	7.10–7.40	7.10–7.40
Clay content [2]	(mass-%)	39–62		
CEC[2]	cmol$_c$ kg^{-1}	31–53		
Fe-Oxalate soluble	(g kg^{-1})	0.59–2.12	0.69–2.63	0.41–4.19
Fe-DCB	(g kg^{-1})	5.62–11.24	6.79–11.70	8.06–12.43
Mn-Oxalat soluble	(g kg^{-1})	0.25–1.00	0.31–1.00	0.55–1.00
Mn-DCB	(g kg^{-1})	0.45–0.82	0.39–1.00	0.54–1.02

[1] Arithmetic Mean, [2] Samples n = 12;

Fe/Mn-DCB = dithionite-citrate-bicarbonate soluble fraction of free (pedogenic) amounts of crystalline + amorphous iron and manganese oxides. Fe/Mn-Oxalate soluble = fraction of amorphous iron and manganese oxides

a) Soil investigations

Soil samples were taken in fields, house gardens, grape fields, wine gardens and orchards from the Ap horizon (0–30 cm) at 10 sites along double-diagonal transects. Eight volume-equivalent cores were taken with an aluminium auger within an area of 4 x 4 m at each site. The fine earth (<2mm) of the air-dried samples, ground in a porcelain mortar, was investigated in the laboratories of the Institute of Soil Science and Soil Conservation of the Justus-Liebig University Giessen, Germany.

The *pH* was determined after DIN 10390 in suspension with 0.01 M $CaCl_2$ with a pH-meter pH90 (WTW). The amount of *carbonates* was determined by the gas-volumetric method using a calcimeter, following DIN 18129. *Total amounts of carbon* (C_t) *and nitrogen* (N_t) were determined on fine ground samples by gas-chromatography using a C-N-S element analyzer (Heraeus). *Anorganic C* was calculated from the carbonate content by using the factor 0.1199, while the amounts of *organic carbon* (C_{org}) resulted from the difference between C_t and anorganic carbon. The amounts of *organic matter* were calculated by $C_{org} * 1.724$. *Particle size distribution* was determined by the combined sieving (and fractions) and pipette method (silt and clay) after decomposition of carbonates (HCl) and organic matter (H_2O_2) and dispersion in Na-Pyrophosphate, following DIN 19683. *Amorphous iron* (Fe_{ox}) *and manganese oxides* (Mn_{ox}) were determined by extraction with buffered oxalic acid, pH 3.25, under dark conditions as described in Schlichting et al. (1995). *Pedogenic iron* (Fe_{DCB}) *and manganese* (Mn_{DCB}) oxides were extracted following the procedure of Mehra & Jackson, as described in Schlichting et al. (1995).

The *mobile and exchangeable fractions of HM*, which are eco-toxicologically relevant because they are potentially plant available and easily leachable, were extracted with NH_4NO_3 according to Zeien & Brümmer (1989, 1991). They are designated in the text as HM_{AN}. The *total amounts of subsequent deliverable HM*, which is the *supply fraction* and includes the soluble and exchangeable fractions as well as the HM strongly adsorbed to carbonates, oxides and organic substances, were extracted by EDTA. Deviating from the method described by Hornburg & Brümmer (1993), EDTA was dissolved in a buffered solution of ammonium acetate at pH 7. Elements of this fraction are designated in the text as HM_{EDTA}. The *total amounts of HM* were extracted from finely-ground samples by using aqua regia following DIN ISO 11466. Elements of this fraction are designated in the text as HM_{AR}.

Element concentrations in the extracts were determined with an atomic adsorption spectrometer FAAS 4100 (Perkin Elmer). For determination of Cd in the NH_4NO_3 extracts, a GFAAS SIMAA 6000 spectrometer (Perkin Elmer) was used due to the low concentrations.

The SPSS statistical package was used for the data analyses.

b) Field and pot experiments

The bioavailability of the accumulated heavy metals was analyzed in pot and field experiments. The pot experiments were carried out with 3 soils at the greenhouse experimental station in Giessen. The soil samples for the pot experiments were taken from 0.20 m depth at three experimental sites near Bolnisi village. Soil samples were air-dried, ground and sieved through a 4-mm sieve. Six small Mitscherlich pots were filled with 5 kg of soil each. Before spinach (*Spinacia oleracea* L. cv. Calata) and summer wheat (*Triticum aestivum* L. cv. Thasos) were grown, the soil in the pots was treated with 15 g of a combined fertilizer (12% N, 5% P, 14% K as sulphate, 6% S, 2% Mg). After emergence, wheat and spinach seedlings were thinned to 20 plants per pot. Summer wheat was fertilized with 0.5 g N per pot as NH_4NO_3 at the shooting stage. Spinach was grown for 41 days and wheat for 105 days.

The field experiment was carried out by growing spinach (*Spinacia oleracea* L. cv. Calata) at three irrigated sites with a different degree of HM pollution (for soil data and contents of HM see Tab. 5). Spinach was sown with 4 g seeds/m^2. At each experimental site spinach was cultivated in 8 plots (10 m^2). Before plant samples were dried at 105°C, part of the spinach shoots were washed with demineralized water in order to carry out comparative analysis of washed and unwashed samples. The concentration of heavy metals in plants was determined by AAS after a dry ashing of the ground plant samples at 420°C and dissolution of the ash in HNO_3 (VDLUFA, 1976).

RESULTS AND DISCUSSION

Results of the investigation of soil properties, the total amounts and mobile fractions of heavy metals in topsoils of un-irrigated and irrigated fields, meadows, house and wine gardens and orchards are presented and discussed in detail in Felix-Henningsen et al. (2007 a,b).

Screening investigations of the concentrations of diverse heavy metals in topsoils of the Mashavera valley showed that only Cu, Zn and Cd are problem elements, which accumulated in the course of irrigation and dust deposition, originating from the deposits of mining waste in the Kazreti mountainous area. Other heavy metal species such as Pb, Cr, V, Co, Ni and Hg occur in negligible low concentrations.

The ecological importance of the soil pollution by HM must be assessed by threshold values for contaminated soils, which are documented in bodies of laws of several European industrial countries. Up until now, such values do not exist for Georgia. Therefore the total amounts of HM in the aqua regia extract (HM_{AR}) and the dissolved and weakly adsorbed fraction in the NH_4NO_3 extract (HM_{AN}) will be compared with the threshold values of the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV, 1999) based on the Federal Soil Protection Act (BBodSchG, 1998). Another source of threshold values based on total amounts (AR) is the "Dutch List" (Rosenkranz et al., 1993).

The concentrations of HM in the EDTA-extract (= HM_{EDTA}) indicate the available plus potentially available supply fraction, more or less strongly adsorbed amounts of HM, bound on free Fe- and Mn-oxides, carbonates and organic substances (Zeien & Brümmer, 1989, 1991). They indicate the future risk potential of soil pollution (Smith et al., 1996) because the HM_{EDTA} can be mobilized when the soil conditions influencing the adsorption (e.g. pH, contents of carbonates and organic matter, redox-conditions etc.) change. Therefore this fraction was also included in this study.

The spatial distribution of the problem elements Cu, Zn and Cd shows soil loading, which depends on the kind of land use. A significant increase of the concentrations follows the sequence: Reference soils (un-irrigated) << arable fields < house gardens << orchards and vineyards.

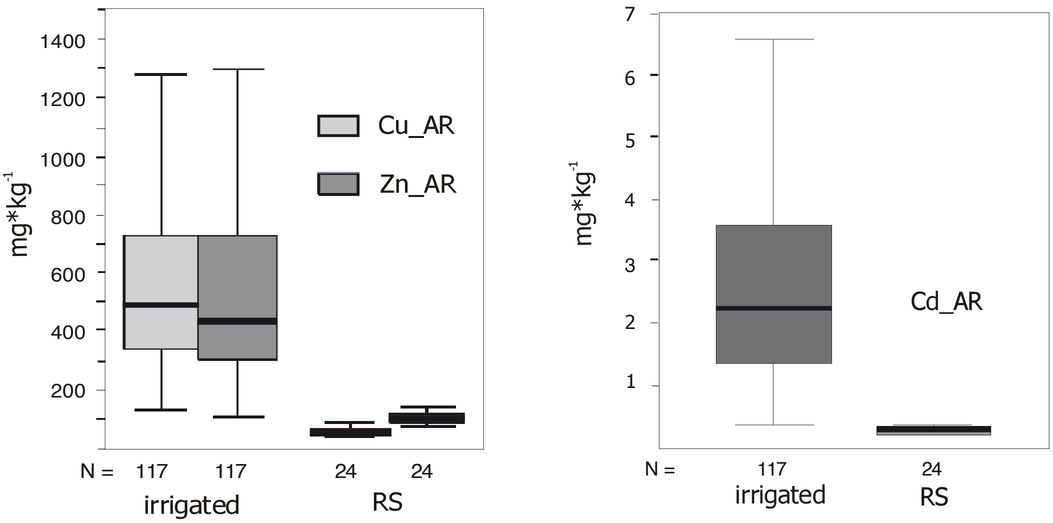

Figure 2. Total amounts (box plots with medians, 25 and 75 percentiles, minimum and maximum) of heavy metals in topsoils of non-irrigated arable fields (RS = reference soils) in comparison to topsoils of irrigated sites of different land use.

Non-irrigated soils of arable fields used for growing cereals and maize are situated on slopes above the irrigation channels. The concentrations comply with the background values in the study area and are related to the parent material and eolian dust deposition from the mining waste deposits (Burnod-Requia, 2003). With respect to the precaution values (BBodSchG, 1998), the HM concentrations in the non-irrigated topsoils are in the uppermost range. For about 30% of the investigated sites the soil concentration of Cu_{AR} already exceeds the precaution value of 60 mg*kg-1, while the maximum value of the mobile Cu_{AN} fraction was 0.31 mg*kg^{-1}, clearly below the trigger value for the pathway soil–food crop. The Zn_{AR} and Cd_{AR} concentrations fall below all threshold values and therefore pose no concern at present for the non-irrigated soils.

Most of the *irrigated soils under different land use* display a strong enrichment with HM that can be traced back to irrigation with polluted water from the Mashavera river over a period of several decades (Fig. 2). The concentrations of Cu_{AR}, Zn_{AR} and Cd_{AR} are narrowly and significantly correlated ($r = 0.94–0.96$) due to the same source. The span of the HM concentrations in irrigated soils is by far wider than in the non-irrigated topsoils, especially towards higher concentrations above the 75th percentile. Differences in the duration, frequency and amounts of irrigation as well as changes in the type of land use and soil cultivation (e.g. depth of plowing) are the reasons for this high spatial variability. This shows that the degree of soil pollution by HM in the Mashavera valley cannot be estimated but must be investigated for each cultivated field, house garden and orchard in order to evaluate the hazard to the food chain and the consumer.

Table 2. Proportion (%) of non-irrigated and irrigated sites of different land use, exceeding relevant threshold values of the German *Protection and Contaminated Sites Ordinance* (BBodSchV, 1999).

Land use (number of investigated sites)	Precaution value	Trigger value soil – food crop	Action value
arable land, non-irrigated (10)	Cu: 30%		
arable land, irrigated (42)	Cu: 100% Zn: 77 % Cd: 27 %		
permanent meadows (15)	Cu: 100 % Zn: 100 % Cd: 80 %		Cu: 60 %, in case of grazing of sheep
vegetable gardens (67)	Cu: 100 % Zn: 100 % Cd: 85 %	Cu: 50 % Zn: 15 %	Cd: 21 %, in case of non-accumulating crops; Cd: 40 %, in case of accumulating crops
orchards and grape fields (49)	Cu: 100 % Zn: 100 % Cd: 100 %	Cu: 85 % Zn: 45 %	Cd: 82 %, in case of mixed cropping with vegetables; Cd: 45 %, in case of wine grapes only

The medians of the EDTA fractions in topsoils *of irrigated arable fields* amount to 9 (Cu), 13 (Zn) and 6 (Cd) times greater than in the non-irrigated reference soils. About 33 % (Cu), 12 % (Zn) and 67 % (Cd) of the total amounts belong to this supply fraction, which indicates, especially in the case of Cd, a high potential risk of soil pollution with heavy metals.

As Cd is the most mobile heavy metal, an increasing uptake by plants already occurs under slightly acid conditions below pH 6.5. At present the arable soils also contain small amounts of calcium carbonate in the A-horizon, mostly in the range of 2–5 mass%. Because agriculture and irrigation favors decalcification and acidification, an increase of the Cd mobility must be taken into account in the future.

Permanent grassland of the alluvial floodplains along the Mashavera river, which occasionally becomes submerged by floodwaters of the river, is polluted by settled fines with a high concentration of HM, distributed on the soil surface and the leaves of vegetation. Eighty per cent of the samples from A-horizons of meadows exceed the precaution value for Cd_{AR}, and 100% of the samples for Zn_{AR} and Cu_{AR}. The meadows are used for extensive grazing of cattle, sheep herds and horses, which also use the river water for drinking. Due to a sandy texture and partly low pH values, humus and carbonate contents, the alluvial soils display a higher proportion of HM in the mobile fraction as compared to irrigated arable soils.

Vegetable gardens are distributed on the lower terrace of the Mashavera valley, adjacent to villages and farms, where they are irrigated manually with water from the river. Other vegetable gardens adjoin the irrigation channels, where they concentrate around settlements. Compared to the arable land, vegetable gardens are irrigated over a longer period in the year, more intensively and with a greater amount of water brought by buckets and pumps or distributed from irrigation channels by furrow irrigation. Therefore the concentrations of the total amounts of HM_{AR} are much higher than in topsoils of arable fields. The same trend is shown by the supply fraction (EDTA). Forty per cent of Cu, 20% of Zn and 79% of Cd belong to the supply fraction. This indicates that with increasing transfer of HM from the irrigation water, the supply fraction increased non-proportionally.

Nearly all site threshold values are exceeded according to BBodSchV (1999) and the target values of the "Dutch List" (Tab. 2). This means that especially due to the strong toxicity of Cd and a potentially high transfer into the food chain, further investigations are necessary of all irrigated vegetable gardens in the Mashavera valley. According to BBodSchG (1998), restrictions of land use would be necessary in order to protect the population.

The high total amounts of HM in topsoils of irrigated soils used for agriculture, house gardens, orchards and grape fields as well as occasionally submerged meadows of the Mashavera floodplain, indicate strong contamination due to the deposition of fines with sulphidic metal particles and dissolved HM in acid mine drainage waters.

The bulk of immobile, specifically adsorbed plus mobile or weakly adsorbed HM forms the supply fraction. The proportion of this fraction, soluble in EDTA, ranges from 20 to 45% of the total amounts (HM_{AR}). Highly significant correlations exist between amounts of the supply fraction and the amounts of adsorbents in the topsoils. The important organic substances for the adsorption of the supply fraction increases in the sequence Cd ($r = 0.43$) < Zn ($r = 0.56$) < Cu ($r = 0.58$). The highly significant correlations between the amounts of Fe and Al oxides and the supply fraction increase in the sequence Cu ($r = 0.80$ Fe_{ox}, 0.85 Al_{ox}) < Zn ($r = 0.58$ Fe_{ox}, 0.64 Al_{ox}) < Cd (no significance Fe_{ox}, 0.62 A_{ox}). This shows that the adsorption of Cu and Zn on soil particles is stronger than that of Cd, which therefore has the highest mobility and risk potential to the food chain, also indicated by the lowest threshold values displayed in the BBodSchV (1999) and the "Dutch List".

Herms and Brümmer (1984) referred to the great environmental importance of the supply fraction, due to significant correlations between supply (HM_{EDTA}) and mobile (HM_{AN}) fractions. The latter are relevant for the amount of HM uptake in food plants (Brümmer et al., 1986; Zeien & Brümmer, 1989, 1991, Hornburg & Brümmer, 1993; Allen et al., 1995). In this study the highly significant correlations (r) between the supply fractions (*EDTA*) and the mobile fractions (NH_4NO_3-extractable) increase in the sequence Cu 0.75 < Zn 0.82 < Cd 0.86.

The supply fraction of HM in topsoils represents a high future risk potential, which is presently still increasing due to continuous irrigation with polluted water from the Mashavera and Kazretula rivers. In case of a slow change of soil properties due to land use, which influences conditions for specific HM adsorption, parts of the supply fraction will become more available. Decomposition of organic matter, decalcification, increasing acidity or intermittent reducing conditions (Charlatchka and Cambier, 2000), due to excess of irrigation water or logging of surface water, would be the main factors.

Due to the recent high adsorption capacity of the soils for HM (Tiller et al., 1984 a,b), only small amounts of HM in the mobile fraction were found with proportions of less than 1% of the total amounts for Cu and Zn and a maximum of 1.5% for Cd. Nevertheless trigger values (for Cu and Zn) and action values (for Cd), which are based on the concentrations of the NH_4NO_3 soluble fraction (BBodSchV, 1999), are exceeded at most irrigated house gardens, orchards and grape fields, especially those used for growing vegetables in mixed cropping systems. As measured by the threshold values of the German Soil Protection Law, land use restrictions and remediation measures would apply to 40 % of the investigated house gardens and to about 80 % of the grape fields, wine gardens and orchards with mixed cropping of vegetables.

In order to indicate the actual risk of an HM transfer to food crops, herbs and vegetables from single house gardens were investigated.

First results from (non-systematic) screening investigations of HM concentrations in herbs and vegetables of irrigated house gardens and grass from an occasionally submerged meadow of the Mashavera floodplain (Table 3) show that the Cu and Zn concentrations in many cases exceed the tolerance threshold for plants. Therefore garden owners of the Mashavera valley have low yields and poor quality crops, often visible by growth depressions and chloroses or necroses of the leaves. In many cases, the Cd concentrations of the herbs and vegetables exceed the tolerance thresholds for animals and human beings and therefore endanger the health of the population. One important source for the HM uptake into the food chain is the adhesion of fines to leaves and stems of herbs, which have direct contact with the irrigation water. Therefore washing of the crops in clean water diminishes the HM concentrations (Table 3). The opposite can be observed in the Mashavera valley. Directly after harvest and before going to market, farmers often wash fruits and vegetables in the Mashavera river bed or with water from the river. This behavior causes another high risk for direct contamination of market fruits and crops.

Furthermore, pot and field experiments with summer wheat (*Triticum aestivum*), as a non-accumulating crop, and spinach (*Spinacia oleracea* L. cv. Calata) as an accumulating crop, were carried out on different polluted soils from the Mashavera valley. While the pot experiment was carried out with soil material from the Mashavera valley under controlled conditions in a green house, the field experiment was influenced during the growing season by the natural environmental factors of the study area.

Table 3. Screening of Cd-, Cu- and Zn-contents in mg* kg^{-1} dry matter (dm) of herbs and vegetables from irrigated house gardens and of grass from an occasionally submerged meadow of the alluvial plain of the river Mashavera. Tolerance thresholds for vegetation, animals and human beings, after Sauerbeck (1985).

Plant species	Organ	Cu mg* kg^{-1} dm	Zn mg* kg^{-1} dm	Cd mg*kg^{-1} dm
Pepperoni	leaf	50.1	268.4	4.1
Pepperoni	stem	16.3	80.1	1.46
Pepperoni	fruit	20.3	52.6	1.29
Tomato	fruit	6.5	23.9	0.4
White cabbage	external leaf	9.2	68.7	1.19
	internal leaf	19.9	47.9	0.32
Red beet	stem	15.7	52.2	0.33
	leaf	4.0	6.8	0.16
Grass, washed	leaf	20.3	96.4	0.73
Grass, without washing		23.1	93.5	0.72
Basil, washed	leaf	5.7	17.2	0.10
Basil, without washing	leaf	56.7	78.5	0.72
Parsley, washed	leaf	4.3	14.6	0.09
Parsley, without washing	leaf	6.7	96.4	0.13
Spinach, washed	leaf	19.5	237.7	2.65
Spinach, without washing	leaf	37.2	253.2	2.93
Tolerance threshold for plants		15-20	150-200	5-10
Tolerance threshold for animals and human beings		30-100	500	0.5-1.0

The topsoils of the experimental fields are rich in clay and organic matter and the low contents of calcium carbonate stabilize the pH in the weak alkaline range (Table 4). Only site 4 displays weakly acidic conditions due to the absence of carbonates. At all sites the concentrations of HM greatly exceed the precaution values (BBodSchG, 1999). Trigger values for the pathway soil – food crop are exceeded by Cu at sites 1P and 2 PF, while action values for Cd-accumulating vegetables (Cd > 0,04 mg*kg^{-1}), are exceeded at sites 2 PF, 3PF and 4 F, and for non-accumulating crops (Cd > 0,1 mg*kg^{-1}) at site 4F.

Table 4: Physical and chemical characteristics and contents of total (HM_{AR}) and plant available amounts (HM_{AN}) of heavy metals in topsoils of irrigated Kastanozems of the Mashavera valley used for pot and field experiments.

Soil P = pot F = field	pH (0,0 M $CaCl_2$)	Clay mass-%	$CaCO_3$ mass-%	OM mass-%	Cu_{AR} mg*kg^{-1}	Cu_{AN} mg*kg^{-1}	Zn_{AR} mg*kg^{-1}	Zn_{AN} mg*kg^{-1}	Cd_{AR} mg*kg^{-1}	Cd_{AN} mg*kg^{-1}
1 P	7.57	49.18	1.29	2.76	527	1.23	352	0.23	1.63	0.01
2 PF	7.39	50.18	0.21	3.24	761	1.43	658	0.66	4.00	0.04
3 PF	7.52	42.84	0.44	3.32	242	0.56	269	0.10	0.94	0.05
4 F	6.67	54.39	0	3.48	933	1.99	782	1.40	3.58	0.12

Table 5. Heavy metal concentrations (mg*kg^{-1} dry matter) in grains and straw of summer wheat, grown in a pot experiment. For tolerance thresholds for plants and animals see Table 3 and for soil data see Table 4.

Soil	Cu		Zn		Cd	
	Grain	Straw	Grain	Straw	Grain	Straw
1 P	12.2	11.2	60.0	69.5	0.26	0.41
2 PF	12.3	11.4	65.3	119.3	0.29	0.66
3 PF	9.5	7.0	50.9	42.7	0.13	0.26

Because summer wheat belongs to a vegetation type with a reduced uptake or which excludes HM, tolerance thresholds (Sauerbeck, 1985) were not exceeded, except for Cd accumulation in the straw of site 2 PF. However, at all sites the Cd concentrations in the wheat grains exceed the "guideline value for Cd concentrations in bread wheat" of 0.1 mg*kg^{-1} according to the German Food Ordinance (ZEBS, 1990), which means that wheat with such Cd concentrations should not be used for human nutrition. The threshold value according to the German Animal Feed Ordinance (FuttermittelVO, 1988) of 1 mg Cd*kg^{-1} for straw, which is used as fodder for animals, is not exceeded.

The results of the spinach field and pot experiments show that this plant species accumulates heavy metals, especially Zn and Cd. At sites 1 P with Cd concentration in the soil below the action value of 0.04 mg*kg^{-1} (Tab. 5), the transfer factors (Cd in plant / Cd_{AR} soil) are clearly above 1. The tolerance thresholds for plants as well as for humans and animals are partly reached or exceeded, especially for Cd. In the field experiment, the spinach of fields 2 and 4 showed severe growth depressions, possibly due to the high Cu and Zn concentrations. Washing of the spinach leaves of the field experiment leads to a marked reduction of the Cu concentrations and reduces the Zn and Cd contents to a smaller extent. Obviously washing removes HM, which are adsorbed at the plant surface as a consequence of direct contamination with polluted irrigation water.

Table 6. Heavy metal concentrations (mg*kg^{-1} dry matter) in the green mass of spinach (*Spinacia oleracea* L. cv. Calata) grown in a pot experiment (P) and a field experiment (F). Spinach from the field experiment was investigated unwashed (F uw) and washed (F w). For tolerance thresholds for plants and animals, see Table 3 and for soil data, see Table 4.

Soil	Cu			Zn			Cd		
	F uw	F w	P	F uw	F w	P	F uw	F w	P
1 P			27.2			182.4			2.99
2 PF	22.0	10.3	33.9	206.7	182.3	209.3	3.04	2.21	4.20
3 PF	13.0	5.8	5.1	123.3	124.1	87.7	1.23	1.29	1.25
4 F	37.2	19.5		253.2	237.7		2.93	2.65	

The threshold for leaf-vegetables of 0.2 mg Cd *kg^{-1} in fresh plant material is exceeded at most sites if a dry matter content of 10 % is assumed, according to the EU Food Ordinance (Verordnung EG Nr. 466/2001 8. March 2001). The majority of the irrigated soils show high total amounts of Cu, Zn and Cd and high concentrations in the supply fraction, which indicates the severe long-term risk of heavy metal pollution to the food chain. In spite of the high HM_{AR} and HM_{EDTA} fractions the proportion of the mobile and weakly adsorbed HM_{AN} fraction, solubility in NH_4NO_3 is rather low and reaches only < 1% (Cu, Zn) – 1.5 % (Cd) of the total amounts. The reason for this rather low mobility is the high sorption capacity of the soils, due to high contents of clay and organic matter, and pH values > 7 (c.f. Blume and Brümmer, 1987). Nevertheless, the concentrations of the mobile Cd fraction exceed the precaution, trigger and action values in topsoils of many sites according to the BBodSchV (1999) and the target and action values of the "Dutch List". According to the German Soil Protection Law, land use restrictions and remediation measures would apply to 30 % of the investigated house gardens and to more than 50 % of the grape fields, wine gardens and orchards with mixed cropping of vegetables (Table 3). Therefore the actual risk of Cd transfer into the food chain is established, which affects the local population as well as people in cities up to the capital Tbilisi, where crops from the Mashavera valley are sold at the open markets.

The first results from screening investigation of crops from house gardens as well as field and pot experiments with wheat and spinach indicate a high uptake of Cu, Zn and Cd in cereals and vegetable leaves that exceed tolerance thresholds for plants, animals and human beings and threshold values for human consumption and animal feed. This indicates that, in spite of a high sorption capacity of the soils, plant availability of HM still exists. Although Cu is specifically adsorbed mainly on organic matter and therefore the least mobile element in neutral to weakly alkaline soils (established by results of the NH_4NO_3 extractions), the Cu contents in vegetation indicates a rather strong uptake. Correlations between HM_{AN} and organic matter content are highly significant and increase in the sequence Cu ($r = 0.38$) < Cd ($r = 0.45$) < Zn ($r = 0.52$). According to Brümmer et al. (1986) and Welp and Brümmer (1998) the mobility of Cu and other metal ions increases in alkaline soils in the sequence Zn < Cd < Cu due to the formation of soluble organic complexes. This could be a reason for the higher mobility and HM uptake by crops. While correlations between pH values and Zn_{AN} ($r = -0.43$) and Cd_{AN} ($r = -0.31$) are weak and negative, the correlation between pH and Cu_{AN} is weak and positive. On the other hand, the direct contact of root hairs with the surfaces of HM adsorbents and the excretion of acid root exudates could favor the dissolution and uptake of HM at a microscale.

While the high affinity of Cu to different fractions of organic substances is well known (Brümmer and Herms, 1983; Atanassova, 1995, 1999; Alloway, 1999), the adsorption of Zn, as reflected by the coefficient of correlation reflects specific conditions. McGrath & Cegarra (1992) showed that the high adsorption of Zn on organic matter indicates a strong loading situation. Due to relatively low amounts and therefore limited adsorption capacity for HM ions of Fe and Al oxides in the Kastanozems, Zn is bound first to humic acids and then with time migrates into the oxide minerals where it is specifically adsorbed. Similar observations were made by Sposito et al. (1985) and Han et al. (2001).

Apart from the soil reaction, the decrease of the redox potential during the irrigation periods can cause a higher HM mobility due to the dissolution of Mn and Fe oxides (e.g. Charlatchka and Cambier, 2000), which have a high binding capacity for HM at pH values > 7. However, in our field and pot experiments the periods of irrigation were short, such that dissolution of oxides by reduction can be excluded.

CONCLUSIONS

The irrigated soils of the Mashavera valley are fertile and have a high agricultural yield potential. Accordingly they are an important resource for the production of food crops in Georgia. The river water used for irrigation, however, is polluted with high concentrations of potentially toxic sulphidic heavy metals. Thus the topsoils of irrigated arable fields, vegetable and wine gardens, grape fields, orchards and occasionally submerged meadows are contaminated in the region with Cu, Zn and Cd. At most of the investigated sites the concentrations exceed the precaution values defined in the Federal Soil Protection and Contaminated Sites Ordinance or the target values in the "Dutch List". A high proportion of the HM is bound by specific and unspecific adsorption in the supply fraction, which is potentially plant available.

Exceeding action values for Cd would justify land use restrictions in many irrigated house and wine gardens, grape fields and orchards, due to a presumable transfer of this highly toxic element into the food chain. High concentrations of Cu and Zn in topsoils and the uptake of these elements in crops cause limitations in yield and crop quality. Furthermore, there is a high risk of direct contamination of people and animals by direct uptake of HM using unwashed crops, or with the use of washing and drinking water from the Mashavera river.

Further systematic investigations are in progress to assess the uptake of HM by crops based on the spatial distribution of soil pollution and through additional field experiments.

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