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MOBILITY OF HEAVY METALS IN ARABLE SOILS FROM BREGU I MATIT PLAIN, NW ALBANIA

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Abstract: In this study, the surface soil samples collected from irrigated soils of Bregu i Matit Plain were analysed for mobile forms of heavy metals in order to evaluate the risk of soil pollution with metals. The NH_4EDTA extractable As, Cr and Ni and NH_4NO_3 extractable Cr, Cu, Ni and As increased significantly in the irrigated soils as compared to non-irrigated soil. The higher metal proportions extracted with EDTA are found for Cd (33.6%), Cu (11.34%), Pb (11%) and Ni (1.37%), and for Cd (0.70%) and Cu (0.28%) extracted with NH_4NO_3. The order of metal extractability in EDTA was: Cd>Cu>Pb>Ni>Zn>As>Cr indicating that Cd and Pb are associated with organic matter more than Cu and Ni, and in NH_4NO_3 was: Cd>Cu>Pb> Ni>As>Zn>Cr which corresponds to the sequence of metal mobility. Only the Pb was proportional to the total content in aqua regia. The mobility of Cd, Cu, Ni, Pb and Zn is controlled by pH. Although there is no actual harmful pollution of soils with heavy metals, a potential risk of soil pollution with Cd, Cu and Pb exists, because their mobility and bioavailability can be increased due to soil acidification.

Keywords: ecological risk, heavy metal fraction, NH_4-EDTA, NH_4NO_3 soil pollution, Albania.

1. INTRODUCTION

The use of irrigation, fertilizers and pesticides is a common practice in modern agriculture. Increasing demand for food and fiber will encourage farmers to use large amounts of these soil inputs. These inputs are the major sources of heavy metals to arable soils (Matchavariani & Kalandadze, 2012; Kibria et al., 2012; Felix-Henningsen et al., 2010; Aydinalp et al., 2010; Micó et al., 2006; Mapanda et al., 2005), causing their chemical degradation. Accumulation of heavy metals in arable soils poses a potential risk to food chain contamination, and consequently to human health. In order to prevent this risk, assessing the heavy metal accumulation in soil is necessary. Bregu i Matit Plain is an important producing area of food crops in northwestern Albania. The main food crops are maize, wheat, vegetables, and forages. The major soils of the area were alluvial and meadow grey cinnamon soils after the National Soil Classification System (1954) or Calcaric and Gleyic Fluvisol and Gleyic and Fluvic Cambisol, respectively, after the World Reference Base for Soil Resources (FAO, 2006). Fluvisols were generally developed on younger fluvial deposits of the Mati and Drini Rivers. Cambisols were developed on the older fluvial deposits and are characteristic of central and northeastern parts of Bregu i Matit Plain. These soils had received agricultural inputs, including irrigation with polluted water from Mati River (Gjoka et al., 2010), over many years. In the first part of the study (Kasa et al., 2014), the total contents of heavy metals Cd, Cr, Ni, Cu, Zn, Pb and As are investigated, revealing significant accumulation of Cd, Cr and Ni in surface irrigated soils of the Bregu i Matit Plain (NW Albania), as compared to non-irrigated soil. In the present study, we analysed the mobile and organically binding forms of Cd, Cr, Ni, Cu, Zn, Pb and As in order to evaluate the pollution level and potential ecological risk of these heavy metals. The knowledge of content of the bioavailable forms of heavy metals is important to potential risk assessment (Takáč et al., 2009). This is because the ecological effect of metals are related to mobile fractions rather than to total contents in the soil (Erhart et al., 2008).

2. Materials and methods

2.1 Soil sampling

Surface (0-25 cm) soil samples were taken with soil auger from plots under various crops and with different history of irrigation in four soils from the Bregu i Matit Plain (Fig. 1). The soil 1 (L1/1 - control, Pllane village) was a non-irrigated soil and planted to alfalfa; the soil 2 (L2/1, L2/2, L2/3 L2/4, Gajush village) and the soil 3 (L3/1, L3/2, L3/3, L3/4, L3/5, L3/6, Shenkoll village) were soils irrigated more frequently (more than six irrigation events per year) and planted to maize and vegetables, respectively; and the soil 4 (L4/1, L4/2, L4/3, L4/4, Rrile village) was a soil irrigated less frequently (up to 3-4 irrigation events per year) and planted to wheat, sunflower, maize and fodder. The details of each sampling points are given in table 1.

The results of chemicophysical properties and total metals content of soils under the study were described in detail in Kasa et al., (2014). The mean values of the soil properties and total heavy metal contents are given in Table 2. Soil pH, organic carbon, clay and heavy metal contents ranged: pH from 6.2 to 7.4 with a mean value of 7.1; organic carbon (OC) from 1 to 1.8% with a mean value of 1.3%; clay from 14.3 to 48.7% with a mean value of 24.8%, cation exchange capacity (CEC_{pot}) from 17.5 to 34.7 cmol(+)kg^{-1} with a mean value of 25.8 cmol(+)kg^{-1}. There were no statistically significant differences in soil properties between irrigated soils (as the average) and control soil, except for pH and CEC.

The mean contents of Cr and Ni in irrigated soils exceeded the maximum permissible levels set by the Council of the European Communities (CEC, 1986), and the contents of Cr, Ni and Cu exceeded the critical values of the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV, 1999). Geo-accumulation index (I_{geo}) indicated that soils were unpolluted to moderately polluted with Cd, Cr and Zn and moderately to strongly polluted with Ni and As.

2.2 Soil analyses

The soil samples were air dried at room temperature and crushed to pass a 2-mm stainless steel sieve. Portions of soil samples (about 50g of < 2-mm soil) were ground in a special mill and stored in closed bottles. Soil samples were analysed for selected soil properties and total, mobile and potentially plant available forms of heavy metals Cd, Cr, Ni, Pb, As, Cu and Zn in the labs of the Institute of Soil Science and Soil Conservation of the Justus-Liebig University Giessen (Germany).

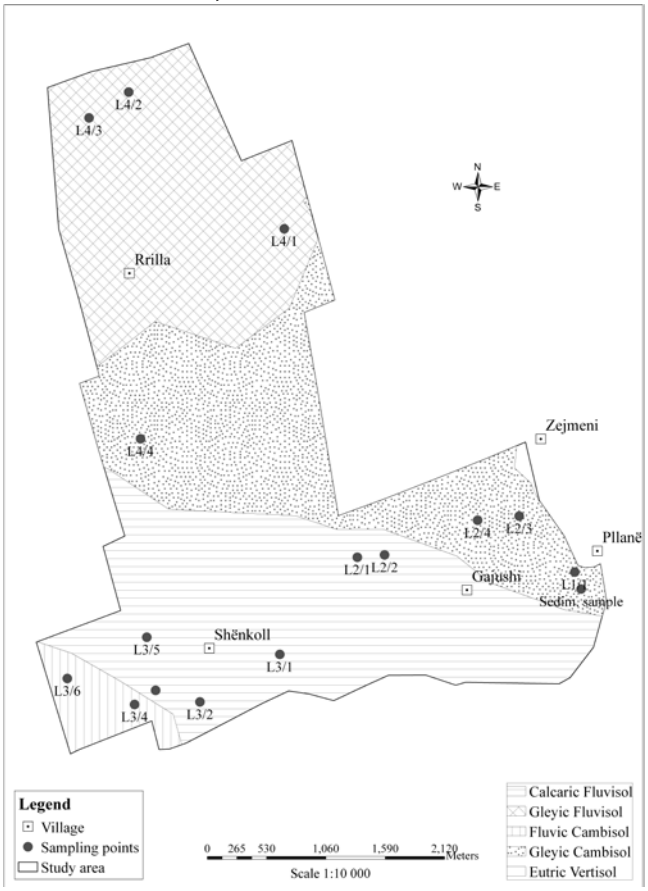

Figure 1. The soils map for the study area and sampling points

Table 1. Geographic coordinates of sampling points

Sampling point	*Location*	*Altitude*	*East*	*North*
L1/1	Pllane	10	19°41'35"	41°41'52"
L2/1	Gajush	5.2	19°40'11"	41°41'56"
L2/2	Gajush	5.3	19°40'21"	41°41'56"
L2/3	Gajush	6.7	19°41'13"	41°42'8"
L2/4	Gajush	6.7	19°40'57"	41°42'7"
L3/1	Shenkoll	14	19°39'41"	41°41'27"
L3/2	Shenkoll	10	19°39'11"	41°41'13"
L3/3	Shenkoll	13	19°38'54"	41°41'16"
L3/4	Shenkoll	13	19°38'46"	41°41'12"
L3/5	Shenkoll	10	19°38'50"	41°41'32"
L3/6	Shenkoll	17	19°38'20"	41°41'19"
L4/1	Rrile	7	19°39'41"	41°43'30"
L4/2	Rrile	10	19°38'40"	41°44'9"
L4/3	Rrile	13	19°38'25"	41°44'2"
L4/4	Rrile	5	19°38'46"	41°42'29"

Table 2. Basic chemicophysical properties and total metal contents in the surface soils

	pH CaCl2	OC %	Clay (%)	CEC cmol(+) kg^{-1}	Cd	Cr	Cu	Ni	Pb	Zn	As
					mg kg^{-1}						
Soil 1 (control)	6.2	1.2	22.0	17.5	0.1	128.6	54.9	179.2	16.3	102.8	7.3
Soil 2	7.4	1.4	26.4	26.5	0.2	209.9	66.7	358.9	12.4	98.2	4.9
Soil 3	7.2	1.1	17.6	24.6	0.2	228.2	66.8	409.3	8.08	79.5	3.3
Soil 4	6.8	1.5	34.6	26.9	0.2	237.1	55.5	418.3	12.2	87	6.0
Min	6.2	1	14.3	17.5	0.1	165.2	39.8	232.7	6.7	72.2	2.5
Max	7.4	1.8	48.7	34.7	0.2	280.9	73.6	464.6	17.4	114.5	9.3
Mean	7.1	1.3	24.8	25.8	0.2	225.5	63.5	397.5	10.5	87	4.5
SD	0.40	0.20	9.50	4.00	0.00	26.30	11.40	62.90	3.30	13.30	1.90
Mean value in irrigated soils	7.13	1.33	26.20	26.00	0.20	225.1	63.00	395.50	10.9	88.23	4.73
LSD ($p<0.05$)	0.50	0.30	14.40	7.80	0.04	56.20	21.90	124.90	5.20	20.30	3.00

SD – Standard deviation; LSD – Least significant difference

Soil pH was measured in 2.5:1 soil 0.01 M $CaCl_2$ suspension (10 g soil and 25 ml $CaCl_2$) by pH-meter (DIN ISO 10390); total carbon was determined by the gas chromatography using a CNS element analyzer (Heraeus); cation exchange capacity (CEC_{pot}) as the sum of exchangeable cations was measured according to Mehlich (1948), in buffered $BaCl_2$-TEA solution (0.1 M, pH 8.2), percolation for 8 h, by atomic adsorption spectrometer (Varian AA240FS); texture was determined by sieving and pipetting method (DIN 19683); total form of heavy metals were extracted with aqua regia (AR) (3 g soil and 24 ml aqua regia) (DIN 11466, 1995), mobile form was extracted with NH_4NO_3 (20 g soil and 50 ml 1 M NH_4NO_3) (DIN 19730, 2009) and carbonate and organically bound form was extracted by NH_4EDTA (5 g soil and 50 ml 0.025 M NH_4EDTA). The element concentrations in the extracts were measured with an inductively coupled plasma optical emission spectrometry (ICP-OES). The precision of the analyses was checked by analysing a certified reference sample (CRS).

2.3 Data analysis

Analysis of variance (one-way ANOVA) and least significant difference (LSD) test were used to find out statistical differences in mobile contents of heavy metals between sampling soils. Significance threshold was $p<0.05$. Statistics were performed using SPSS 19. Level of soil metal pollution was determined based on comparison with threshold values by BBodSchV (1999).

3. RESULTS AND DISCUSSIONS

3.1 Mobility of heavy metals in soil

The mobility of heavy metals in soil depends on the nature of metal ion, the nature of extractant

and soil pH (Sabienë et al., 2004). To extract the mobile fraction of metals from the soil, several extractants have been used *(*Aikpokpodion et al., 2012; Atanassova et al., 2012; Kashem et al., 2007). In this study, mobility of heavy metals was expressed in terms of content extractable with EDTA and NH_4NO_3. As a strong metal binding agent, NH_4EDTA (0.025 M, pH 7) is used to extract the soluble and exchangeable fractions as well as the heavy metals strongly adsorbed to carbonates, oxides and organic substances, while NH_4NO_3 (1 M) is used to extract the mobile and exchangeable fractions (Felix-Henningsen et al., 2010).

The NH_4EDTA fraction gives a good estimate of the potentially plant available metals (Cappuyns, 2012; Felix-Henningsen et al., 2007), and the NH_4NO_3 fraction gives an indication of the immediately plant available metals (Barbooti et al. 2010). The contents of these two fractions in the studied soils are given in Table 3 and Table 6.

The NH_4EDTA metal fraction varied: for Cd 0.03-0.08 mg kg^{-1}, Cr 0.03-0.06 mg kg^{-1}, Cu 4.08-9.81 mg kg^{-1}, Ni 2.39-10.04 mg kg^{-1}, Pb 0.69-2.9 mg kg^{-1}, Zn 0.31-1.83 mg kg^{-1}, and As 0.002-0.016 mg kg^{-1}, with the higher mean values for Ni and As in the irrigated soils as compared to non-irrigated soil. However, only the As in three sampling points of Soil 2 and in one sampling point of Soil 3, Cr in one sampling point of Soil 3 and Ni in one sampling point of Soil 3 and in two sampling points of Soil 4 contents showed higher statistically significant differences. The amounts of heavy metals extracted with EDTA decreased as follows: Cu>Ni> Pb> Zn>Cd>Cr>As.

The percentages of heavy metals in this fraction varied considerably between sampling soils (Table 4). The highest extractability of Cd (48%), Cu (16.4%), Pb (13.4%), Ni (2.0%) and Zn (1.3%) was found in Soil 1, where the soil pH is lower (see Table 2). In general, the extractability of heavy metals by EDTA in the studied soils was as follows: Cd>Cu>Pb>Ni>Zn>As>Cr. This order does not corresponds to the constant of metal–EDTA complex stability (Harmsen, 1977). This suggests that Cd and Pb are respectively associated with organic matter more than Cu and Ni. The low extractability of Cr (0.02%) is explained by its solubility that decreases above pH 4 (Alloway, 1995), and of As (0.05%) by the fact that EDTA does not form stable complexes with arsenic (Tokunaga & Hakuta, 2002).

The EDTA extractable metal contents were proportional to the total content in AR only for Pb ($r=0.80$, $p<0.001$), while the non-significant correlations were found for other metals (Table 5). This suggests that the NH_4EDTA (0.025 M, pH 7) is a very good extractant for Pb, a good extractant for Cu, Zn and Ni, a moderate extractant for Cd and a weak extractant for As and Cr in the studied soils. The amounts of metals extracted by NH_4NO_3 are markedly smaller than those extracted by EDTA. This is expected after NH_4NO_3 is a weaker extractant than EDTA.

Table 3. NH_4EDTA extractable metal contents (mg kg^{-1}) in the studied soils

	Cd	Cr	Cu	Ni	Pb	Zn	As
Soil 1 (control)	0.06	0.04	9.00	3.60	2.18	1.35	0.000
Soil 2	0.06	0.05	7.40	2.98	1.71	0.98	0.008
Soil 3	0.06	0.04	5.92	4.95	0.91	0.84	0.001
Soil 4	0.05	0.04	5.63	6.73	0.88	0.43	0.001
Min	0.03	0.03	4.08	2.39	0.69	0.31	0.002
Max	0.08	0.06	9.81	10.04	2.90	1.83	0.016
Mean	0.05	0.04	6.44	4.81	1.20	0.80	0.007
SD	0.01	0.01	1.68	2.55	0.67	0.47	0.006
CV(%)	21.43	23.1	26.15	53.13	55.98	58.85	88.83
Mean metal content for irrigated soils	0.05	0.04	6.26	4.89	1.13	0.76	0.007
LSD ($p<0.05$)	0.02	0.01	2.87	4.18	0.98	0.90	0.01

SD – Standard deviation; CV – Coefficient of variation; LSD – Least significant difference

Table 4. NH_4EDTA extractable metal contents as a percent of total content

	Cd	Cr	Cu	Ni	Pb	Zn	As
Soil 1 (control)	48.02	0.03	16.40	2.01	13.38	1.31	0.00
Soil 2	38.71	0.03	11.16	0.86	12.78	0.96	0.15
Soil 3	35.82	0.02	8.86	1.20	11.22	1.05	0.02
Soil 4	26.36	0.02	10.19	1.57	7.34	0.49	0.01
Mean metal content for all soils	33.63	0.02	11.34	1.37	11.03	0.93	0.05
Mean metal content for irrigated soils	33.63	0.02	10.07	1.21	10.45	0.83	0.06

Table 5. Pearson correlation among EDTA and total fractions of soil heavy metals

	TOTAL						
EDTA	Cd	Cr	Cu	Ni	Pb	Zn	As
Cd	0.39						
Cr		-0.16					
Cu			0.50				
Ni				0.49			
Pb					0.80[a]		
Zn						0.50	
As							0.21

[a]Correlation is significant at the 0.001 level

Table 6. NH_4NO_3 extractable metal contents (mg kg^{-1} in the studied soils)

	Cd	Cr	Cu	Ni	Pb	Zn	As
Soil 1 (control)	0.003	0.002	0.168	0.130	0.015	0.031	0.000
Soil 2	0.001	0.004	0.217	0.043	0.006	0.002	0.002
Soil 3	0.001	0.004	0.158	0.070	0.005	0.004	0.001
Soil 4	0.001	0.003	0.163	0.290	0.005	0.010	0.000
Min	0.001	0.002	0.120	0.014	0.001	0.002	0.001
Max	0.003	0.010	0.235	0.794	0.015	0.031	0.007
Mean	0.001	0.004	0.176	0.125	0.006	0.007	0.001
SD	0.001	0.002	0.035	0.197	0.004	0.010	0.002
CV (%)	49.73	55.45	20.17	157.31	61.75	89.45	71.26
Mean metal content for irrigated soils	0.001	0.004	0.179	0.134	0.005	0.005	0.001
LSD ($p<0.05$)	0.001	0.001	0.028	0.428	0.004	0.013	0.002

This metal fraction varied: for Cd 0.001-0.003 mg kg^{-1}, Cr 0.002-0.01 mg kg^{-1}, Cu 0.12-0.235 mg kg^{-1}, Ni 0.014-0.794 mg kg^{-1}, Pb 0.001-0.015 mg kg^{-1}, Zn 0.002-0.031 mg kg^{-1}, and As 0.001 to 0.007 mg kg^{-1}, with the higher mean values for Cr, Cu, Ni and As in the irrigated soils as compared to non-irrigated soil.

But only the Cr in one sampling point of Soil 2, in two sampling points of Soil 3, and in one sampling point of Soil 4; Cu in three sampling points of Soil 2 and in one sampling point of Soil 3; Ni in one sampling point of Soil 4; and As in one sampling point of Soil 2 and in two sampling points of Soil 3 contents showed higher statistically significant differences. The amounts of heavy metals extracted with NH_4NO_3 in non-irrigated soil followed the order Cu>Ni>Zn>Pb>Cd>Cr>As, and in irrigated soils the order Cu>Ni>Zn=Pb> Cr>Cd= As. This means that Cu had the highest chance of being accumulated in plants.

The percentages of heavy metals in this fraction varied greatly between sampling soils (Table 7). The highest extractability of Cd (2.6%), Ni (0.07%), Pb (0.09%) and Zn (0.03%) was found in Soil 1. The extractability of the metals by NH_4NO_3 followed the order of Cd>Cu>Pb>Ni>As>Zn>Cr. This corresponds well to the sequence of metal mobility and to metal extractability by EDTA for the first four metals.

The NH_4NO_3 extractable metal contents were proportional to the total content for Pb ($r=0.64$, $p<0.01$), while the non-significant correlations are found for other heavy metals (Table 8). This indicates that the NH_4NO_3 (1 M) is a good extractant for Pb, and a weak extractant for other metals. The significant correlation between the NH_4NO_3 and NH_4EDTA metal contents are found for Ni ($r= 0.72$, $p<0.005$) and Pb ($r= 0.57$, $p<0.025$). The correlation analysis has shown that this fraction of Cd, Cu, Ni, Pb and Zn is controlled by soil pH.

Table 7. NH_4NO_3 extractable metal contents as a percent of total content

	Cd	Cr	Cu	Ni	Pb	Zn	As
Soil 1 (control)	2.560	0.002	0.310	0.070	0.090	0.030	0.000
Soil 2	0.673	0.002	0.330	0.013	0.048	0.003	0.060
Soil 3	0.682	0.002	0.238	0.017	0.048	0.005	0.037
Soil 4	0.738	0.001	0.320	0.063	0.038	0.008	0.000
Mean metal content for all soils	0.703	0.002	0.285	0.031	0.044	0.005	0.023
Mean metal content for irrigated soils	0.698	0.002	0.296	0.031	0.045	0.005	0.032

Table 8. Pearson correlation among NH_4NO_3 and total fractions of soil heavy metals

NH_4NO_3	TOTAL						
	Cd	Cr	Cu	Ni	Pb	Zn	As
Cd	-0.12						
Cr		0.14					
Cu			0.02				
Ni				0.31			
Pb					0.64[b]		
Zn						0.30	
As							-0.32

[b]Correlation is significant at the 0.01 level

Similar results were reported by other authors (Shaheen et al., 2013; Felix-Henningsen et al., 2010; Abollino et al., 2002).

3.2 Soil pollution and risk assessment

The NH_4NO_3 fraction of heavy metals is available for the plant immediately, and therefore possess the environmental risk. This fraction can be used as a basis for assessing the level of pollution and potential ecological risk of heavy metals in soil. For this study, the pollution level was determined by threshold (trigger and action) values from BBodSchV (1999). The results show that the content of heavy metals in all the studied soils lies under these values (Table 9). This means there is no actual harmful pollution of soils with Cd, Cu, Ni, Pb, Zn and As. Nevertheless, having low content of heavy metals extracted by NH_4NO_3 does not always mean a lower risk of metal transfer into the food chain. Narimanidze et al., (2003) reported severe accumulations of Cu, Zn and Cd in spinach and other food crops despite of a low concentration of heavy metals in the NH_4NO_3 extract. In an ecotoxicological study of these soils, the knowledge of heavy metal contents in plants is important. On the other hand, the relatively high proportion of Cd, Cu and Pb in EDTA fraction (see Table 4), suggest a potential risk of soil pollution by these metals associated with increasing their mobility and bioavailability due to soil acidification. Intensive agriculture with nitrogen fertilizers or manures can result in soil acidification. The NH_4NO_3 fraction of Cd above 2% in non-irrigated soil and close to 1% in all the studied soils indicates a low actual ecological risk to the environment.

4. CONCLUSIONS

The results of this study indicate that NH_4EDTA extractable As, Cr and Ni and NH_4NO_3 extractable Cr, Cu, Ni and As increased significantly in the irrigated soils in comparison to non-irrigated soil. The EDTA shows a higher extractability of heavy metals than NH_4NO_3. The higher proportions of heavy metals extracted with EDTA are found for Cd (33.6%), Cu (11.34%), Pb (11%) and Ni (1.37%), and for metals extracted with NH_4NO_3 are found for Cd (0.70%) and Cu (0.28%).

The extractability of the metals with EDTA follows the order of Cd>Cu>Pb>Ni>Zn>As>Cr suggesting that Cd and Pb are associated with organic matter more than Cu and Ni, and the extractability with NH_4NO_3 follows the order of Cd>Cu>Pb>Ni>As>Zn>Cr.

The EDTA and NH_4NO_3 extractable metal contents are proportional to the total content in aqua regia only for Pb, while the non-significant correlations are found for other metals.

The mobility of Cd, Cu, Ni, Pb and Zn is controlled by soil pH. There is no actual harmful pollution of the studied soils with heavy metals, but the relatively high proportion of Cd, Cu and Pb in EDTA fraction indicates a potential risk of soil pollution related to increasing their mobility and bioavailability due to soil acidification.

Table 9. The measured and trigger/action values for NH_4NO_3 heavy metals ($mg.kg^{-1}$)

	Cd	Cr	Cu	Ni	Pb	Zn	As
Soil 1 (control)	0.003	0.002	0.168	0.130	0.015	0.031	0.000
Soil 2	0.001	0.004	0.217	0.043	0.006	0.002	0.002
Soil 3	0.001	0.004	0.158	0.070	0.005	0.004	0.001
Soil 4	0.001	0.003	0.163	0.290	0.005	0.010	0.000
Trigger value		-	1	1.5	0.1	2	0.4
Action value	0.04*/0.1						

*for soils of fields used for cultivation of bread wheat and Cd accumulating vegetables

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