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Heavy Metal Pollution of Soils and Food Crops due to Mining Wastes in the Mashavera River Valley

Peter Felix-Henningsen[*], **Tengiz F. Urushadze**[**], **Eliso I. Narimanidze**[J], **Lars-Christoffer Wichmann**[J], **Dietrich Steffens**[§], **Besik B. Kalandadze**[Ґ]

* *Institute of Soil Science and Soil Conservation, Justus-Liebig-University, Giessen, Germany*
** *Academy Member, Georgian State Agricultural University, Tbilisi*
J *Centre for International Development and Environmental Research, Giessen, Germany*
§ *Institute of Plant Nutrition, Justus-Liebig-University, Giessen, Germany*
Ґ *Iv. Javakhishvili Tbilisi State University*

ABSTRACT. The fertile irrigated soils of the Mashavera valley, Georgia, have high agricultural yield potential. The river water used for irrigation, however, is polluted with mining waste from a copper and gold mine situated in the mountainous region of the middle reaches of the Mashavera river. Furthermore waste water from a floatation plant, erosion material from floatation waste deposits and acid mine drainage leads to high concentrations of dissolved and suspended sulphidic heavy metals. The Cu, Zn and Cd concentrations of mud from irrigation channels and the Mashavera river are extremely high. It is estimated that the annual transfer of heavy metals (HM) by irrigation water is in the range of several g*ha^{-1} for Cd and several kg*ha^{-1} for Cu and Zn. *© 2007 Bull. Georg. Natl. Acad. Sci.*

Key words: *heavy metals, pollution of soils, irrigated and non-irrigated soils.*

Georgia is rich in different mineral resources, which were already known and mined over the past centuries. One of the most important and biggest non-ferrous metal deposits is located in SE Georgia in the province Kvemo Kartli at the mountain fringe of the Small Caucasus. In the region of the small town Bolnisi, located in the transition area between the middle and lower reaches of the Mashavera river, poly-metallic ore deposits, mainly copper, zinc and gold, have been mined since 1974 in a large opencast mine at the village of Kazreti.

Another branch of economic activity is intensive agriculture on the fertile soils of the alluvial and terrace plains of the Mashavera river. Due to the semi-arid climate of East Georgia, with arid phases during the vegetation period, sufficient yields of fruits and food crops from the fertile soils, mainly kastanozems and chernozems, can only be obtained by irrigation with water from the Mashavera. Then 2 to 3 yields per year are possible.

Decades of mining of copper and precious metals have caused severe environmental problems. Mining waste, which is deposited on the mountain slopes around the opencast mine as well as deposits of waste from a flotation plant consisting of fine ground rock debris, cover an area of about 240 ha. Mining and flotation wastes are rich in fines, which contain remains of sulphides. Due to an extremely acid environment from sulfuric acid, caused by oxidation of sulphides near recent surface deposits and the release of heavy metals (HM), the stockpiles are unvegetated. Adequate measures to stabilize the slopes by planting vegetation were never taken. Therefore, runoff from the slopes leads to rill and gully erosion and severe contamination of the Kazretula river and other small creeks near Kazreti, which meet the Mashavera river, by fines with adsorbed heavy metals and remnants of sulphides. The Mashavera presently is one of the most polluted rivers of Georgia.

The use of the Mashavera waters for irrigation led to pollution of the fertile soils by suspended fines, rich in heavy metals. The polluted soils, on the other hand, can also be a potential source for the contamination of the food chain by heavy metals.

Accordingly a research project, generously funded by the German Volkswagen Foundation, focused on amounts and spatial distribution of the heavy metals as a consequence of deposition of mining wastes on irrigated soils of the Mashavera valley as well as on the eco-toxicological importance for the food chain.

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.

The ore deposits of the Bolnisi region show a close relationship to volcano-sedimentary rocks of the Upper Cretaceous (Upper Turonian up to Lower Santonian), locally penetrated by intrusive rocks.

The most important ore deposits of Georgia occur in the Bolnisi district, especially deposits of non-ferrous metals. They show a close relationship to hydrothermal systems that occur in the surroundings of Santonian volcanic dykes, tuff deposits and tectonic faults [1,2].

The hydrothermal fluids caused a diffuse, stratiform dissemination of metals in the superficial rocks as well as a crystallisation of sulphidic ore veins. The metal sulphides are associated with gold, which mainly occurs in metasomatic alterated banks of quartzite-sericite rocks of about 100 m thickness [2,3]. Mining of the copper sulphide deposits started in 1975. The ”Madneuli” mining company produces high-grade copper concentrates by floatation, which are exported to different countries [4]. The extraction of gold from ground quartzite rocks by cyanide (heap-leach procedure) started in 1994. 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 in the west and the Poladauri valley in the east. Therefore 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. In addition, highly contaminated waste water from the Madneuli floatation plant contributes to the pollution of the river Mashavera [2,3]. Violations against existing security regulations caused a temporary closure of mining in the past.

Fine grained floatation 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 release of large amounts of AMD and dissolved HM. The steep slopes of the large heaps are bare and not fixed by vegetation, thus causing sheet and rill erosion and transport of fines to the Mashavera and Kazretula rivers, while AMD runoff directly contaminates the rivers by HM. In addition, the physical state of the deposits was not taken into account and resulted in slope failures [5]. During the dry summer months the heaps of floatation waste are the source of dust, which amounts to about 30 Mg a^{-1} [4] 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.

The natural steppe vegetation formations [6] of the Mashavera valley were changed by agriculture.

This main channel branches off from the Mashavera river directly below the floatation plant and the large deposits of floatation waste at Kazreti. Due to the strong load of the Mashavera river water with fines, which derive from the waste deposits and the floatation plant, the irrigation channels also conduct water heavily contaminated by HM.

The fields of the northern side of the Mashavera valley are irrigated with water from a channel, which branches off from the Mashavera river upstream of Kazreti. Therefore this water is free from contamination.

Due to the continental type of climate the typical main soil orders belong to kastanozems and chernozems [7,8], which frequently degraded to phaeozems as a consequence of long periods of intensive irrigation. The main soils of the study area are calcic kastanozems, which show an accumulation of calcium carbonate in the form of concretionary mottles in the subsoil but lower humus content and a more brownish colour than chernozem. They are associated with calci-vertic chernozems with clay contents up to 65 mass-%. The medium to strong humic topsoils show a blocky to polyhedral structure due to the high clay content. They are weakly alkaline and have a rather high CEC.

The humus content decreases with increasing intensity of soil cultivation in the sequence grape fields and vineyards, orchards, house gardens, and arable fields. As a further reason for the high humus contents in topsoils of vineyards, 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 [9]. 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.

The clay minerals of chernozems and kastanozems mainly consist of chlorite-smectite mixed-layer minerals (corrensite) and the composition shows no difference between the saprolite from pyroclastics (rhyolitic tuff and ignimbrite) and the soil horizons above, although the clay contents rise from 20 mass-% in the saprolite to about 60 mass-% in the topsoil.

Orientation in the field was based on Russian topographical military maps 1:50,000, Landsat TM 5 scenes and aerial photographs.

Soil samples were taken in fields, house gardens, grape fields, vineyards 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 Justus-Liebig University in 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 $C_{org} \cdot 1.724$.

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 [10].

Pedogenic iron (Fe_{DCB}) *and manganese* (Mn_{DCB}) oxides were extracted following the procedure of Mehra & Jackson, as described in [10].

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 [11,12]. 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 [13], 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 the 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.

Due to the discharge of waste waters from the floatation plant, as well as suspensions and acid mine drainage (AMD) from the mining waste deposits, the water and sediments of the Mashavera and Kazretula rivers and the branching irrigation channels are loaded by HM. pH values < 4 of the flowing waters indicate that HM are temporarily dissolved. The concentration of the river and channel waters greatly exceeds the threshold values of the German Waste Water Regulation and the German Drinking Water Regulation, although a dilution occurs when the mine waters enter the river. The population of the villages along the rivers and channels use the water not only for irrigation but also for washing of fruits and vegetables, clothes and dishes as well as for personal hygiene. Therefore the residents are exposed to a high risk of direct contamination with HM.

Liming of the Kazretula river, sporadically disposed by the Madneuli Mining Company, raised the pH to a weakly alkaline range and diminished the concentration of dissolved HM

Fine-grained sediments of the rivers and the irrigation channels are contaminated to a high degree with HM. They consist of fine ground sulphidic rock fragments and organic matter from bacteria and algae, which absorb a part of the dissolved HM fraction. According to the German Sludge Ordinance [14], the concentrations exceed the threshold values for Cu_{AR} by factors of 10-40, for Zn_{AR} by 3 and for Cd_{AR} by 1.2-3.4. A proportion of 30 (Cu, Zn) to 60 % (Cd) of the total amounts belong to the supply fraction, which is potentially plant available .

In the course of irrigation, suspended fines are distributed with the irrigation water on the fields and gardens. Under the assumption that the irrigation water contains a concentration of suspended fines of 1 g l^{-1}, an irrigation of only 50 mm a^{-1} causes an annual deposition of 500 kg mud ha^{-1} with up to 16 kg Cu ha^{-1}, 3.6 kg Zn ha^{-1} and several 100 g Cd ha^{-1}.

At the end of the annual irrigation period the irrigation channels are cleaned from mud sediments. The mud is excavated and deposited at the field margins along the irrigation channels. Then erosion distributes the fines over the adjacent field areas and causes another source of soil pollution by HM.

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 spatial distribution of the problem elements Cu, Zn and Cd shows a 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. Therefore the presentation and discussion of the results must take the type of land use into account (Fig. 1).

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 with the parent material and eolian dust deposition from the mining waste deposits [4]. With respect to the precaution values [15], 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 lies with 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 of HM that can be traced back to irrigation with polluted water from the Mashavera river over a period of several decades (Fig. 1). 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 population.

In topsoils of arable fields the Cu$_{AR}$ concentrations considerably exceed the regional background values (by a factor of 5), the German precaution values (factor 2–7) and the target values of the Dutch List (factor 2–9). The low concentrations of the mobile fraction, < 1 % of the potentially available supply fraction (HM$_{EDTA}$), indicates the high sorption capacity of the soils rich in humus, bases and clay for Cu. Nevertheless, at two sites the trigger value is exceeded for the path soil–food crop according to [16].

In 77 % of the investigated sites the Zn$_{AR}$ concentrations exceeded the precaution values [16] and the target values (Dutch List) up to a factor of 3. Due to an obviously strong adsorption of Zn, from which the rather low concentrations of the available fraction (Zn$_{AN}$) is a result, the trigger value for the path soil–food plant of more than 2 mg*kg^{-1} was reached at one site. Therefore it can be assumed that up to now the growth of food crops is not severely affected by the Zn concentrations.

In 27 % of the investigated topsoils of arable fields, the concentrations of Cd$_{AR}$, with amounts up to 5.7 mg·kg^{-1} exceeded the precaution value of 1.5 mg*kg^{-1} according to [16] for soils rich in clay. The action value for topsoils of fields used for the cultivation of bread wheat is defined as 0.04 mg Cd$_{AN}$*kg^{-1}. In three fields the action value was reached or exceeded, but in most sites 50 % or more of the range below the action value was reached. Therefore the growth of bread wheat on irrigated fields of the

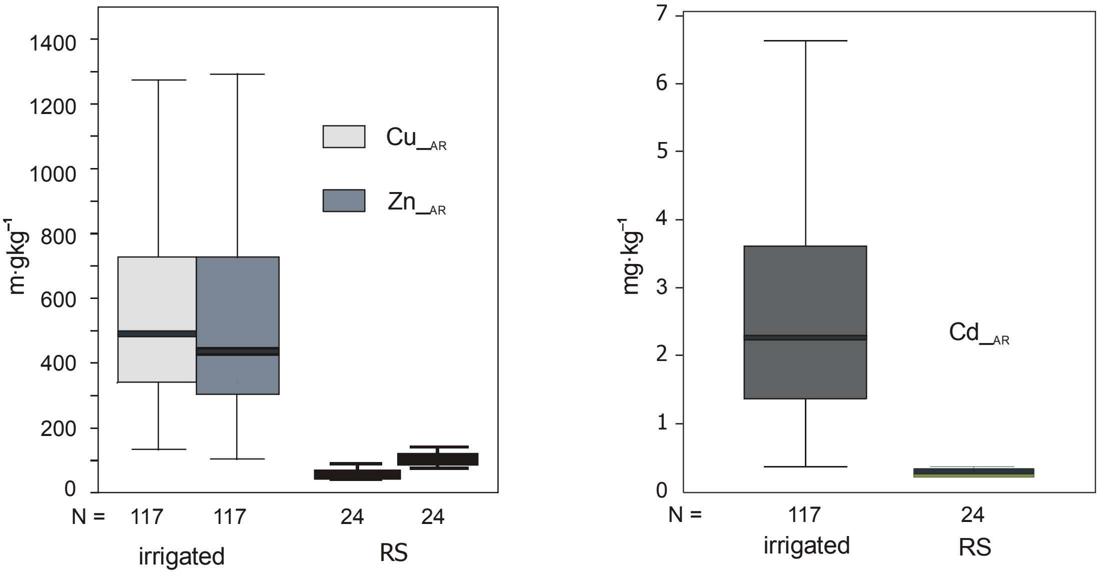

Fig. 1. Total amounts (box plots with medians, 25 and 75 percentiles, minimum and maximum) of heavy metals in topsoils of non-irrigated arable fields (RS = reference soils) in comparison to topsoils of irrigated sites of different land use.

Mashavera valley should be controlled with respect to the Cd pollution of the soils.

The medians of the EDTA fractions 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.

The alluvial floodplains along the Mashavera river are covered by permanent grassland, which becomes occasionally submerged by flood waters of the river. Due to the pollution of the river water by mining wastes, settled fines with a high concentration of HM are distributed on the soil surface and the leaves of vegetation. The meadows are used by extensive grazing of cattle, sheep herds and horses, which also use the river water for drinking. Although the span of the HM concentrations is lower, the medians are in the same range compared to topsoils of arable fields. This shows that due to flooding, the spatial distribution of the HM is more uniform. Due to a sandy texture and partly low pH values, humus and carbonate contents, the alluvial soils display a higher proportion of HM_{AN} in the mobile fractions as compared to irrigated arable soils. The lower sorption capacity of soils, mostly rich in sand, results in the precaution values being lower than for clayey soils [16]. They are 0.4 $mg*kg^{-1}$ for Cd_{AR}, 20 $mg*kg^{-1}$ for Cu_{AR} and 60 $mg*kg^{-1}$ for Zn_{AR}. 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} und Cu_{AR}. On the other hand the action values (for grassland in the AR fraction, [16]) are relatively high (Cu_{AR}: 1,300 $mg*kg^{-1}$, Cd_{AR}: 20 $mg*kg^{-1}$, Zn_{AR}: not defined) and not reached by the actual HM_{AR} concentrations, with one exception: for meadows used for sheep grazing, which is frequently the case in the Mashavera valley, the action value for Cu_{AR} is 200 $mg*kg^{-1}$. More than 60 % of the samples from permanent meadows of the valley floor exceed this action value. This means that the pollution of the meadow soils can be dangerous for sheep, but also other grazing animals are affected through direct uptake of HM with fines adhering to the leaves of the grass vegetation and dispersed in the river water used for drinking. Therefore the meadows of the alluvial plain of the Mashavera river bear a high risk for the transfer of HM into the nutrient chain.

The 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 (Table 1) belong to the supply fraction. This indicates that with increasing transfer of HM with the irrigation water, the supply fraction increased non-proportionally.

At nearly all sites the precaution values are exceeded according to [16] and the target values of the “Dutch List”. The median of the soluble Cu_{AN} fraction exceeds the trigger value of 1 $mg*kg^{-1}$ for the pathway soil–food plant. For 10 % of the investigated house gardens, extreme concentrations up to eight times the trigger value were found. Due to toxic effects, frequent growth depressions of the cultivated crop plants must be taken into account.

The Zn_{AR} concentrations in topsoils of house gardens exceed the precaution value of 200 $mg*kg^{-1}$ in nearly all samples and surpasses this value by up to a factor of 12. Fifteen per cent of the samples exceed the trigger values of 2 mg $Zn_{AN}*kg^{-1}$. Therefore Zn may also cause frequent reductions in growth, yield and quality of the garden crops.

Due to high Cd concentrations, 85 % of the samples exceed the precaution value of 1.5 mg $Cd_{AR}*kg^{-1}$. Because in vegetable gardens crops with a high affinity for HM accumulation are frequently grown, the action value of 0.1 mg $Cd_{AN}*kg^{-1}$ was reduced to 0.04 mg $Cd_{AN}*kg^{-1}$ according to [16]. In the case of growing non-accumulating species of vegetables, 21 % of the investigated samples from vegetable gardens exceed the action value of 0.1 mg $Cd_{AN}*kg^{-1}$. Since there is mainly a mixed cropping of accumulating and non-accumulating vegetable species, the lower action value has to be taken into account, which is exceeded in about 40 % of the samples. This means that 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 [15], restrictions of land use would be necessary in order to protect the population.

An extreme HM load is distributed in topsoils of orchards, grape fields and vineyards (Table 2). Since the 19th century cultivation of fruit trees and wine has a long tradition in the Mashavera valley and its tributaries. These permanent cultures cover most of the area of the Mashavera valley bottom and the lower slopes of the adjacent mountains. Traditional mixed cropping with vegetables between the grape rows requires a high intensity of irrigation and therefore causes a severe HM contamination of the soils. This is clearly indicated by the comparison of the HM concentrations in topsoils of two neighboring, irrigated vineyards, with and without mixed cropping.

Table 1

Concentrations of heavy metal fractions in topsoils of irrigated vegetable gardens of the Mashavera valley and related soil data. *AR* = aqua regia extract, *EDTA* = EDTA extract, *AN* = NH_4NO_3 extract, OM = organic matter; Al/Fe/Mn$_{DCB}$ = free oxides, Al/Fe/Mn$_{ox}$ = amorphous fraction of the free oxides.

		Vegetable Gardens. Irrigated (N = 67)		
		Minimum	Maximum	Median
Cu_{AR}	(mg*kg^{-1})	91.20	2,945.00	553.25
Cu_{EDTA}	(mg*kg^{-1})	15.80	1371.00	227.05
$\mathrm{Cu}_{EDTA/AR}$	%	17.00	55.00	39.50
Cu_{AN}	(mg*kg^{-1})	0.27	7.92	1.44
$\mathrm{Cu}_{AN/EDTA}$	%	0.00	2.00	1.00
Zn_{AR}	(mg*kg^{-1})	157.70	2,441.00	501.50
Zn_{EDTA}	(mg*kg^{-1})	18.10	585.00	94.45
$\mathrm{Zn}_{EDTA/AR}$	%	10.00	60.00	20.00
Zn_{AN}	(mg*kg^{-1})	0.00	31.83	0.33
$\mathrm{Zn}_{AN/EDTA}$	%	0.00	21.00	0.00
Cd_{AR}	(mg*kg^{-1})	0.28	14.50	2.55
Cd_{EDTA}	(mg*kg^{-1})	0.13	11.16	2.00
$\mathrm{Cd}_{EDTA/AR}$	%	46.00	95.00	79.00
Cd_{AN}	(mg*kg^{-1})	0.00	0.56	0.03
$\mathrm{Cd}_{AN/EDTA}$	%	0.00	14.00	1.00
pH (H_2O)		6.67	8.23	7.76
pH ($CaCl_2$)		5.99	7.68	7.37
EC 2.5	(µS*cm^{-1})	83.00	1,297.00	201.50
$CaCO_3$	mass-%	0.00	15.50	1.70
OM	mass-%	0.28	6.50	3.16
Al_{DCB}	mg*g^{-1}	0.50	1.78	1.07
Fe_{DCB}	mg*g^{-1}	5.46	15.30	8.83
Mn_{DCB}	mg*g^{-1}	0.32	1.06	0.67
Al_{ox}	mg*g^{-1}	0.67	3.14	1.82
Fe_{ox}	mg*g^{-1}	0.79	6.78	1.88
Mn_{ox}	mg*g^{-1}	0.04	1.00	0.63

Table 2

Concentrations of heavy metal fractions in topsoils of irrigated orchards and wine gardens of the Mashavera valley and related soil data. *AR* = aqua regia extract, *EDTA* = EDTA extract, *AN* = NH_4NO_3 extract, OM = organic matter; Al/Fe/Mn$_{DCB}$ = free oxides, Al/Fe/Mn$_{ox}$ = amorphous fraction of the free oxides.

		Orchards. Wine Gardens. Irrigated (N = 49)		
		Minimum	Maximum	Median
Cu_{AR}	(mg*kg^{-1})	127.30	2,366.00	605.40
Cu_{EDTA}	(mg*kg^{-1})	56.90	1,006.00	280.10
$\mathrm{Cu}_{EDTA/AR}$	%	28.00	79.00	45.00
Cu_{AN}	(mg*kg^{-1})	0.23	6.59	1.22
$\mathrm{Cu}_{AN/EDTA}$	%	0.00	1.00	0.00
Zn_{AR}	(mg*kg^{-1})	139.30	3,735.00	614.00
Zn_{EDTA}	(mg*kg^{-1})	8.30	842.00	134.60
$\mathrm{Zn}_{EDTA/AR}$	%	4.00	56.00	22.00
Zn_{AN}	(mg*kg^{-1})	0.00	19.30	1.15
$\mathrm{Zn}_{AN/EDTA}$	%	0.00	7.00	1.00
Cd_{AR}	(mg*kg^{-1})	0.40	13.80	3.37
Cd_{EDTA}	(mg*kg^{-1})	0.17	7.87	2.76
$\mathrm{Cd}_{EDTA/AR}$	%	20.00	88.00	82.00
Cd_{AN}	(mg*kg^{-1})	0.00	0.32	0.05
$\mathrm{Cd}_{AN/EDTA}$	%	1.00	6.00	2.00
pH (H_2O)		7.05	8.15	7.65
pH ($CaCl_2$)		6.49	7.54	7.20
EC 2.5	(µS*cm^{-1})	103.00	483.00	197.00
$CaCO_3$	mass-%	0.00	20.00	0.10
OM	mass-%	2.63	5.06	3.46
Al_{DCB}	mg*g^{-1}	0.71	2.33	1.14
Fe_{DCB}	mg*g^{-1}	7.17	12.43	10.00
Mn_{DCB}	mg*g^{-1}	0.45	1.03	0.85
Al_{ox}	mg*g^{-1}	1.39	3.57	1.80
Fe_{ox}	mg*g^{-1}	0.33	4.19	1.65
Mn_{ox}	mg*g^{-1}	0.42	1.00	0.82

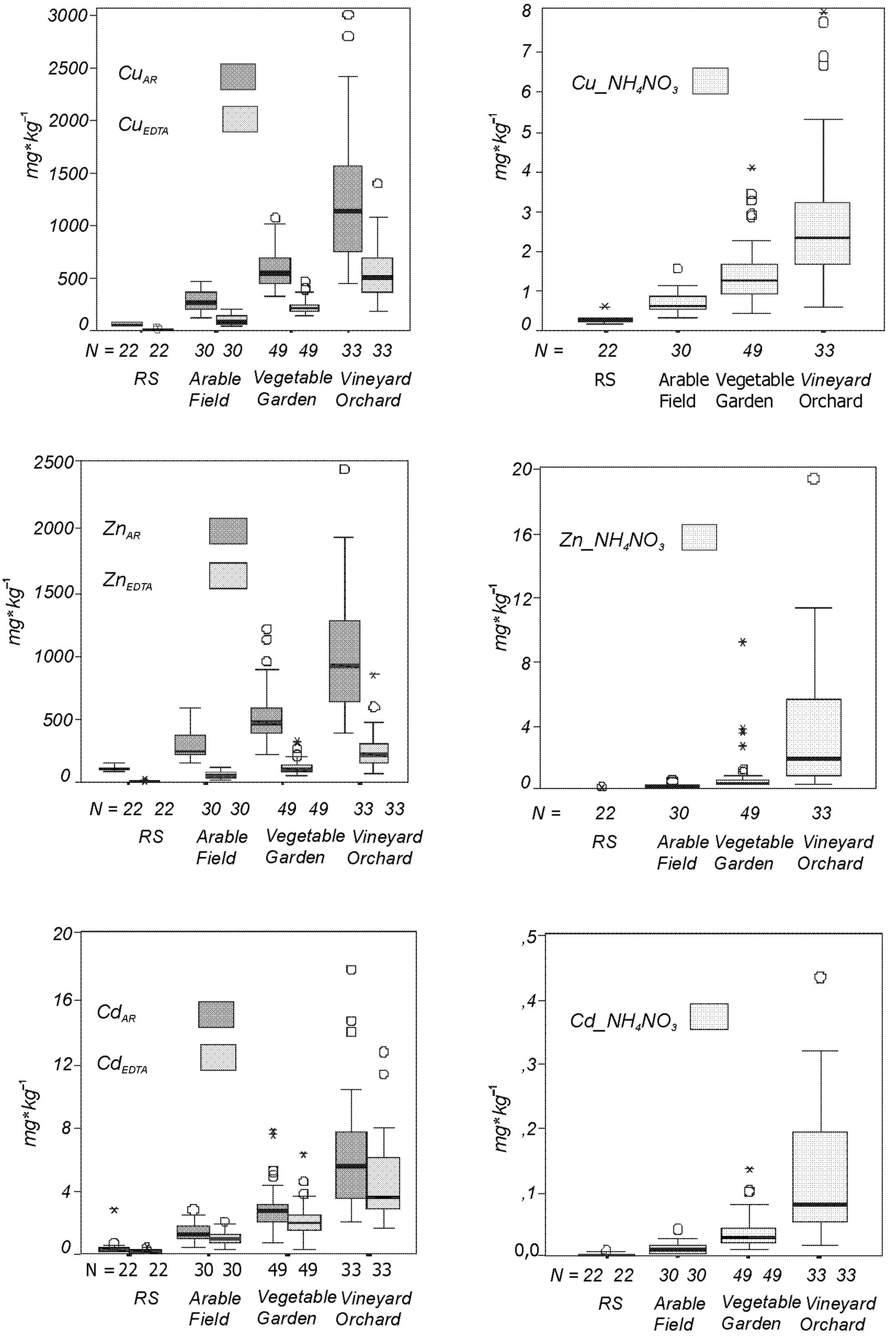

Fig. 2. Total amounts (box plots with medians, 25 and 75 percentiles, minimum and maximum) of heavy metals in topsoils of nonirrigated arable fields (RS = reference soils) in comparison to topsoils of irrigated sites with different land use.

Forty-five percent of Cu$_{AR}$, 22 % of Zn$_{AR}$ and 82 % of Cd$_{AR}$ belong to the supply fraction (*EDTA*, Table 4) and cause a high and long-term risk potential to the environment and food chain.

Background, precaution and target values of all three HM species are exceeded many times. The amounts of Cu$_{AR}$ exceed the precautions values [16] by between 7 to 49 times. The Zn$_{AR}$ concentrations are up to 18 times higher and the Cd$_{AR}$ concentrations up to 12 times higher than the corresponding precaution value. The amounts of Cu$_{AR}$ exceed the site-specific intervention values of the "Dutch List" (250 - 260 mg Cu$_{AR}$ ·kg^{-1}) at all sites up to a factor of 11. At 45 % of the investigated sites the amounts of Zn$_{AR}$ exceed the intervention value (210–214 mg Zn$_{AR}$·kg^{-1}). This threatens both the soil functions and growth conditions of the vegetation.

Trigger values for the mobile fraction of Cu (1 mg Cu$_{AN}$·kg^{-1}, [16]) are exceeded in 85 % of the investigated sites and those of Zn (2 mg Zn$_{AN}$·kg^{-1}, [16]) in 45 %.

The evaluation of the Cd concentrations with respect to the relevant action values must take the mixed cropping into account. Grapevine are not strong accumulators of heavy metals. Therefore the higher action value of 0.1 mg Cd$_{AN}$·kg^{-1} [16] is valid, which is exceeded in about 45 % of the investigated sites. On the other hand, for growing vegetables, which are partly strong accumulators of HM, the lower action value of 0.04 mg Cd$_{AN}$·kg^{-1} [16] is applicable, which is exceeded in 82 % of the investigated sites.

The high concentrations of HM in topsoils of irrigated soils used for agriculture, house gardens, orchards and vineyards indicate strong contamination due to the deposition of fines with sulphidic metal particles and dissolved HM in acid mine drainage waters. The intra-element correlations show that all metals derive from the pollution of the Mashavera river by sulphidic mining wastes in the form of fines and acid mine drainage. The total amounts of HM in the topsoils depend on the type of land use and are related to the kind of crops and the intensity of irrigation (Fig. 2).

The oxidation of sulphides after deposition at the soil surface or incorporation to the topsoil by infiltration, cultivation and bioturbation leads to a dissolution of HM accompanied by the formation of sulfuric acid. Acid conditions at the microscale favor the mobility of HM ions. Due to the carbonate contents of most topsoils, the sulfuric acid is buffered rapidly and dissolved HM become immobile due to adsorption mainly on the surface of clay minerals, carbonates, iron and aluminum oxides and humic acids. Because the chernozems, phaeozems and kastanozems of the Mashavera valley show high contents of clay and organic matter, moderate contents of iron and aluminum oxides, and low to high contents of carbonates, the buffer capacity of the topsoils for HM is rather high.

The bulk of immobile, specifically adsorbed plus mobile or weakly adsorbed HM form the supply fraction. 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 [16] and the "Dutch List".

While the high affinity of Cu to different fractions of organic substances is well proven [17,18,20], the adsorption of Zn, as reflected by the coefficient of correlation, is something special. Obviously the high adsorption of Zn on organic matter reflects a strong loading situation [4]. Due to a relatively low amount of Fe and Al oxides and the saturation of their adsorption capacity for HM ions, Zn is bound first to humic acids and then migrates with time into the oxide minerals where it is specifically adsorbed. Similar observations were made by [21] and [22,23] referred to the great environmental importance of the supply fraction, due to significant correlations between supply (EDTA) and mobile (NH_4NO_3) fractions. The latter are relevant for the amount of HM uptake in food plants [24,11-13, 25]. 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 [26], 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 [27,28], 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.

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 (manuscript in prep.) that exceed tolerance thresholds for plants, animals and human beings. Although Cu is adsorbed specifically mainly on organic matter and therefore the least mobile element in neutral to weakly alkaline soils (indicated by the results of the NH_4NO_3 extractions), the Cu contents in vegetation indicates a rather strong uptake. According to [29] the mobility of Cu and other metal ions increases in alkaline soils due to the formation of soluble organic complexes. In future studies the HM uptake in food crops must be investigated systematically. Furthermore it should be established that the characterization of the mobile fraction with the NH_4NO_3 extraction method after [11,12], which was developed for neutral to acid Middle European soils, is also valid for alkaline soils. Due to the possible volatilization of NH_3 in an alkaline environment, the concentration of NH_4 is probably too low for the exchange of weakly adsorbed HM. In a weakly alkaline milieu they could be mobilized due to direct contact with plant roots by acid root exudates.

Nevertheless, the concentrations of the mobile Cd fraction exceed the precaution, trigger and action values of [16] and the target and action values of the “Dutch List” in topsoils of many sites. 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, vineyards and orchards with mixed cropping of vegetables. Therefore the actual risk of Cd transfer into the food chain is proven, 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.

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მდინარე მაშავერას ხეობაში ნიადაგების და სასოფლო-სამეურნეო ნათესების გაჭუჭყიანება მძიმე ლითონებით

პ. ფელიქს-ჰენინგსენი[*], თ. ურუშაძე[**], ე. ნარიმანიძე[□], ლ. ვისმანი[□],
ს. სტეფენსი[§], ბ. კალანდაძე[#]

* *ნიადაგმცოდნეობის და ნიადაგის დაცვის ინსტიტუტი, იუსტუს-ლიბიხის უნივერსიტი, ჰისენი, გერმანია*
** *აკადემიის წევრი, საქართველოს სახელმწიფო სასოფლო-სამეურნეო უნივერსიტეტი, თბილისი*
□ *საერთაშორისო განვითარების და გარემოსდაცვითი კვლევის ცენტრი, გისენი, გერმანია*
§ *მცენარეთა კვების ინსტიტუტი, იუსტუს-ლიბიხის უნივერსიტეტი, გისენი, გერმანია*
# *ივ. ჯავახიშვილის თბილისის სახელმწიფო უნივერსიტეტი*

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