Assessment of heavy metals contamination in the western Drama plain soils (Macedonia, N. Greece), using combined geochemistry and GIS mapping techniques

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Abstract

Heavy metals (HMs) pollution of rural soils in the vicinity of both active and abandoned mines continues to attract attention because of their potential human health risk via food chain. Long-term manganese mining and ore processing activities in the Drama district, Macedonia (Northern Greece) have resulted in a tremendous legacy of abandoned mining wastes at the "25km Mn-mine" site, without any safety measures. Current research was focused at the western part of Drama plain, lying close to the above mine site. The concentration of 6 health related elements (Mn, Pb, Zn, Cu, Cd, and As) in the surface soils from this area was assessed using the Inductively Coupled Plasma-mass spectrometry (ICP-MS) technique.

The results indicated that total metal concentration ranges (in mg.kg^{-1}) observed in study soils were: 245-130013 for Mn, 11-1996 for Pb , 23-2140 for Zn, 5-153 for Cu, 0.4-28 for Cd, and 2-1077 for As, with mean values of 4133, 183, 134, 33, 2, and 43, respectively.

The overall degree of the total HMs soil pollution and their ecological risks were evaluated using the composite pollution *(CPI)* and the potential ecological risk *(RI)* indices respectively. Geostatistical analysis and GIS mapping techniques were employed to the dataset to produce spatial distribution maps for the 6 studied elements, and 3D graphics for the presentation of the above mentioned indices.

Similar spatial distribution patterns were found in the geochemical maps of metal concentrations, confirming a strong geochemical association and common source of the 6 HMs. Highest values of total HMs concentrations were observed close and along both sides of

the Xiropotamos stream. Soils at these sites display moderate to extremely high degree of contamination and considerable potential ecological risk by multiple HMs.
Thus, an immediate action to remediate the contaminated topsoils is recommended to safeguard the health of residents in the studied area.

Key words: heavy metals, contamination, GIS mapping, ecological risk, Drama plain

1. Introduction

Soils contamination by various pollutants is nowadays one of the most significant environmental problems (Yang et al. 2001, Carr et al.2008, Lee et al. 2009, Lu et al. 2012). Between the wide diversity of pollutants affecting the terrestrial ecosystem heavy metals (HMs) received particular concern considering their strong toxicity even at low concentrations (Li et al. 2006; Sharma et al. 2007; Davis et al 2009; Li et al. 2009). Heavy metals reaching the soil remain present in the pedosphere for a long time due to their non-decay by time and long biological half-lives (Imperato et al. 2003, Wang et al. 2008).

The introduction and concentration of HMs into soils and sediments has been the subject of increasing study in recent decades (Alloway 1995, Adriano 2001, Lee et al. 2006, Sheng et al. 2012).

Sources of HMs pollution can be both natural and anthropogenic (Kabata-Pendias 2011). Mining and mineral processing activities are among human activities which release a variety of toxic and potentially toxic pollutants into the environment (Nriagu 1990; Wong et al. 2002; Navarro and Martinez 2008; El Hamiani et al. 2010; Zornoza et al. 2012).

The most serious problem is that of spilled mine tailings and wastewaters which are usually displayed at the mine places often without any safety measures. Thus, mapping the HMs distribution around and downstream from mining areas is important in the assessment of environmental pollution, land contamination and the human health risk (Carr et al. 2008, Chen et al. 2012, Ripin et al. 2014).

The ecological importance of HMs in rural soils has attracted a great deal of attention because of its close relation to human health. Of particular concern is the geochemistry of soils in agricultural areas. Heavy metals tend to accumulate in topsoil which can then pose a risk to human health as a result of entering the food chain through direct injection of dust or ingestion of plants (Gupta and Gupta 1998; Lu et al. 2004, El Hamiani et al. 2010, Lu et al. 2010; Wang and Lu 2011; Khan et al 2013).

Therefore, a detailed risk assessment of HMs accumulation in agricultural lands around mining places is required for application of inorganic fertilizers, organic wastes, and pesticides to soils in order to ensure the safe crop production. Further, identifying potential anthropogenic sources of HMs in surface soils may help remediation efforts and protect populations at risk (Mullingan et al. 2001, Davis et al. 2009, Wuana and Okieimen, Ye et al. 2012).

Regional geochemical survey along with mapping of the HMs spatial distribution have been applied to environmental and pollution studies of soils in order to identify hot-spot areas and assess the potential anthropogenic sources of pollution (Navas and Machin 2002, Imperato et al. 2003, Li et al. 2004, Lee et al. 2006, Morton-Bernea et al. 2009, Chen et al. 2012, Ripin et al. 2014).

The present study was focused on the western part of Drama plain, constituting the recipient of the effluents from Xiropotamos stream, which flows through the abandoned “25km Mn-mine” place.

The objectives of this study were: 1. to assess the total concentration of the health related elements Mn, Pb, Zn, Cu, Cd, and As in the western Drama plain soils; 2. to portray their spatial distribution patterns using GIS mapping techniques; 3. to assess the overall degree of the total HMs soil pollution and their ecological risk in terms of composite pollution (CPI) and the potential ecological risk (RI) indices respectively.

2. Materials and methods

2.1. Study area

The study area comprises the western part of Drama plain and has an extent of 170km^2. It constitutes the watershed basin of Angitis River and its tributaries. The drift geology of the broader area comprises mica-two mica schists and gneisses, marbles, all intruded by an Oligocene granodiorite, and compact carbonate conglomerates of Miocene age (Fig.1). The land is intensively cultivated mainly for cereals (wheat and maize), vineyards and olive groves.

The Drama district has a long history of Mn mining, with more than 7Mt total ore concentrate production of Mn-oxides at the “25km Mn-mine” (Nimfopoulos et al. 1997). After mining cessation in 1994, enormous amounts of mining waste materials (tailings, low grade ore, ore concentrate) were left at the mine place and within the Xiropotamos stream (a tributary of Angitis river) valley without any safety measures.

2.2. Field sampling procedure

A square grid sampling scheme (cell size 1x1km) was applied for the collection of soils and the coordinates of each sampling point were recorded with a handheld Gobal Positioning System (GPS) receiver. A total of 148 surface (0-20cm) soil samples (2kg) were collected with a plastic shovel and stored in plastic bags. Each soil sample comprised a composite of at least 20 sub-samples taken on a 20x20m square. This sampling procedure was intended to obtain a more representative average sample collected at each site. A simplified geological map of the study area showing the sampling locations is given in Figure 1.

In the laboratory soil samples were air dried, disaggregated and sieved through a stainless steel mesh to isolate the <180μm fraction for the chemical analyses.

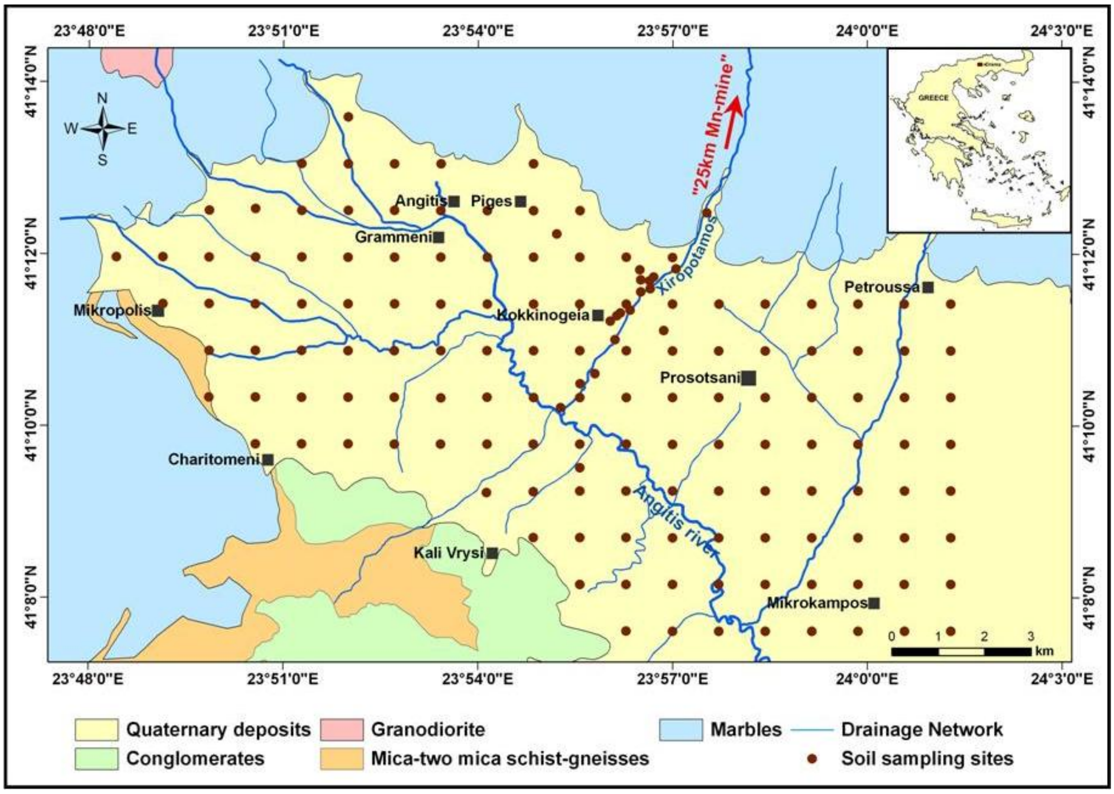

Figure 1. Simplified geological map of the study area with sampling points of surface soils.

2.3. Analytical methods

The determination of total element contents was performed using an aqua regia digestion, followed by ICP-MS analysis for 36 elements, where of 6 elements (Mn, Pb, Zn, Cu, Cd and As) are presented in this study. Analyses were carried out at ACME Analytical Laboratories (Vancouver, Canada). Reagent blanks, analytical duplicates, and certified standards were also used where appropriate to ensure the accuracy and precision of analysis (ACME 2013).

2.4. Quantification of soil pollution

There is a need in environmental quality studies to assess metal concentration with respect to environmental guidelines, relevant background values or threshold values, in order to evaluate the extent of pollution and its possible ecological impact (Wang et al 2011; Sheng et al. 2012, Khan et al. 2013).

The overall degree of contamination was evaluated by means of the combine pollution index (*CPI*), using formula (1) (Abrachim and Parker 2008).

$$CPI = \frac{\sum_{i=1}^{i=n} PI_f^i}{n} \qquad (1)$$

where n is the number of analyzed elements, i is itch element and PI is the pollution index given by formula (2):

$$PI = \frac{Csample}{Creference} \qquad (2)$$

where

Csample is the metal concentration in the sample, and

Creference relevant value of the same metal

The Dutch target value of the metal was used as a reference one in the present study (VROM 2000).

For the classification and description of the degree of contamination (*CPI)* in soils the following graduation was proposed (Abrachim and Parker 2008):

$CPI < 1.5$	Nil to very low degree of contamination
$1.5 \leq CPI < 2$	Low degree of contamination
$2 \leq CPI < 4$	Moderate degree of contamination
$4 \leq CPI < 8$	High degree of contamination
$8 \leq CPI < 16$	Very high degree of contamination
$16 \leq CPI < 32$	Extremely high degree of contamination
$CPI \geq 32$	Ultra high degree of contamination

2.5. Ecological risk assessment

The potential ecological risk of HMs in studied soils was evaluated by a comprehensive method combining the concentrations of HMs in soils with their ecological and environmental effects, and toxicological effects. Based on the calculation formula proposed by the previous reports (Hakanson 1980; Luo et al. 2007, Yu et al. 2012) the indices of potential ecological risk of HMs in study soils were evaluated using formula (3):

$$RI = \sum_{i=1}^{n} E_r^i \qquad (3)$$

where *RI* is a composite index indicating the potential ecological risk of the total HMs in soils; *n* is the total number of the measured HMs, E_r^i is an index of potential ecological risk of an individual element of HMs, which can be evaluated using formula (4)

$$E_r^i = T_r^i \times C_r^i \qquad (4)$$

where T_r^i is the toxic response factor indicating the toxic level of an individual element and the sensitivity of medium to the HMs. Based on the report of Hakanson (1980), T_r^i of Mn, Pb, Cd, As, Cu, and Zn, is assumed to be 2, 5, 30, 10, 5, and 1, respectively. C_R^i is the pollution index of an individual HM, which can be estimated with the concentration of the element in soils (C_i) and the reference value (C_R^i) using formula (5):

$$C_r^i = \frac{C^i}{C_R^i} \qquad (5)$$

where the reference value of C_R^i is referred to the background value of average soils worldwide (Kabata-Pendias 2011) as given in Table 2.

The indices of *RI* as shown in Table 1 were defined as four grades indicating the different levels of potential ecological risk of HMs in sediments based on the study of Hakanson (1980).

Table 1. Level definition of the potential ecological risk of HMs in soils (after Hakanson 1980).

Potential ecological risk index (E_r^i) of an individual HM		Composite index (RI) of the potential ecological risk of the total HMs	
$E_r^i < 40$	Low risk	$RI < 150$	Low risk
$40 \leq E_r^i < 80$	Moderate risk	$150 \leq RI < 300$	Moderate risk
$80 \leq E_r^i < 160$	Considerable risk	$300 \leq RI < 600$	Considerable risk
$160 \leq E_r^i < 320$	Great risk	$RI \geq 600$	Very great risk
$E_r^i \geq 320$	Very great risk		

Further, to aid decisions on site remediation, it is necessary to produce a hazard map showing the overall pollution status of the site.

2.6. Data processing

Descriptive data analysis was performed, including calculation of maximum, minimum, median, mean, SD, skewness, kurtosis. Pearson's correlation analysis of the total metal concentrations was used to find interelements relationships. All statistic analyses were performed using SPSS 19 for Windows software.

Geostatistical analysis and GIS mapping techniques were employed to produce spatial distribution maps for the 6 studied metals and the 3D graphics of the CPI and RI indices, using ArcGIS version 9.2 software.

3. Results and discussion

3.1. Total metal concentration and spatial distribution in soils

Summary statistics for HMs contents in all the studied samples are provided in Table 2, along with reference values for comparison.

Table 2. Descriptive statistical summary of HMs concentrations (values in $mg.kg^{-1}$) in studied soils, along with reference values for comparison.

Element		Mn	Pb	Zn	Cu	Cd	As
Mean		4134	183	134	33	1.9	43
Min		245	11	23	5	0.4	2
Max		130013	1996	2140	153	27.5	1077
Median		851	47.5	79	23	1.3	13
Std. deviation		17786.8	378.3	243.9	29.9	3	137.6
Skewness		5.9	3.3	5.8	2.3	6.1	6.3
Kurtosis		40.5	10.7	38.4	36.2	4.7	43.9
Target values		1500*	85	140	36	0.8	29
Mean concentration of world soils		488	27	70	39	0.4	6.8
*PI***	mean	2.8	2.2	1.0	0.9	1.9	1.5
	range	0.2-86.7	0.1-23.5	0.2-15.3	0.1-4.3	0.4-27.5	0.1-37.1
*E***	mean	8.5	33.8	1.9	4.2	140.6	62.8
	range	0.5-266	2-370	0.3-31	0.6-20	30-2063	2.9-1584

* Phytotoxic level (after Kabata-Pendias 2011)

** *PI:* pollution index; *E*: potential ecological risk index

Total concentrations of HMs in the studied soils showed wide ranges (Table 1) and locally display significantly higher than the background levels of agricultural soils worldwide (Kabata-Pendias 2011). Besides, all metal concentrations were beyond the limits of the European Legislation (Council Directive 86/78/EEC 1986).

Total metal concentration ranges (in $mg.kg^{-1}$) observed were: 245-130013 for Mn, 11-1996 for Pb , 23-2140 for Zn, 5-153 for Cu, 0.4-28 for Cd, and 2-1077 for As, with mean values of 4149, 181, 133, 34, 2, and 42, respectively.

The identification of the potential sources of HMs in Drama plain soils is a prerequisite for the assessment of the contamination risk and a remediation or immobilization strategy (Wuana and Okieimen 2011).

Spatial distribution maps of total HMs concentrations, created on geostatistic and GIS techniques revealed that all six elements tend to follow similar patterns (Fig.2), confirming a strong geochemical association and a common source.

Highest values for all six elements total concentrations were observed close and along both sides of the Xiropotamos stream. Levels of contamination become significantly lower at a distance of about 200m from the Xiropotamos stream course.

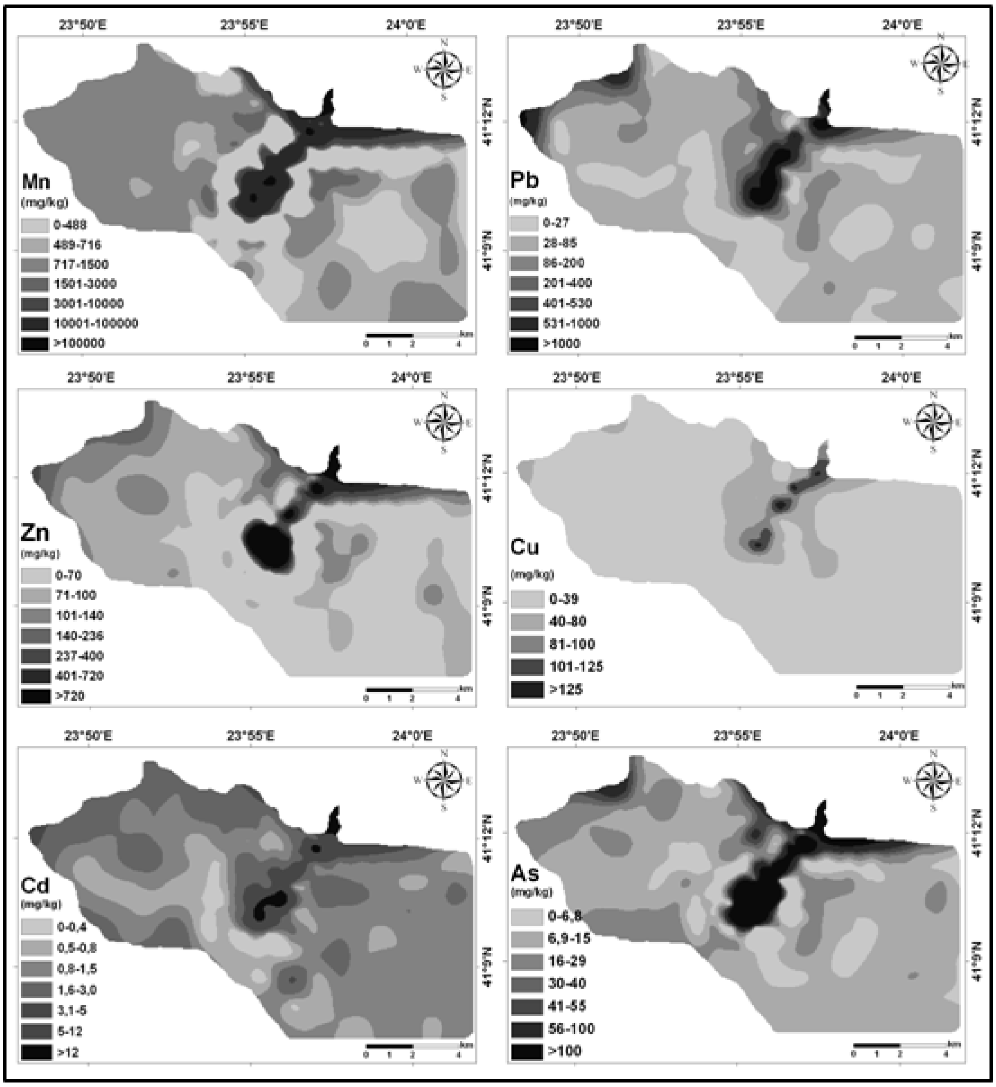

Figure 2. Spatial distribution of heavy metals contents in the western Drama plain surface soil, mapped by geostatistical interpolation using ArgGIS. All units in mg kg^{-1}

Besides, electron probe microanalyses on Mn-oxide minerals present in the contaminated soils revealed high Pb, Cu, Zn, Cd and As contents (Sofianska 2013), which are comparable to those found in the Mn mineralization of the "25Km Mn-mine" (Michailidis et al. 1997). These results would indicate that the current enrichment of the western Drama plain soils in HMs appears to be mainly due to the erosion of the mining wastes, which introduce Mn-oxide minerals into the Xiropotamos stream sediments and further onto the agricultural land.

Table 3. Pearson's correlation matrix of the total metal concentrations in the studied soils (n=148)

	Mn	Pb	Zn	Cu	Cd	As
Mn	1					
Pb	0,60**	1				
Zn	0,93**	0,75**	1			
Cu	0,50**	0,91**	0,65**	1		
Cd	0,93**	0,69**	0,98**	0,60**	1	
As	0,96**	0,61**	0,96**	0,53**	0,97**	1

**. Correlation is significant at the 0.01 level (2-tailed).

Statistical correlations between total metal concentrations in soils (Table 3) showed that Mn was significantly positively correlated with Pb, Cu, Zn, Cd and As, denoting a geochemical association and common pollution pathways (Manda et al. 2002, Imperato et al. 2003; Zhou et al. 2008; Gherfat et al 2012; Yu et al. 2012).

The Xiropotamos stream flowing through the abandoned "25 km Mn-mine" place caused a long time waste downstream transportation. Besides, extensive flooding during winter times and over bank deposition of the mining wastes on the agricultural land was the main source of pollutants in the study area.

These data denote an association of Pb, Cu, Zn, Cd and As with the Mn-minerals present in the mining wastes. The mining wastes cause contamination dispersion along the Xiropotamos stream course mainly by solid transport (even though also dissolution may be present). Consequently, downstream transportation, along with extensive flooding during winter times and overbank deposition of the mining wastes introduced the HMs contamination into the agricultural land.

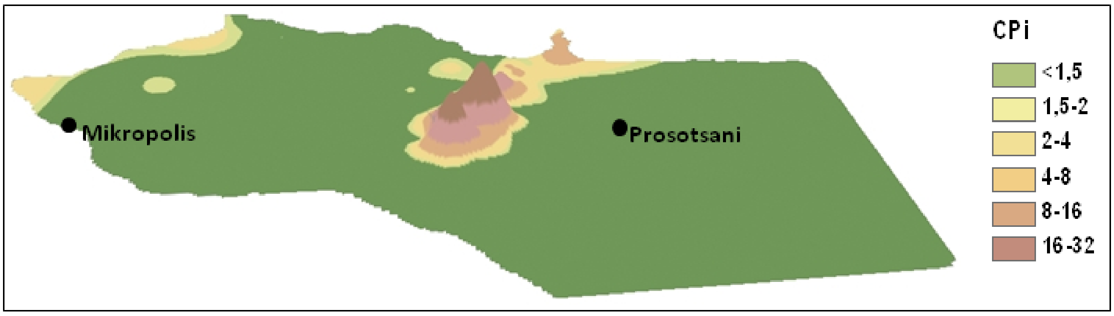

Figure 3. A 3D graphic of the combined pollution index (*CPI*) in soils of the western Drama plain.

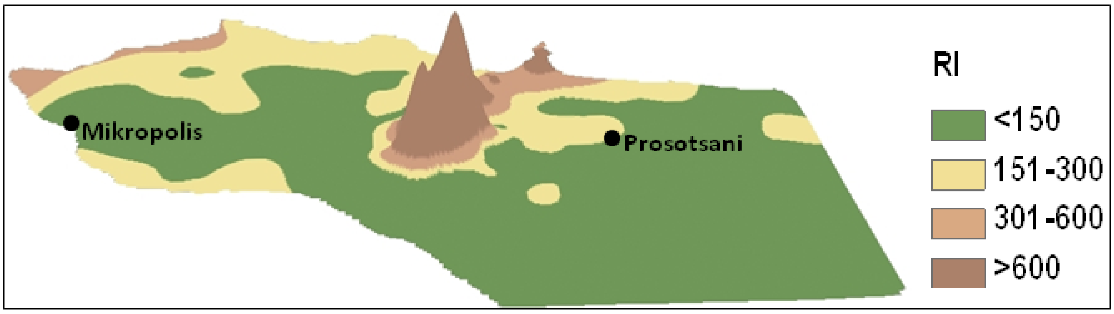

Figure 4. A 3D graphic of the potential ecological risk index (*RI*) in soils in the western Drama plain.

3.2. Environmental significance of HMs in studied soils

In order to display more effectively the multi-elements pollution status and the potential ecological risk of HMs, 3D graphics of the combined pollution index (*CPI*) and risk assessment index (*RI*) were constructed, using ArcGIS software (Fig 3 and 4). The *CPI* of all analysed soil samples varies from 0.30 to 33.12. Approximately 7.5% of all analysed samples have high to ultra high pollution levels, with the metals Mn, Pb, Cd and As contributing most of the pollution in soils. Peak values of *CPI* are found in sampling sites close and along both sides of the Xiropotamos stream (Fig.3).

The *RI* values for most sampling sites (85% of the soil samples) were found lower than 300, suggesting that most areas have low and moderate ecological risk from HMs. However, 15% of the samples have *RI* values ranging from 300 to 600, indicating considerable ecological risk. The highest *RI* values were also observed at sites close and along both sides of Xiropotamos stream. At this district hazard map (Fig.4) shows that a considerable potential ecological risk exists. Overall the elements Cd, Pb and As pose a higher individual ecological risk than the other study metals.

This information enforces the immediate intervention to reduce risk related to HMs. Thus, mining tailings should be encapsulated or treated in order to minimize their HMs contribution to the stream and the agricultural land. In addition, a reclamation strategy has to be considered.

4. Conclusions

This study demonstrates that the combination of geochemistry and GIS base mapping techniques can be a useful tool to characterize the extent and level of HMs pollution. Similar spatial distribution patterns of all six HMs along with the significantly positive correlation among Mn and Pb, Zn, Cu, Cd, As denote a strong geochemical association and a common source of HMs. Highest values of total HMs concentrations were observed at sites close and along both sides of the Xiropotamos stream, which has contributed to the dispersion of mining wastes onto the agricultural land. Based on the calculated CPI and RI values the studied soils in the above sector of western Drama plain are considered moderately to extremely highly contaminate and may pose a considerable potential ecological risk by multiple HMs.

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