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ORE-DRESSING PRODUCTION AND ITS IMPACT ON SOIL AND WATER

Introduction. Nowadays one of the biggest problems in the world is global pollution of the environment. Of course, development of the civilization has changed the world, man uses natural resources more intensively. All the above mentioned is followed by soil pollution, erosion and decreased fertility, accumulation of harmful substances and as a result deterioration of drinking water, poor vegetation cover, etc. This in its turn sharply changes the social environment as well as human health that has global nature and does not refer to any separate the state.

Basic Part. 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 investigated. 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 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.

According a research project, generously funded by 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 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 natural steppe vegetation formations [1] 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 [2; 3], which frequently degraded to phaeozems as a consequence of long periods of intensive irrigation. The main soils of the study area cover 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 color 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 decrease with increasing intensity of soil cultivation in the sequence grape fields and vineyards, orchards, house garden and arable soils. 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 as well as from the use of copper bearing fungicides [2]. 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 ignimritic) 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 : 500 000, Landsat TM 5 scenes and aerial photographs. Soils samples were taken in

fields, house gardens, grape fields, vineyards and orchards from Ap horizon (0–30 cm) in 10 sites along double-diagonal transects. Eight volume-equivalents cores were taken with an aluminum auger within an area of $4 \cdot 4$ at each site. The fine earth (< 2 mm) 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, with a pH-meter pH90 (WTW).

The amount of carbonates was determined by the gas-volumetric method using a calcimeter, following DIN 18129.

Total amount of carbon (C_1) and nitrogen (N_1) 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_1 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 3,25, under dark conditions as described in [3].

Pedogenic iron (Fe_{ox}) and manganese (M_{dcb}) oxides extracted following the procedure of Mehra & Jackson, as described in were determined by extraction with buffered oxalic acid, pH 3,25, under dark conditions as described [3].

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 [4; 5]. 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 [6], 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 11 466. 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 SI (MAA 6000 spectrometer (Perkin Elmer) was used due to the low concentrations.

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. Although Cu is adsorbed

T a b l e 1 — Concentrations of heavy fractions in topsoils of irrigated vegetable gardens, 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 traction of the free oxides)

Heavy fractions		Vegetable Gardens. Irrigated (N = 67)			Orchards. Wine Gardens. Irrigated (N = 49)		
		Minimum	Maximum	Median	Minimum	Maximum	Median
<i>Cu</i> _{AR}	(mg * kg ⁻¹)	91.20	2,945.00	553.25	127.30	2,366.00	605.40
<i>Cu</i> _{EDTA}	(mg * kg ⁻¹)	15.80	1371.00	227.05	56.90	1,006.00	280.10
<i>Cu</i> _{EDTA/ AR}	%	17.00	55.00	39.50	28.00	79.00	45.00
<i>Cu</i> _{AN}	(mg * kg ⁻¹)	0.27	7.92	1.44	0.23	6.59	1.22
<i>Cu</i> _{AN / EDTA}	%	0.00	2.00	1.00	0.00	1.00	0.00
<i>Zn</i> _{AR}	(mg * kg ⁻¹)	157.70	2,441.00	501.50	139.30	3,735.00	614.00
<i>Zn</i> _{EDTA}	(mg * kg ⁻¹)	18.10	585.00	94.45	8.30	842.00	134.60
<i>Zn</i> _{EDTA/ AR}	%	10.00	60.00	20.00	4.00	56.00	22.00
<i>Zn</i> _{AN}	(mg * kg ⁻¹)	0.00	31.83	0.33	0.00	19.30	1.15
<i>Zn</i> _{AN / EDTA}	%	0.00	21.00	0.00	0.00	7.00	1.00
<i>Cd</i> _{AR}	(mg * kg ⁻¹)	0.28	14.50	2.55	0.40	13.80	3.37
<i>Cd</i> _{EDTA}	(mg * kg ⁻¹)	0.13	11.16	2.00	0.17	7.87	2.76
<i>Cd</i> _{EDTA/ ar}	%	46.00	95.00	79.00	20.00	88.00	82.00

End table 1

Heavy fractions		Vegetable Gardens. Irrigated ($N = 67$)			Orchards. Wine Gardens. Irrigated ($N = 49$)		
		Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
Cd_{AN}	$(mg * kg^{-1})$	0.00	0.56	0.03	0.00	0.32	0.05
$Cd_{AN / EDTA}$	%	0.00	14.00	1.00	1.00	6.00	2.00
$pH(H_2\hat{I})$	—	6.67	8.23	7.76	7.05	8.15	7.65
$pH(CaCl_2)$	—	5.99	7.68	7.37	6.49	7.54	7.20
$EC_{2,5}$	$(\mu S * cm^{-1})$	83.00	1,297.00	201.50	103.00	483.00	197.00
$CaCO_3$	mass – %	0.00	15.50	1.70	0.00	20.00	0.10
OM	mass – %	0.28	6.50	3.16	2.63	5.06	3.46
Al_{DCB}	$mg * g^{-1}$	0.50	1.78	1.07	0.71	2.33	1.14
Fe_{DCB}	$mg * g^{-1}$	5.46	15.30	8.83	7.17	12.43	10.00
Mn_{DCB}	$mg * g^{-1}$	0.32	1.06	0.67	0.45	1.03	0.85
Al_{OX}	$mg * g^{-1}$	0.67	3.14	1.82	1.39	3.57	1.80
Fe_{OX}	$mg * g^{-1}$	0.79	6.78	1.88	0.33	4.19	1.65
Mn_{OX}	$mg * g^{-1}$	0.04	1.00	0.63	0.42	1.00	0.82

specifically mainly 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 [7] 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 [4; 5], 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 (table 1).

Nevertheless, the concentrations of the mobile Cd fraction exceed the precaution, trigger and action values of [8] 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 capital Tbilisi, where crops from the Mashavera valley are soils at the open markets.

As a result of lab and field experiments conducted in hothouses the fixation of heavy metals by iron oxides has been stated, decreasing absorption of heavy metals by plants to 35%.

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