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Spatial Distribution and Evaluation of Arsenic and Zinc Content in the Soil of a Karst Landscape

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Abstract: Karst features such as polje are highly vulnerable to natural and anthropogenic pollution. The main objectives of this study were to investigate the soil quality in the Ioannina polje (north-west Greece) concerning arsenic (As) and zinc (Zn), and delineate their origin as well as compare the As and Zn content in soil with criteria recorded in the literature. For this purpose, the geomorphological settings, the land use, and the soil physicochemical properties were mapped and evaluated, including soil texture and concentrations of aqua-regia extractable As and Zn. The concentration of elements was spatially correlated with the land use and the geology of the study area, while screening values were applied to assess land suitability. The results reveal that 72% of the total study area has a very gentle slope. This relief favors urban and agricultural activity. Thus, the urban and agricultural land used cover 92% of the total area. The spatial distribution for As and Zn in the soil of the study area is located on very gentle slopes and is strongly correlated with the geological parent materials and human-induced contamination sources. Arsenic and Zn can be considered enriched in the soil of the area studied. The median topsoil contents (in mg kg^{-1}) for As (agricultural soil 16.0; urban soil 17.8) and Zn (agricultural soil 92.0; urban soil 95.0) are higher compared to the corresponding median values of European topsoils. Land evaluation suitability concerning criteria given from the literature is discussed. The proposed work may be helpful in the project of land use planning and the protection of the natural environment.

Keywords: Ioannina polje; soil quality; agricultural soil; aircraft emissions; GIS

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1. Introduction

Karst terrains occupy about 7–10% of the planet and are mainly developed in carbonate rocks and evaporate [1]. It is estimated that carbonate rocks cover 12% of the Earth's continental area [1]. Karst formations consist of surface and subsurface forms such as poljes and caves. Polje represents an extraordinary element in a karst landscape. A polje is an extensive and closed basin with a flat bottom, karstic drainage, and a steep slope at least on one side [2].

Karst landscapes are areas of abundant resources, such as water supplies, limestone quarries, and minerals. Thus, karst aquifers constitute 25% of the Earth's groundwater resources. Worldwide, the vast majority of surface karstic formations have some form of urban and agricultural activity [1,3]. In Greece, carbonate rocks have a widespread outcrop and occupy about 40% of the surface area [3,4]. Karst regions are fragile landscapes and highly vulnerable to contamination [5–10]. Anthropogenic activities may lead to the degradation of a karst landscape and loss of karst landforms and can cause soil erosion and contamination [11–13]. Since water moves very rapidly in karstic systems and regions, pollutants can be transported for long distances in a short period [14–26].

The leaching of soluble contaminants from the soil in a karst landscape may deteriorate water resources. The chemical composition of water flowing through and out of the rocks and soils of a karst landscape reflects the element's content in the weathering material. Furthermore, karst systems are highly vulnerable compared to other systems because potential contaminants can easily reach groundwater [27,28]. Therefore, the proposal of protection measures to preserve soil quality in a karst region is a crucial issue.

In recent years, environmental studies revealed high contents of potentially toxic elements in soils, sediments, and groundwater [28–40]. Several research studies revealed that the total concentration of metals could not indicate deficiency and toxicity [41–43]. Furthermore, several soil properties, such as pH, Cation Exchange Capacity (CEC), and organic matter, should be studied in combination with trace element contents to better understand the trace elements' behavior [40–45].

Many researchers reported a high concentration of toxic elements such as arsenic (As) and zinc (Zn) in the soils of urban, suburban, industrial, traffic, and mining areas [30–34,40–46]. Therefore, the assessment of As and Zn contents in the soil of a karst area is a necessary step for proposing remedial measures and protecting the natural environment.

In the present study, an attempt was made to identify and evaluate the spatial distribution of As and Zn in the soil of the polje of the Ioannina karst basin (north-west Greece). The specific aims of this study were: (a) to determine the quality status of the soil in the Ioannina basin concerning As and Zn; (b) to investigate the origin of As and Zn in relation to land uses.

The findings of this study may contribute to the international database of investigations on As and Zn content in soil and provide a stable scientific basis for further investigating the specific sources of As and Zn accumulation and their geochemical mobility in the urban and suburban environment. The novelty of this study lies in the fact that in this research work, As and Zn content in the soil of the Ioannina basin are investigated and evaluated to assess the land suitability for residential and agricultural use, applying criteria provided by the literature. The outcome of this study may be helpful for stakeholders and policymakers monitoring the area. No other previous studies reported a potentially toxic elements content in the soil (or any other sampling material) of the Ioannina basin to the best of the authors' knowledge.

2. Materials and Methods

2.1. Primary Data

The data collected for this study include four topographic maps with a scale of 1:50,000, published by the Hellenic Army Geographical Service (H.A.G.S.), along with four geological maps of Greece on a scale of 1:50,000 (sheets Ioannina, Klimatia, Doliana, Tselepovo), published by the Institute of Geology and Mineral Exploration-IGME [47–50]. The land cover of the study area was obtained from the CORINE 2012 Land Cover (CLC) map of the Copernicus Program [51]. The soil map of Greece (scale 1:500,000) published by O.P.E.K.E.P.E. [52] was used for the soil classification of the study area. The soil groups were digitized and inserted as a polygon layer in the GIS database, using the Soil Map Of Greece [52]. GIS-based data have been used in this study for manipulating, analyzing, and presenting.

2.2. Study Area, Geological, Geomorphological, and Land Use Setting

The studied area is a part of the Ioannina karstic basin, and it is located in Epirus, in north-west Greece (Figure 1A). The altitude in the plain that is part of the study area varies between 460 and 760 m, while the eastern edge of the basin is bound by the Mitsikeli mountain (Figure 1B). The study area hosts several settlements and a part of the Ioannina city, and lies on the western shore of Lake Pamvotis (Figure 1B). The dominant wind in the Ioannina basin blows from the of West [53].

The geological formations of the study area are presented in Figure 1C. Rocks from the Ionian geotectonic zone and post-alpine sediments are part of the study area's geological structure [47–50]. The alpine rocks of this zone include (a) Sinion-Pantokrator limestone of the Late Triassic (Early Lias) age; (b) Jurassic shales and carbonate rocks; (c) Upper Jurassic Vigla limestones; (d) Senonian micro-breccia limestones; (e) Eocene limestones [49]; (f) Eocene-Oligocene lignite deposits [49,54]; and (g) Upper Eocene (Priabonian) to Early Miocene flysch [49,55]. The post-alpine sediments consist of Pliocene limnic sediments and Quaternary deposits such as terra-rossa and Fe-Mn oxides, old siliciclastic deposits, soil talus cones and scree, recent lacustrine and fluvial deposits, and some glacial scree deposits [56–60].

The morphology of an area is often related to the development of land uses, soils, and spatial distribution of the trace elements [5,25]. Geomorphologic features such as slope angle are considered. The slope of the study area was computed by using a digital elevation model (DEM). The slope values are categorized into five classes (Figure 2), as follows: (i) < 5°, (ii) 5–10°, (iii) 10–20°, (iv) 20–30°, and (v) > 30°. The slopes were correlated with the spatial distributions of land uses and soils, as well as the As and Zn content in the soil.

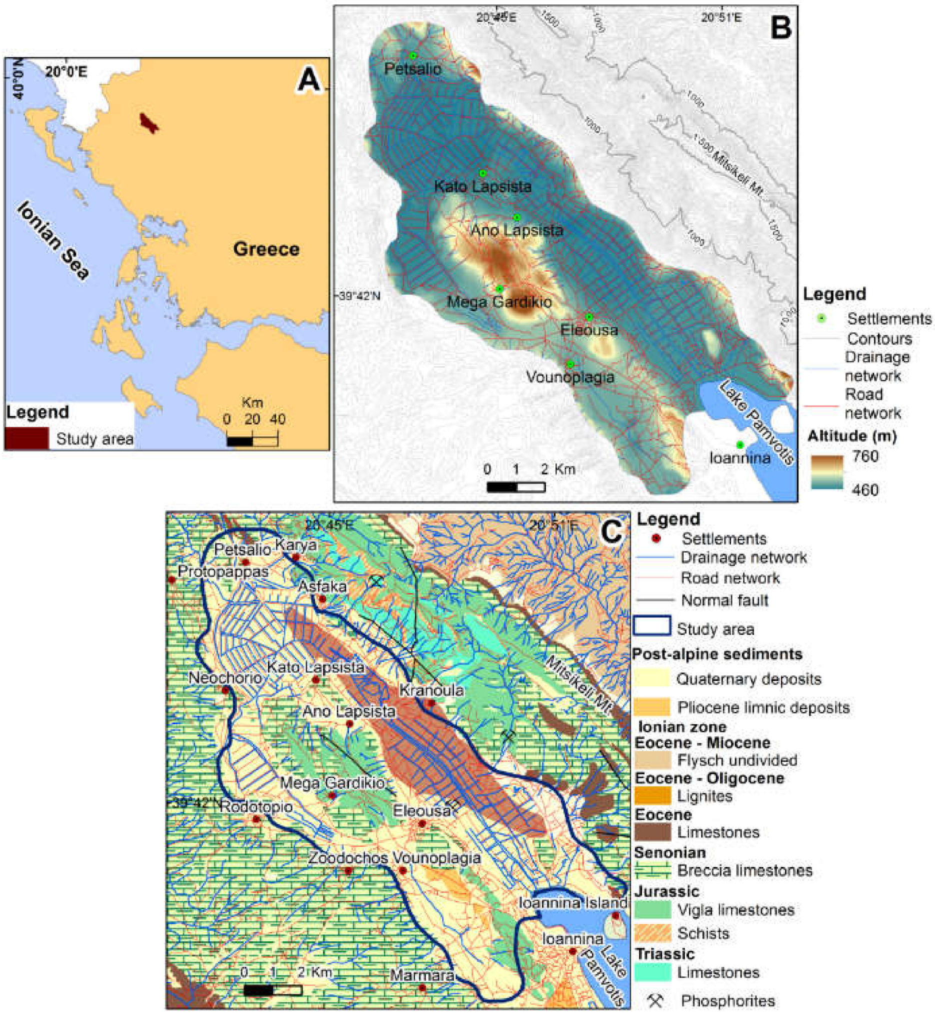

Figure 1. (**A**) Location map of the study area; (**B**) Road network, hydrographic network, and elevation of the study area; and (**C**) Geological map of the area studied.

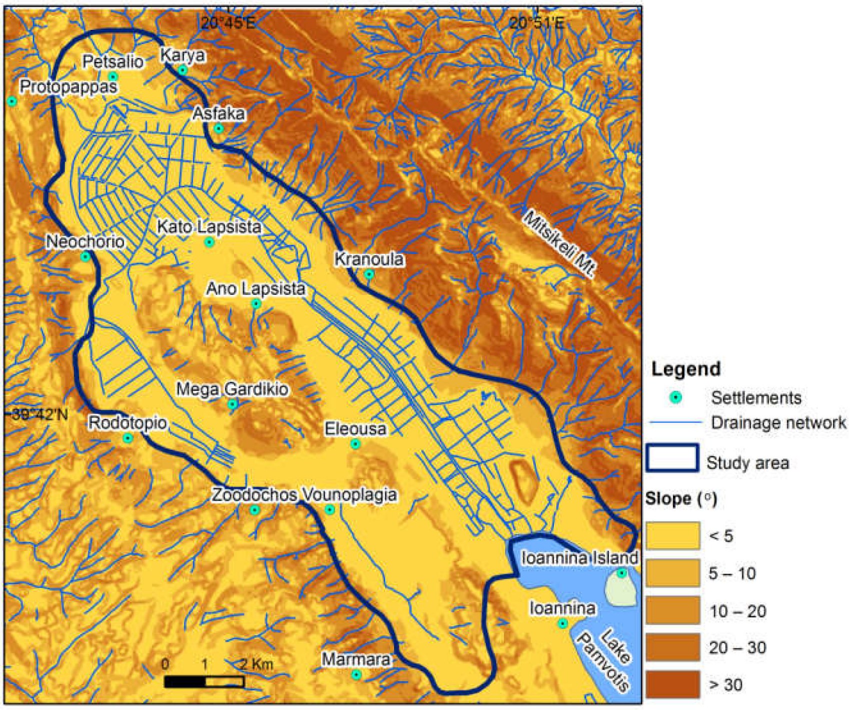

Figure 2. Map showing the morphologic slopes of the study area.

Land use was divided into urban areas, agricultural areas, shrub and sparsely vegetation areas, and wetlands (Figure 3). Urban fabric, roadway network, cottage industries, the Ioannina city's airport, and a vehicle recycling, crushing, and dismantling plant are anthropogenic activities and land-use types in the study area.

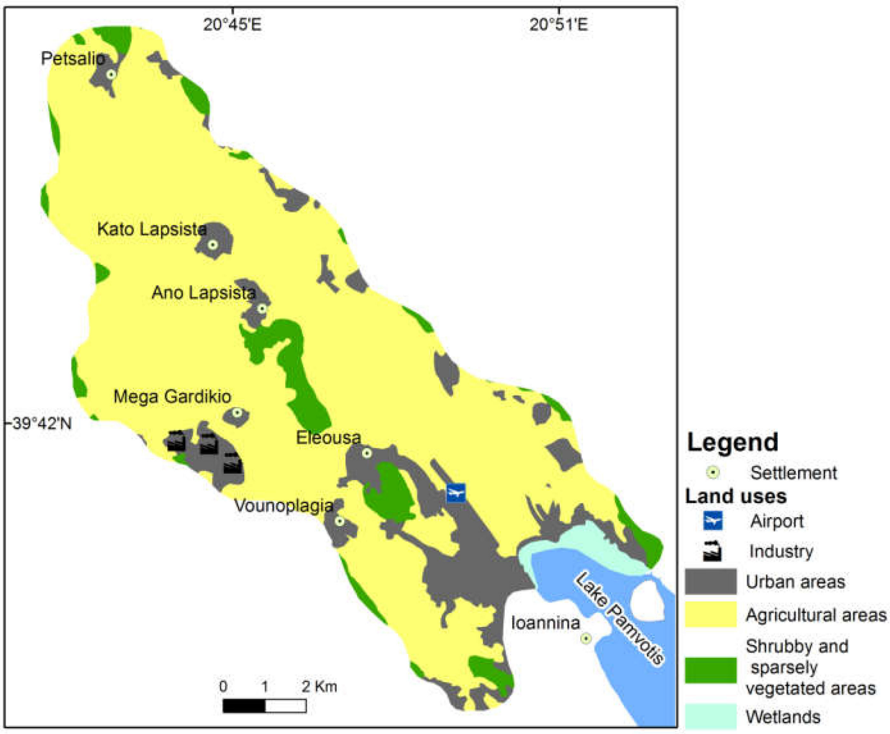

Figure 3. Map showing the land uses of the study area.

2.3. Soil Sampling and Laboratory Procedures

Topsoil samples (0–30 cm) were collected at 112 sampling sites from the Ioannina karst basin (Figure 4) following the soil sampling procedure of Papadopoulou-Vrynioti et al. [28]. Sampling sites were selected by applying the square grid procedure (1 km × 1 km), covering about 110 km^2. Composite soil samples for each sampling site consisted of five topsoil sub-samples which were taken from five points over a patch of land of 5 m^2, approximately. Soil samples were mixed thoroughly to obtain a composite sample (about 2 kg) for each sampling site.

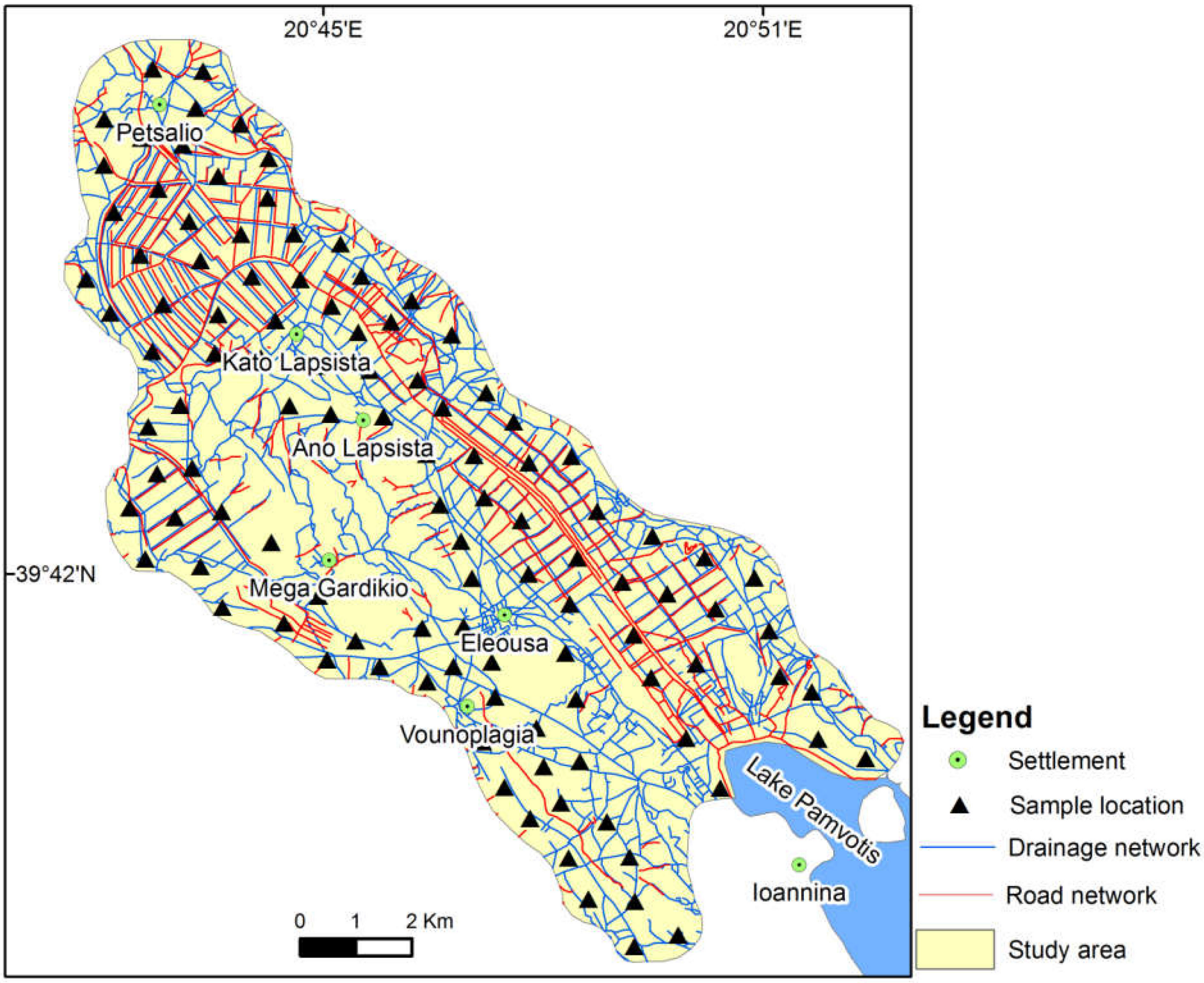

Figure 4. Map showing soil sampling locations in the studied area.

The soil samples were further treated using procedures as described by Papadopoulou-Vrynioti et al. [28]. All soil samples were dried at room temperature (< 25 °C) and divided into two soil subsample sets: (a) subsamples that have been stored in clean polythene bags for the determination of soil grain size and organic matter; and (b) subsamples that had passed through a 2.00 mm sieve and were stored in clean polyethene bags for the analysis of aqua-regia extractable elements including As and Zn.

The Bouyoucos hydrometer method [61] has been applied to determine the clay (<0.002 mm), silt (0.002–0.020 mm), and sand (0.02–2.00 mm) contents (in %). The organic matter content was determined by the dichromate oxidation method [62]. The dichromate oxidation method was also used by many researchers for the determination of the organic matter and organic carbon in soil [28,46,63,64]. To measure the aqua-regia extractable element concentration, 2.5 g of the fine-grained fraction of each sample was placed into glass tubes, and then aqua regia (HCl-HNO_3-H_2O) was added [28]. The glass tubes were heated until fuming on a hot plate. The solutions were left to cool down and made up a final volume of 50 mL with deionized double-distilled water [28]. The soil contents of As and Zn were measured by atomic absorption spectroscopy (AAS). The reference samples and method blanks were analyzed throughout the entire laboratory process to record the chemical analysis quality. Prepared blanks were always below the instrumental detection limits. The chemical analyses were repeated until an accuracy of 95–105%, and the precision of ± 5% was accomplished. The treatment of soil samples was performed at the laboratory of the Institute of Geological and Mineral Exploration (IGME).

2.4. Data Treatment

The software code Surfer 11.0 (Golden Software®, Golden, CO, USA) was used for the triangular diagram. The inverse distance weighted (IDW) technique was applied to interpolate the textured classes' values and the spatial distribution of soil properties. The numerical values were categorized applying the natural breaks classification method using the software code ArcMap 10.8 GIS (ESRI®) (Environmental Systems Research Institute; Redlands, CA, USA). The contents of the elements recorded in the soil of the study area were compared with the corresponding median values for European topsoil [65]. The software codes Microsoft® Excel (Redmond, Washington, DC, USA) and IBM® SPSS 26.0 (International Business Machines Corporation; Statistical Product and Service Solutions; Armonk, NY, USA) for Windows were applied for the data treatment. The Pearson correlation coefficient (r) of the examined variables was estimated applying Equation (1):

$$r_{i,m} = \frac{\sum_i (x_i - x_m)(y_i - y_m)}{\left\{\left[\sum_i (x_i - x_m)\right]^2 \left[\sum_i (y_i - y_m)\right]^2\right\}^{1/2}} \tag{1}$$

where x and y are the *i-th* values of the standardized variables x and y and x_m, y_m are their respective means.

The land suitability evaluation in the studied area was performed by adopting criteria for the soil content of As and Zn established by the Environmental Protection Agency (EPA) [66], the Canadian Council of Ministers of the Environment (CCME) [67], and the Department of Environment and Conservation (DEC) [68].

3. Results and Discussion

3.1. Geomorphologic and Land Use Characteristics

Carbonate rocks control the karst characteristics of the basin. According to Papadopoulou-Vrynioti et al. [69], alluvial sediments primarily derived from the flysch outcrops in the north-eastern part of the area. The transport capacity of the surface runoff increases from the steep slopes of the western flank of the Mitsikeli mountain [70–75].

The slopes of the Ioannina karst basin are shown in Figure 2. The percentage proportion of the area for each slope class in the study area was estimated. More specifically, 72% of the total study area has a very gentle slope (<5°), 15% a gentle slope (5–10°), 10% moderate slopes (10–20°), 5% a steep slope (20–30°) and 1% very steep slopes (>30°). The very gentle slopes appear in the Ioannina karst basin, while the steep slopes are presented mainly in the hilly area and the western edge of the Ioannina karst basin. The percentage proportion of the area for each land use in the study area was estimated. The urban land covers 15% of the total area, the agricultural land 77%, the shrubby and sparsely vegetation 6%, and the wetlands 2%. The urban and the agricultural areas are the most extensive land uses of the study area, covering 92% of the total area. Many researchers reported that the relief controls the land uses in an area [76–78]. The smooth morphology supports urban development and agricultural activity [79,80]. As much as 69% of the urban area is located on very gentle slopes, 22% on gentle slopes, and 9% on moderate slopes. Thus, the urban area includes an urban pattern, a dense roadway network, cottage industries, the Ioannina city's airport, and a vehicle recycling, crushing, and dismantling industry. Regarding the other land uses, 78% of the agricultural land is located on very gentle slopes, 14% on gentle slopes, and 8% on moderate slopes, and 6% of the shrubby and sparsely vegetation area is situated in very gentle slopes, 14% on gentle slopes, 8% on moderate slopes, and 5% on steep slopes, while 100% of the wetlands is located on very gentle slopes. The Ioannina Airport has served as a civil airport since 1965. It is a mid-sized airport with an annual mean of 2219 flights. During the period 1994–2016, 48,732 flights carried 2,615,336 passengers [53].

3.2. Physicochemical Characteristics of the Soil

There is a high variability of soil pH values across the studied area, ranging from 5.0 to 7.8 [69]. The study area's soil pH values suggest acid to alkaline conditions for all agricultural soil samples. The main geological factors controlling the distribution of pH in the studied area involves the weathering process of the calcareous material and the decomposition process of the organic matter of the lignite/peat occurrences. The CEC values ranged from 7.70 to 40.90 meq/100 g, with a median value of 17.50 meq/100 g [69]. The CEC values suggest that the mobility of As and Zn would be expected to be low in the agricultural soil of the study area. The calcium carbonate ($CaCO_3$) content in the soil of the study area ranged from 0.05 to 59%, with a median of 0.9% [69]. According to the O.P.E.K.E.P.E. [52], the following Reference Soil Groups are recorded in the Ioannina basin (Figure 5A): (a) Cambisols (CM), which are characterized by the absence of appreciable quantities of organic matter, illuviated clay, and compounds of Al or Fe; (b) Fluvisols (FL) accommodate genetically young soils in alluvial deposits. Fluvisols present a layering of the sediments rather than pedogenic horizons; (c) Histosols (HL) are shallow soils over hard rock and comprise very gravelly or highly calcareous material; (d) Leptosols (LP) are shallow over hard rock and comprise highly calcareous material; and (e) Luvisols (LV) are fertile soils suitable for a wide range of agricultural uses.

The spatial correlation of the soil groups and slopes proved that 68% of Cambisols are located in very gentle slopes, 23% in gentle slopes, and 9% in moderate slopes. As much as 91% of Fluvisols are situated on very gentle slopes, 6% on gentle slopes, and 3% on moderate slopes, while 93% of Histosols are located in very gentle slopes, 4% on gentle slopes, and 3% on moderate slopes. Regarding Leptosols, 52% are on very gentle slopes, 21% on gentle slopes, 23% on moderate slopes, and 4% on steep slopes. Finally, 80% of Luvisols are located in very gentle slopes, 21% on gentle slopes, and 5% on moderate slopes. Consequently, the vast majority of soil groups are located on very gentle slopes. The Fluvisols and Luvisols soils containing the highest proportion of clay are recorded mainly in the central part of the study area (Figure 5A). The Fluvisols are mainly derived from the erosion of flysch (Figure 1). The Histosols are observed in the eastern part of the polje, while the Leptosols are distributed primarily in the northern and western parts of the area (Figure 5A). These two soil groups include calcareous material and can be attributed to the karstification process of the carbonate rocks outcropping in the study area.

The mean, median, minimum, and maximum values of organic matter, clay, silt, and sand content in the soil of the studied area are tabulated in Table 1. The soil of the study area presents high proportions of silt and clay (Table 1). The spatial distribution of organic matter in the soil of the study area is shown in Figure 5B. The higher organic matter content is recorded mainly in the eastern part of the studied area, suggesting a higher capacity of immobilization for As and Zn (Figure 5B).

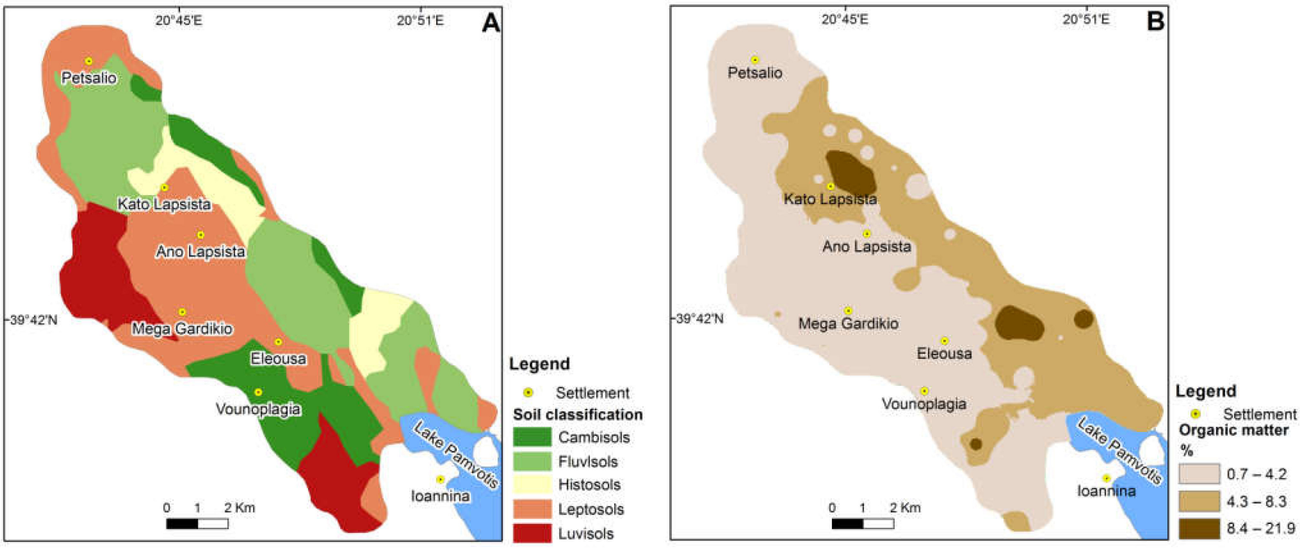

Figure 5. (**A**) Classification of soils in the studied area; (**B**) Spatial distribution of organic matter in the soil of the study area.

Table 1. Organic matter, clay, silt, and sand content (%) in the soil of the Ioannina basin.

	Organic Matter	Clay	Silt	Sand
		Agricultural land use (n = 102)		
Mean	4.2	32.3	38.1	29.8
Median	3.3	31.0	38.5	27.0
Minimum	0.7	5.0	13.0	4.0
Maximum	22.0	64.0	64.0	82.0
		Urban land use (n = 8)		
Mean	4.1	35.9	36.5	27.8
Median	3.6	31.5	37.5	23.5
Minimum	1.0	11.0	20.0	7.0
Maximum	6.9	65.0	56.0	69.0
		Wetlands (n = 2)		
Minimum	4.4	42.0	31.0	12.0
Maximum	6.8	57.0	35.0	23.0

The mean, median, minimum, and maximum values of aqua-regia extractable element contents at the Ioannina karst basin's soils and the analytical methods' detection limits are presented in Table 2. The study area's soil is highly enriched with the elements As and Zn, as shown by their median values, which are higher than that of the corresponding values given by Salminen et al. [65].

Table 3 tabulates the Pearson correlation coefficient (r) matrix for soil data of the studied area. It is shown that only some of the correlation coefficients are statistically significant (p-value < 0.05). Sand showed a significant negative correlation with the clay and silt contents (Table 3). In contrast, there are significant positive weak correlations for As-OM, Zn-OM, and Zn-Clay, indicating weak associations of these elements with organic matter and Zn with clay, respectively (Table 3). This finding suggested an additional anthropogenic or geological source, except for the known lignite deposits and clay minerals, which control the distribution of the As and Zn content in the soil of the study area.

Table 2. Detection limits and descriptive statistics of As and Zn concentration (in mg kg^{-1}) in the soil of the Ioannina basin compared to criteria provided from the literature.

	As	Zn
Detection limit	2	2
Agricultural land use (n = 102)		
Mean	19.8	94.6
Median	16.0	92.0
Minimum	3.6	17.0
Maximum	76.0	465.0
Urban land use (n = 8)		
Mean	18.7	94.9
Median	17.8	95.0
Minimum	13.0	60.0
Maximum	27.0	146.0
Wetlands (n = 2)		
Minimum	23.0	143.0
Maximum	33.0	173.0
European topsoil [65]	6.0	48.0
EPA Residential soil [66]	0.68	2300
EPA Plant-Avian-Mammalian [66]	5.7	6.62
CCME Agricultural land use [67]	12	200
CCME Residential land use [67]	12	200
DEC Ecological Investigation level [68]	20	200

Table 3. Pearson correlation coefficient (r) matrix for soil data (n = 112) of the study area. The *p*-value is calculated at the 95% confidence level (OM: Organic matter).

		As	Zn	OM	Clay	Sand	Silt
As	r	1.00	−0.10	0.27	−0.03	0.10	−0.13
	p-value		*0.317*	*0.004*	*0.774*	*0.309*	*0.166*
Zn	r		1.00	0.24	0.17	−0.18	0.09
	p-value			*0.010*	*0.082*	*0.065*	*0.323*
OM	r			1.00	−0.12	0.11	−0.04
	p-value				*0.197*	*0.249*	*0.710*
Clay	r				1.00	−0.82	0.16
	p-value					*0.000*	*0.104*
Sand	r					1.00	−0.70
	p-value						*0.000*
Silt	r						1.00

3.3. Spatial Distribution of Elements in Soil

3.3.1. Arsenic

The spatial distribution of As in the soil of the Ioannina basin is illustrated in Figures 6 and 7. The concentration of As in soil at the eastern and western part of the studied area is higher than the European topsoil's median value [65]. The elevated As (> 33.1 mg kg^{-1}) content in soil is recorded north of the Pamvotis lake and the areas lying between Petsalio and Ano Lapsista-Kato Lapsista (Figure 7A,B). The vast majority (93%) of elevated As concentration is found on very gentle slopes. The elevated As concentration is mainly observed in the Fluvisols and Leptosols soil classes (Figure 6A). The elevated As content in the Ioannina basin's soil is spatially related to the highest organic matter content (Figure 6B) and lignite deposits (Figure 7B), consequently reducing the mobility of As and leading to the high content of As in soil. A similar enrichment mechanism of trace elements in soil involving organic matter is also reported by Li et al. [81] in the soil of Tongguan

County (China). Furthermore, the elevated As concentration in soil is also well related to agricultural land use (Figure 7A), suggesting that an additional anthropogenic source of As in the soil of the study area is the application of agricultural chemicals, phosphate, and nitrogen fertilizers. Since there are no detailed data about the doses of the fertilizers applied in the study area and their As content, only relevant information from the literature can be reported and discussed. According to Kabata-Pendias and Pendias [82], the As concentration (mg kg^{-1}) in phosphate and nitrogen fertilizers range from 2 to 1200 and 22 to 120, respectively. Furthermore, according to Kabata-Pendias and Mukherjee [42], agricultural practices may be a significant source of As, as its concentration is often elevated in sludge, manure, fertilizer, and pesticides.

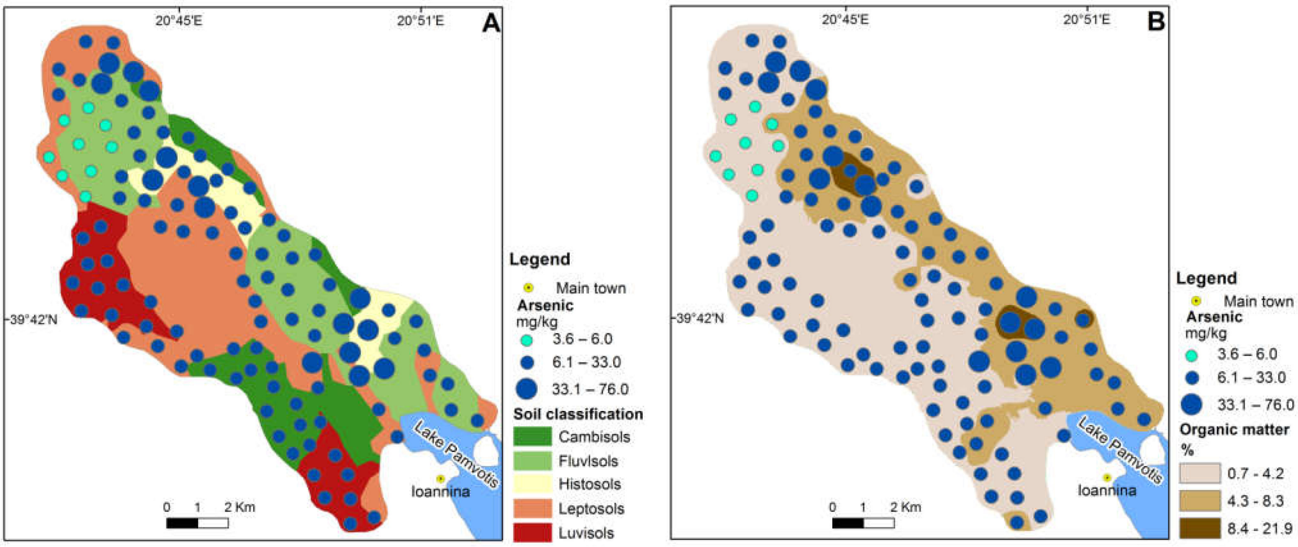

Figure 6. Graduated symbol plots of As content in the soil of the Ioannina basin in relation to the Reference Soil Groups (**A**); and organic matter (**B**).

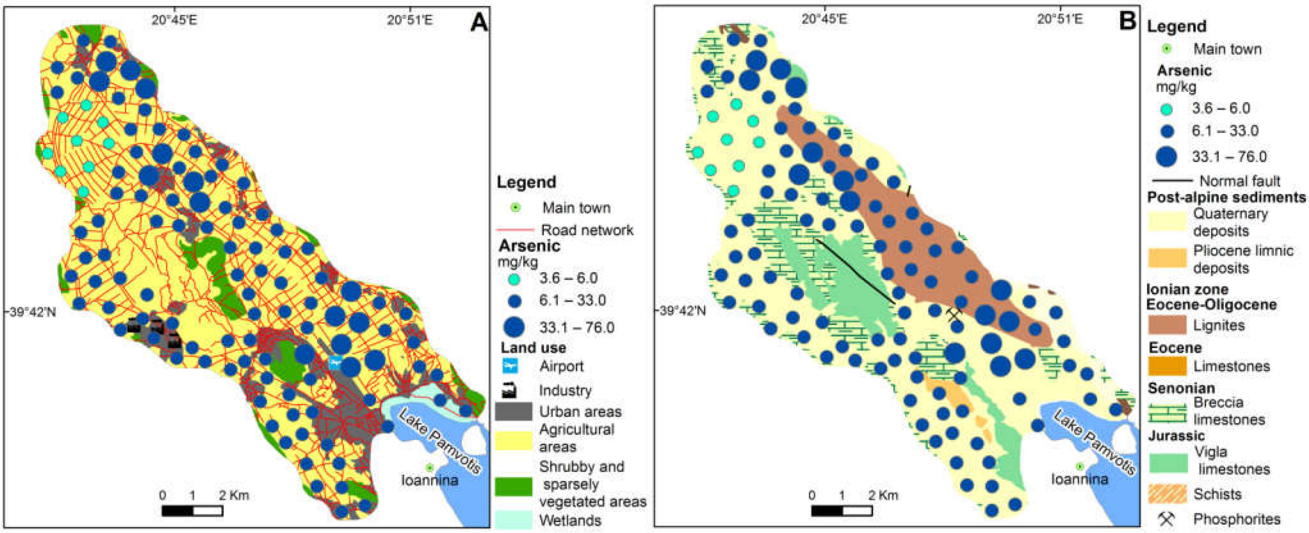

Figure 7. Graduated symbol plots of As content in the soil of the Ioannina basin in relation to land uses (**A**) and geology (**B**).

The arsenic content in the lignite deposits of the Ioannina basin varies between 1.93 and 46.40 mg kg^{-1} [54], suggesting that lignite deposits are a natural source of As in the soil of the Ioannina karst basin. Similar findings regarding the contribution of lignite deposits as a contamination source of As for soil and groundwater have also been reported by many researchers in the Oropos-Kalamos basin (Greece) [83,84]. According to Golfinopoulos et al. [85], the most important reason for the As occurrence in the environment of Greece is the geogenic sources. The airborne particulate matter, especially the lighter particles, attributable to aircraft operations, is another possible anthropogenic source of the As content in the soil of the Ioannina basin. Amato et al. [86] reported that aircraft operations at Barcelona airport (Spain) resulted in As contents of up to 6.3 ng m^{-3} in particulate matter samples. Agrawal et al. [87] studied emission indices of various elements for four planes as a function of engine load and reported that the As emission by jet engines is up to 0.00487 mg per 1 kg of combusted fuel. Moreover, the As content in PM_{10} collected at Barcelona airport is up to 6.3 ng m^{-3} [86]. The AsO_3 content in brake abrasion dust reaches up to 0.01% [88], suggesting that road traffic emissions are also an additional source of As in the Ioannina karst basin's soil. An increase of As concentration in roadside soil was also reported by Wiseman et al. [89] in Toronto (Canada).

An arsenic content in soil exceeding the plant-avian-mammalian screening level (P,A,M) established by EPA is recorded in the 99.9% (14.8 km^2), 91.8% (71.4 km^2), 91.6% (6.0 km^2), and 99.8% (1,6 km^2) of the urban agricultural, shrubby-vegetated, and wetland areas, respectively (Figures 8A and 9A). All the sampling sites at the Ioannina karst basin present an As content in soil higher than the EPA (RS) (Figure 9A).

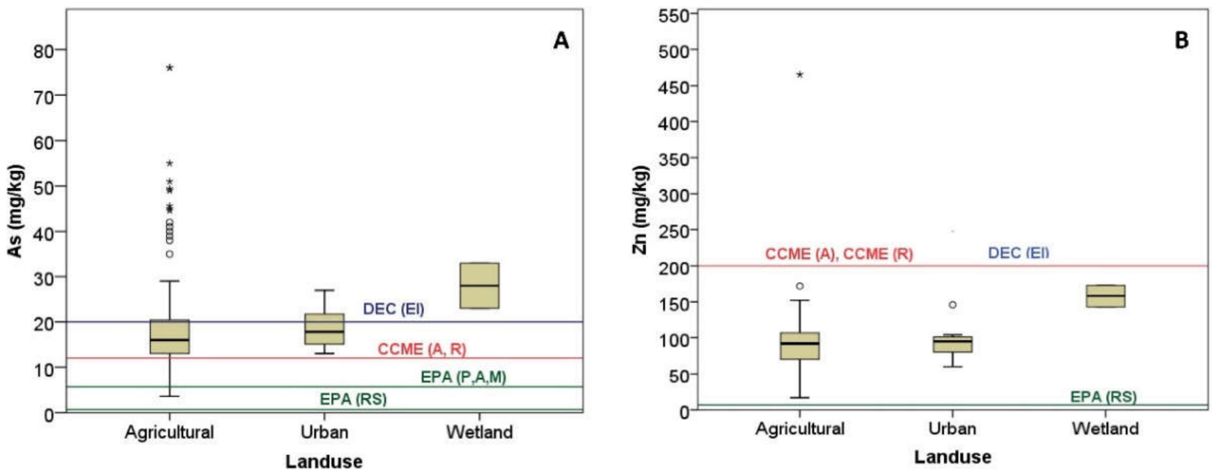

Figure 8. Boxplots for: (**A**) As and (**B**) Zn, comparing the elements' concentration to standards from the literature [65–67]. EPA (RS): Residential soil's regional screening level; EPA (P,A,M): Plant-Avian-Mammalian screening level; EPA (A,M): Avian-Mammalian screening level; CCME (A): Soil quality guideline for agricultural land use; CCME (R): Soil quality guideline for residential land use; DEC (EI): Ecological investigation level; asterisks and circles indicate outliers.

An arsenic concentration in soil that exceeds CCME (A) and CCME (R) is recorded in 83.6% (12.4 km^2), 74.7% (58.1 km^2), 75.8% (5 km^2), and 99.8% (1.6 km^2) of the urban, agricultural, shrubby-vegetated, and wetland area, respectively (Figure 9B). In the 37.5% (5.5 km^2), 28.2% (21.9 km^2), 25.5% (1.7 km^2), and 99.8% (1.6 km^2) of the urban agricultural, shrubby-vegetated, and wetland area, respectively, the As content in soil is higher than the DEC (EI) (Figure 9C). The median As values in the soil of agricultural, urban, and wetland land uses are higher than the CCME (A), CCME (R), EPA(P,A,M), and EPA (RS) values, suggesting a potential threat to residents, plants, and terrestrial ecological receptors of the study area. Only the median value for As in the soil of wetlands of the Ioannina karst basin exceeds the DEC (EI) (Figure 9A). A decrease in the growth of vegetables and chlorosis is among the expected impacts of As on plants [90], while As is known to deactivate enzymes in animals [91]. Adverse effects of As-contaminated vegetables on human health include, among others, abnormalities of the nervous system and endocrine disruptions [92].

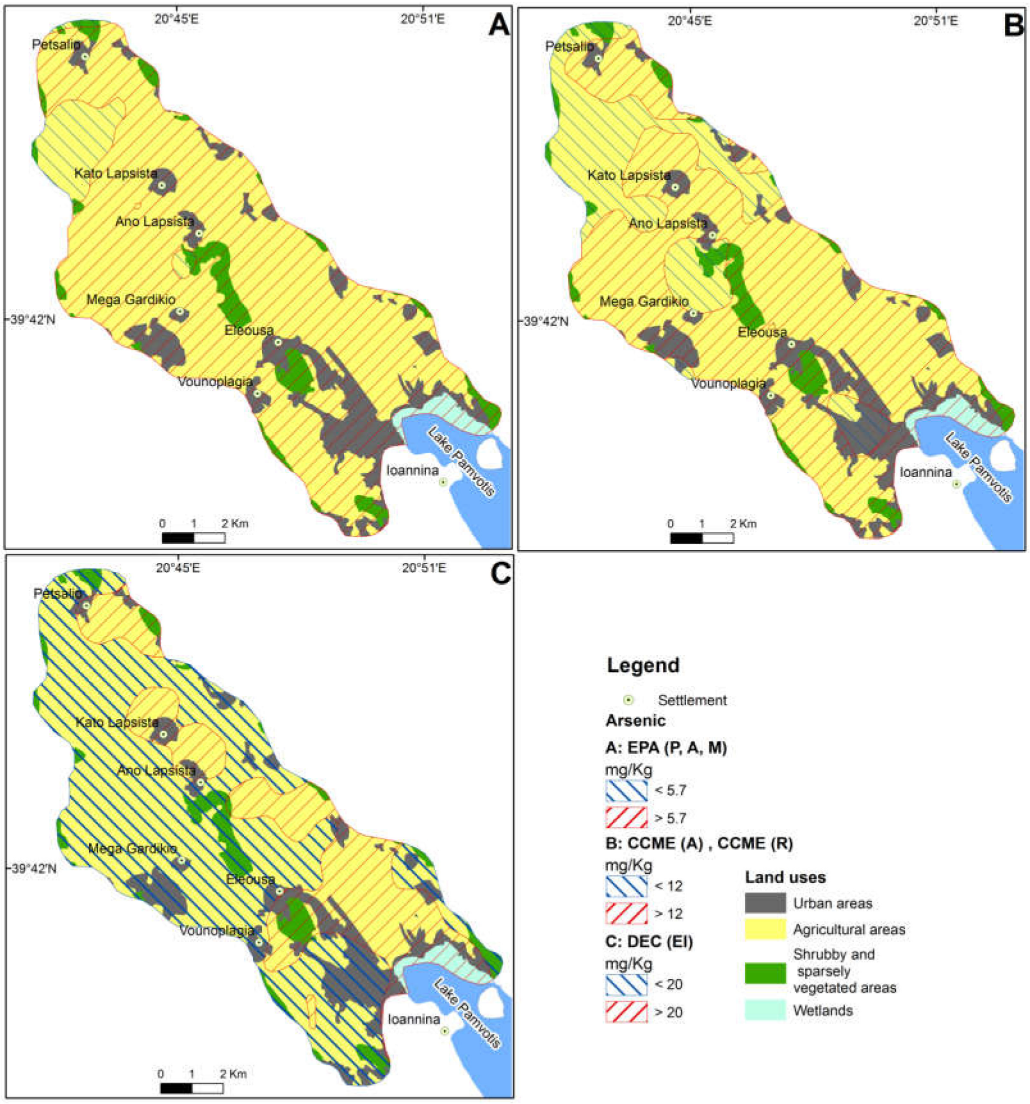

Figure 9. Suitability map comparing As content in the soil of the Ioannina basin in relation to EPA (P,A,M) (**A**); CCME (A) and CCME (R) (**B**); and DEC (EI) (**C**).

3.3.2. Zinc

Only 5% of the sampling sites contained a Zn concentration in soil lower than the European topsoil's median value [65]. The vast majority (94%) of the maximum Zn concentration is located on very gentle slopes. The highest Zn content is mainly recorded in the Fluvisols, Leptosols, and Luvisols soil classes (Figure 10A). The highest Zn concentration in the soil of the studied area is spatially related to the highest organic matter content, as depicted in the eastern edge of the Ioannina basin (Figure 10B). The spatial pattern of Zn is not very complex, probably because its sources are distributed all over the study area, suggesting that the Zn content in soil is attributed mainly to geogenic sources (Quaternary deposits and Fe-Mn oxides) (Figure 11A,B), as also reported by Vryniotis [93], who concluded that Fe-Mn oxides are the primary geological source of Zn in the soil of the Ioannina karstic basin. Automobile emissions, aircraft operations, usage of fertilizers, vehicles scrap, and related activities are also continuous anthropogenic sources of Zn in the soil of the Ioannina basin. Many researchers [94,95] measured Zn levels in the soil surrounding airports and have revealed a direct link between aircraft operations and Zn, thus supporting the results of this study. According to Kabata-Pendias and Mukherjee [42], agricultural practices are considered among the main Zn sources which significantly contribute to Zn level in soils, suggesting that agricultural activities in the studied area are an additional anthropogenic source of contamination. The Zn concentration in fertilizers varies between 61 and 625 mg kg^{-1} [42]. Furthermore, Zn content is a well-known key tracer of traffic emissions [96–99]. Alexakis [100] reported a high Zn content (up to 720 mg kg^{-1}) in a road sediment of the West Attica region (Greece), which can be explained by the wear of vehicle tires and traffic emissions. Agrawal et al. [87] observed up to 0.0441 mg Zn per kg of fuel combusted in aircraft engines, while the Zn content in PM_{10} samples collected at Barcelona airport (Spain) was up to 646 ng m^{-3} [86]. Zinc is primarily applied in galvanized iron and steel products, which are used in automobile door panels. Zinc is also used for grills, carburettors, and pumps, and is also required for paints [101]. Jaradat et al. [101] studied the heavy metal distribution at a scrapyard of discarded vehicles (Zarqa city, Jordan) and observed an elevated Zn concentration in the plants gathered inside (58.35 mg kg^{-1}) and outside (52.11 mg kg^{-1}) of the scrapyard. Jaradat et al. [101] suggested that crushing and dismantling activities are a source of contamination in the vicinity of vehicle scrapyards.

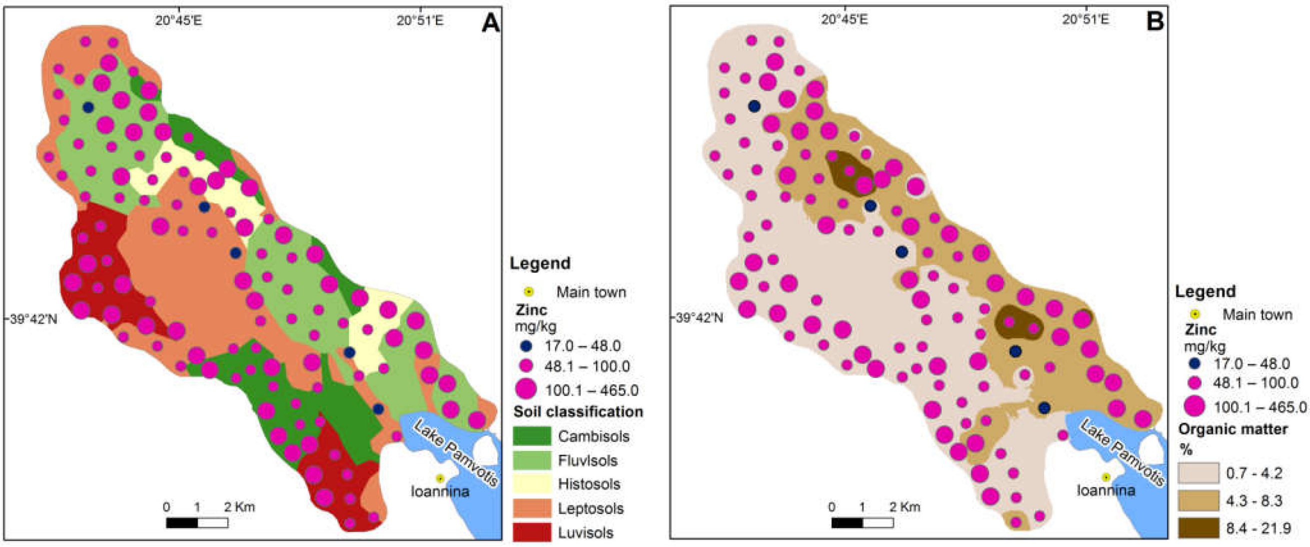

Figure 10. Graduated symbol plots of Zn content in the soil of the Ioannina basin in relation to the Reference Soil Groups (**A**); and organic matter (**B**).

All the sampling sites at the study area present a Zn content in soil [except only one sampling site for the screening values of CCME (A), CCMR (R), and DEC (EI)] higher than EPA (P,A,M) and lower than CCME (A), CCME(R), and DEC(E) screening values (Figure 11). Because Zn content in the soil does not exceed CCME (A), CCME(R), EPA (RS), and DEC (EI), there is no potential risk to human health and cultivated plants (Figure 12). Only 0.6% (0.1 km^2) and 1.1% (0.9 km^2) of the urban and agricultural land use areas, respectively, present Zn values higher than the screening values given by CCME (A), CCME (R), and DEC (EI) (Figure 12). Zinc causes alterations in plants' chloroplast structure [102], while Zn-rich vegetables' adverse impacts on human health mainly include kidney and liver failure, icterus, and bloody urine [103].

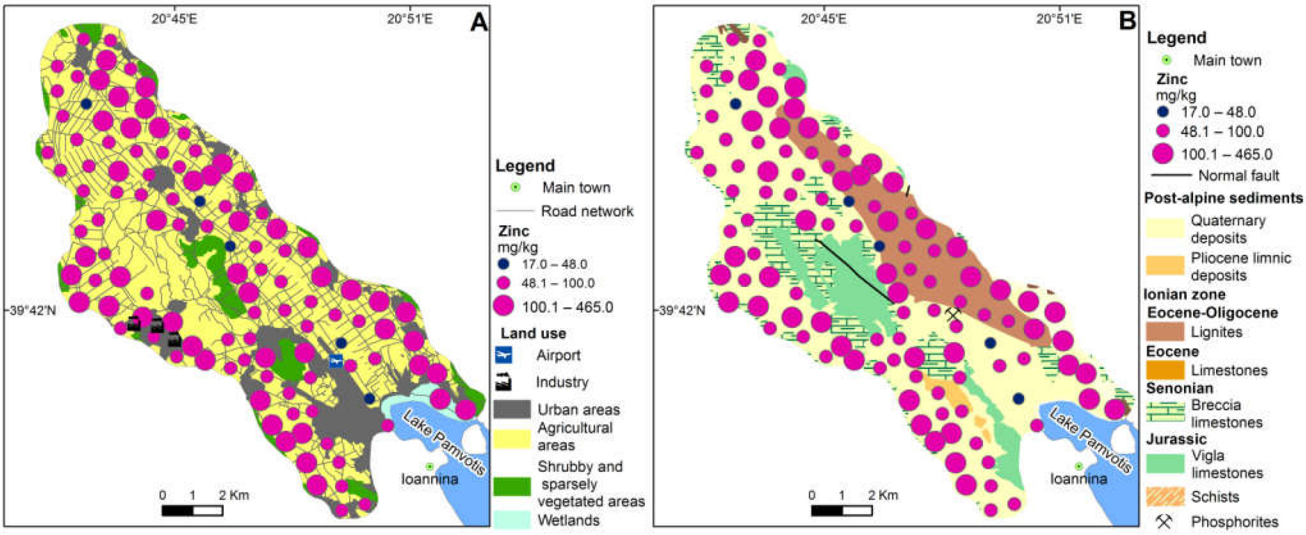

Figure 11. Graduated symbol plots of Zn content in the soil of the Ioannina karst basin in relation to land use (**A**) and geology (**B**).

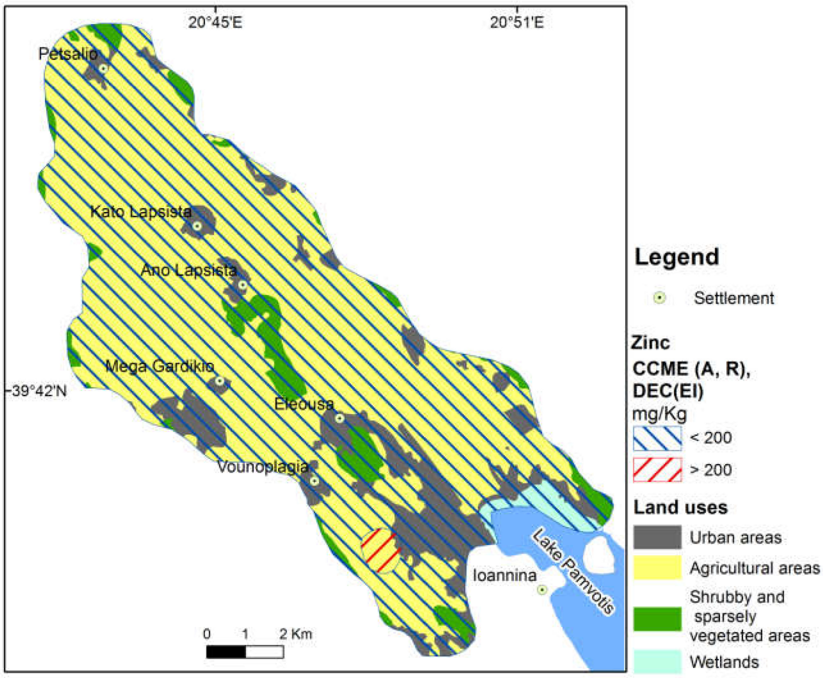

Figure 12. Suitability map comparing the Zn content in the soil of the study area to CCME (A), CCME (R) and DEC (EI).

4. Conclusions

This study delineates the spatial distribution of As and Zn content in the soil of a karst landform and assesses the land suitability for residential and agricultural use. Almost 72% of the total study area has a very gentle slope, favoring urban and agricultural land, which covers 92% of the total area. The median topsoil content for As and Zn is higher than the corresponding median values of European topsoils and was found to be in areas presenting very gentle slopes. The arsenic concentration in the topsoil of the karst landscape appeared to be influenced mainly by lignite deposits. The arsenic content in the soil of the Ioannina basin exceeds at least one or more of the criteria provided by the literature, and hence poses a potential risk to human and terrestrial ecological receptors. The comparison of Zn concentration in topsoil with the literature's criteria revealed that Zn does not pose a potential threat to human health and cultivated plants, except for 0.6% and 1.1% of the urban and agricultural land-use area, respectively. The evaluation of the land suitability of the study area revealed that the As content poses a potential risk to plants, avians and mammals. All the soil sampling sites in the study area present an As concentration higher than the screening value for residential soil. Moreover, the As content in soil is higher than the criteria given by CCME for 83.6% and 74.7% of the urban and agricultural areas, respectively. Scientists, engineers, stakeholders and planners may utilize the outcomes of this study in the environmental monitoring of the area and the forthcoming projects of spatial planning. Additionally, the local authorities may use this work for proposing remedial measures and policies to protect the natural environment.

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