CONTENTS OF HEAVY METALS AND ORGANOCHLORINE INSECTICIDES (HCH AND DDT) IN AGRICULTURAL MONITORING SITES (16X16 KM) FROM THE WEST REGION

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Abstract: *Soil loading of with heavy metals and organochlorile insecticedes pose a risk to the environment and therefore their monitoring is required. Land angricultural monitoring system, level I (16x16 greed), in West Region include 89 sites. In the top soil samples of these sites were determined, also, the contents of heavy metals (Cu, Pb, Zn, Cd, Co, Ni, Mn) and organochlorine insecticides (HCH and DDT). Most of studied elements have maximum values below alert threshold for sensitive use. Except, Cd and DDT with values belong to normal value class. The contents of heavy metals and organochlorile insecticedes (DDT and HCH) were presented according to land uses, soil classes, soil types, textural classes, soil reaction classes and humus content. The variation of heavy metal contents according to soil classes reveals highest values of Cu, Co, Ni, Mn on Protisols and Anthrisols, of Pb on Podzols, of Zn on Solonetz, of Cd on Vertisols. The lowest values of Cu, Zn, Cd were recorded on Luvisols and in case of Ni, Mn on Podzols. Generally, the values of these elements are lower compared to the obtained contents at the national level.*

Key words: *soil, monitoring, heavy metals, HCH, DDT*

INTRODUCTION

The report of the European Commission "Towards a Thematic Strategy for Soil Protection", identified eight restrictions for European soils, among them being the soil contamination with heavy metals. A contaminant is a substance that in an environment is present in excess of the natural background concentration (CCME, 2006). The accumulation of heavy metals in surface soil is determined by environmental variables (parent materials and soil properties) and human activities (VON SOTHERN, 2001, HU et al., 2013). Accumulation of heavy metals can affect soil quality, soil organisms, agricultural products quality and the ecosystem (NAGAJYOTI et al., 2010).

After 1985, chlorinated pesticides were forbidden throughout our country, but HCH and DDT residues are still found in agricultural soils (DUMITRU et al., 2011).

In this paper are presented the loading of topsoil in the sample plots of the soil monitoring sites of level I (16x16 km) from West Region (Arad, Timis, Caras, Hunedoara counties) with heavy metals (total forms), DDT and HCH (total forms)-second determination.

MATERIAL AND METHODS

In West Region, the the agricultural monitoring greed at level I (16x16 km) totalize 89 agricultural sites. Methodology the achievement of agricultural soil-land monitoring systems at level I (16 x 16 km) was done in accordance with the Ordinance 38/2002, approved with amendments by Law 444/2002, and with the Order of the Minister of Agriculture, Food and Forestry (MAFF) no. 223/2002. The content of heavy metals in soil monitoring plots of level I was determined by acid mixture digestion (nitric, perchloric, sulphuric, 2:1:0,2 report) and Atomic Absorption Spectrophotometric dosage. The content of Organochlorine insecticides content (HCH, DDT – total forms) was determined by extraction with petroleum ether-acetone 2:1 mixture and gas chromatographic determination Interpretation of results is made following

the Order no. 756/1997. The soil classification was made according WRB-SB 1998 (Bridges et al., 1998).

RESULTS AND DISCUSSIONS

On the whole agricultural land of West Region, the agricultural monitoring greed (16x16 km) totalizes 89 sites. For the agricultural land, most plots are found on arable land (50 sites), followed by grassland (25 sites), meadows (13 sites) and orchards (1 site). At this region, 9 soil classes are found from the whole 12 existent classes and 15 of the 32 soil types listed in SRTS, 2012 (FLOREA &MUNTEANU, 2012).

Soil is the major sink for heavy metals released into the environment and the heavy metals persist for a long time in soils (LOMBI et al., 1998).

Table 1 presents the pollutants contents in topsoil of agricultural monitoring plots using interval of values and some statistical parameters as: arithmetic mean ($\bar{x}$) standard deviation (±σ), variation coefficient, 25%, 50%, 75% and 90% percentiles.

Except Zn, the values of studied elements are lower compared to the obtained contents on the whole greed (DUMITRU et. 2011).

Table 1

Contents of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of agricultural soil monitoring sample plots, level I (16 x 16 km), in West Region– mg·kg^{-1}

	Plots	Range	$\bar{x}$	±σ	CV, %	25%	50%	75%	90%
Cu	89	7.4-63	24.6	10.54	43	19	24	28	33
Pb	89	7-44	18.7	6.5	35	15	17	20	26
Zn	89	35-254	94.8	42.5	44.8	67	83	107	151
Cd	89	0.16-0.95	0.40	0.22	54.5	0.26	0.33	0.41	0.86
Co	89	4-30	11	4.9	43	8	10	13	17
Ni	89	5.5-71	28.7	12.0	42	22	27	32	41
Mn	89	45-1092	444	173	39	319	451	541	641
Total DDT	89	0.005-0.035	0.014	0.006	44	0.009	0.012	0.018	0.020
Total HCH	89	0.002-0.032	0.008	0.005	66	0.004	0.007	0.012	0.016

$\bar{x}_1$ - arithmetic mean; ±σ- standard deviation; CV, %- variation coefficient; 25%, 50%, 75% and 90% percentiles.

According to Order no 756/1997, most of studied elements have maximum values below alert threshold for sensitive use. Except, Cd and DDT with values belong to normal value class (fig. 1). For Cu, Ni and HCH, the values of arithmetic mean and median are between normal values and the alert threshold for sensitive use. The studied elements contents according to land uses (tab. 2) highlights small differences between land uses, both in the interval of values, and the average value. In case of Cu, Cd and DDT, higher average values were recorded on arable land and in case of Pb, Zn, Co, Ni, the higher values were recorded on medows.

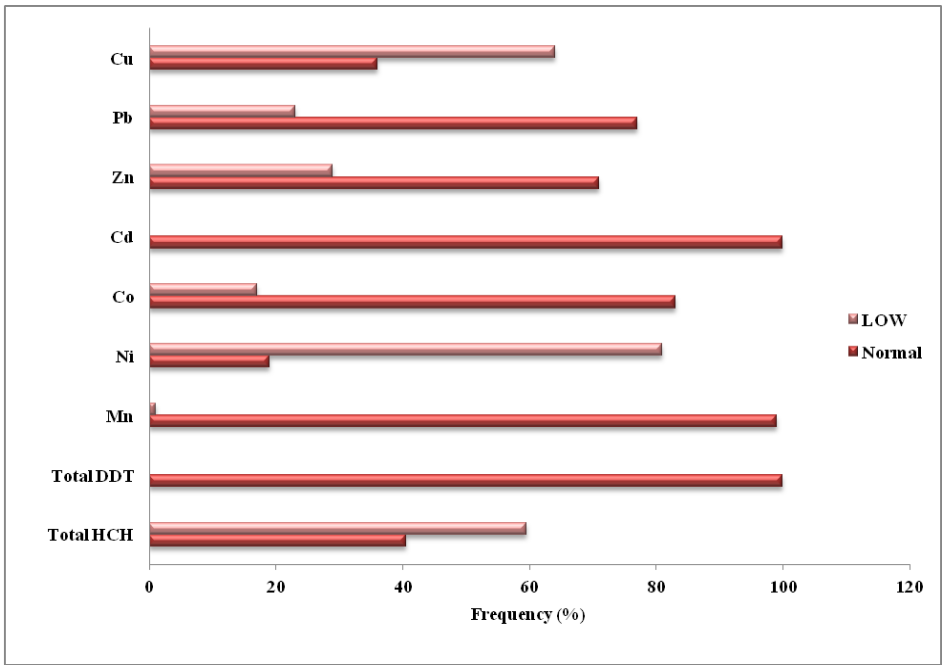

Figure 1. Distribution of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of monitoring sample plots, level I (16x16 km) from West Region, by loading classes – mg·kg^{-1}

Table 2

Average contents of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of monitoring sample plots, level I (16x16 km) from West Region, by main agricultural land uses – mg·kg^{-1}

	Arable land		Orchards		Pastures		Meadows	
	Range	$\bar{x}$	Range		Range	$\bar{x}$	Range	$\bar{x}$
Cu	9-61	27	23	25	7.4-49	20.4	12.3-63	25
Pb	7-38	16	20	25	12.8-40	22	13.8-43.5	23
Zn	35-254	85	228	25	39-191	93	72.5-224	126
Cd	0.16-0.95	0.44	0.29	25	0.19-0.75	0.35	0.19-0.90	0.37
Co	3.8-18.9	9.7	10	25	4.3-29.7	12.2	8.1-29.5	15.2
Ni	11.7-46	29	25	25	9.6-55	25.7	5.5-71	34
Mn	142-742	436	357	25	45-1092	436	237-821	501
Total DDT	0.005-0.035	0.016	0.016	25	0.006-0.031	0.012	0.006-0.020	0.010
Total HCH	0.003-0.023	0.007	0.005	25	0.002-0.032	0.010	0.004-0.018	0.010

The variation of heavy metal contents according to soil classes reveals highest values of Cu, Co, Ni, Mn on Protisols and Anthrisols, of Pb on Podzols, of Zn on Solonetz, of Cd on Vertisols. The lowest values of Cu, Zn, Cd were recorded on Luvisols and in case of Ni, Mn on Podzols (tab. 3).

Variation of heavy metals concentration in different soils from different countries is due to different parent materials from which soil develops, the variety of pedogenetic processes from different climatic regions (Cataldo and Wildung, 1978). Maximum values of Cu, Pb, Co, Ni. Mn were recorded in mountains soils (Leptosols, Dystric Cambisols, Podzols), which shows the influence of parent materials (tab. 4).

Table 3

Average contents of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of agricultural soil monitoring sample plots, level I (16x16 km) from West Region, by soil classes – mg·kg^{-1}

	PRO	CER	CAM	LUV	POD	VERT	SAL	HID	ANT
Cu	32	28	23	18	19	28	32	28	34
Pb	20	14.6	21	19	28	17	24	18	10
Zn	113	79	117	72	87	91	139	127	100
Cd	0.50	0.37	0.41	0.33	0.39	0.62	0.41	0.37	0.35
Co	14	8.7	14	9.5	13	10	9	11	15
Ni	41	29	30	21.6	17	32	23	33	41
Mn	525	455	494	408	246	390	445	468	319
Total DDT	0.016	0.015	0.013	0.013	0.016	0.010	0.007	0.014	0.013
Total HCH	0.007	0.007	0.011	0.008	0.015	0.004	0.008	0.005	0.005

PRO- Protisols; CER- Cernisols; CAM- Cambisols; LUV- Luvisols; POD- Podzols;VER- Vertisols; SAL- Salsodisols; HID-Hidrisols; ANT- Anthrosols

Except selenium, a significant positive correlation between the total heavy metals content and the soil clay content was found by Mermut et al. (1996). Soil texture has a major influence on the concentration of Cd, Co, Cr, Cu, Ni and Zn, the median is 3-5 times higher in clay soils compared to sandy soils (Zhao et al., 2007).

As regarding the variation of heavy metals according to soil textural classes, the lowest Cu content was recorded on sandy loamy soil (19 mg/kg) and the highest value on clay soil (30 mg/kg). Also, the Ni content increased from sandy loam soils to clay soils (tab. 5).

Table 4

Average contents of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of agricultural soil monitoring sample plots, level I (16x16 km) from West Region, by soil types – mg·kg^{-1}

	LS	RS	FS	CZ	FZ	EC	DC
Cu	63	22	30	29	19	23	22
Pb	28	19	20	14	17	18	25
Zn	127	80	118	79	77	117	116
Cd	0.29	0.53	0.52	0.38	0.35	0.47	0.29
Co	30	12	13	8	10	13	16
Ni	71	42	38	30	26	32	25
Mn	790	516	497	440	544	491	497
Total DDT	0.010	0.016	0.017	0.014	0.020	0.014	0.011
Total HCH	0.015	0.005	0.007	0.006	0.009	0.010	0.013

LS-Leptosols; RS-Regosols; FS-Fluvisol; CZ-Chernonozems; FZ-Phaeozems; EC-Eutric Cambisols; DC-Dystric Cambisols;

Table 4 (continuation)

	HL	LV	EP	VS	GS	SN	AT
Cu	22	16	19	28	28	32	33
Pb	18	19	28	17	18	24	12
Zn	72	72	87	91	127	139	146
Cd	0.28	0.36	0.39	0.62	0.37	0.41	0.35
Co	10	9	13	10	11	9	15
Ni	28	18	17	32	33	23	36
Mn	469	372	246	390	468	445	385
Total DDT	0.013	0.012	0.016	0.010	0.014	0.007	0.010
Total HCH	0.008	0.008	0.015	0.004	0.005	0.008	0.005

HL-Haplic Luvisols; LV-Luvisol; EP-Entic Podzols; GS-Gleysols; SN-Solonetz; AT-Anthrosols

Table 5

Average contents of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of the agricultural monitoring sample plots, level I (16x16 km) from West Region, by textural classes – $mg \cdot kg^{-1}$

	Textural classes				
	Loamy sand	Sandy loam	Loam	Clay loam	Clay
Cu	25	19	24	25.5	30
Pb	35	20	20	17	17
Zn	55	121	95	88	102
Cd	0.75	0.30	0.36	0.45	0.41
Co	20	12	12	9.6	13
Ni	25	23	26	29.7	42
Mn	500	367	482	424	450
Total DDT	0.031	0.011	0.013	0.015	0.013
Total HCH	0.016	0.011	0.009	0.008	0.008

According to soil reaction, the average content of Cu and Cd increased from strongly acid soils to slightly alkaline soils, respectively, moderately alkaline soils (tab. 6). The Pb content increased from strongly acid soils to neutral soils. According to humus content classes, as a general trend, the Pb and HCH contents increased with increasing soil humus content (tab. 7).

Table 6

Average contents of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of the agricultural soil monitoring sample plots, level I (16x16 km) from West Region, by soil reaction classes – $mg \cdot kg^{-1}$

	SOIL REACTION CLASSES					
	Strongly acid	Moderately acid	Slightly acid	Neutral	Slightly alkaline	Moderately alkaline
Cu	23.7	23.8	24.4	24.1	30	18
Pb	18	23.1	23.6	28.9	17.4	12
Zn	86	70	71	67	82	114
Cd	0.28	0.35	0.52	0.42	0.47	0.60
Co	11	15	16	16	15	13
Ni	31	34	39	34	43	28
Mn	396	588	588	578	556	330
Total DDT	0.009	0.050	0.056	0.028	0.031	0.040
Total HCH	0.013	0.017	0.016	0.014	0.010	0.008

Table 7

Average contents of heavy metals and organochlorine insecticides (HCH and DDT) in topsoil of the agricultural soil sample monitoring plots, level I (16x16 km) from West Region, by humus content classes – $mg \cdot kg^{-1}$

	HUMUS CONTENT CLASSES					
	Very low	Low	Moderate	High	Very high	Excessively high
Cu	34	22	25	23	36	13
Pb	10	13	17	21	30	40
Zn	100	50	91	110	88	52
Cd	0.35	0.5	0.44	0.32	0.52	0.23
Co	15.1	7.5	10.2	12.7	19.7	13.6
Ni	41	21.6	30	26	37.7	10
Mn	319	303	457	447	519	45
Total DDT	0.013	0.020	0.014	0.012	0.016	0.013
Total HCH	0.005	0.010	0.006	0.011	0.013	0.017

CONCLUSIONS

Except, Cd and DDT, according to Order no 756/1997, the studied elements have maximum values below alert threshold for sensitive use.

For Cu, Ni and HCH, the values of arithmetic mean and median are between normal values and the alert threshold for sensitive use.

The studied elements contents according to land uses highlights small differences between land uses, both in the interval of values, and the average value.

In case of Cu, Cd and DDT, higher average values were recorded on arable land and in case of Pb, Zn, Co, Ni, the higher values were recorded on meadows.

The highest Cu and Ni contents were recorded on clay soils, and the Pb and HCH contents increased with increasing soil humus content.

Except Zn, the values of studied elements are lower compared to the obtained contents at the national level.

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