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The contribution of karstic rocks to soil quality, Ioannina plain (Epirus, Hellas)

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ABSTRACT

Soil is a significant link to the food chain as trace elements and compounds are provided, directly or indirectly, to plants, animals and people. In certain areas, soil quality depends mainly on karstic rocks, such as limestone and dolomite, on which a certain type of ecosystem (karst ecosystem), is developed.

Ioannina plateau in NW Hellas constitutes a large karstic basin. According to the analytical results of 112 soil samples from the plain to the north-west of the city of Ioannina, a 100 km^2 area, which is part of the same karstic system (polje) there is a sufficient amount of samples with over 4% of $CaCO_3$ in about 23.20% of the sampled area. The highest values of $CaCO_3$, water extractable Ca^{2+}, Mg^{2+} cations, bicarbonate (HCO_3^-), Cation Exchange Capacity (CEC), exchangeable Ca^{++} cations and pH are observed specifically in a NW–SE trending zone near to the foothills of the limestone of Mitsikeli mountain. This is mainly due to the higher supply of material, derived from the dissolution of carbonate rocks, transportation and deposition of $CaCO_3$ of soil originating from the Mitsikeli mountain. The foothills of Mitsikeli mountain are enriched in the detritus derived from the weathering of limestone, and subsequent fluvial erosion and deposition of the calcium carbonate detritus downstream. The transport capacity of the many streams, that drain the slopes of Mitsikeli mountain, is increased, because the inclination is up to 30° and, therefore, with concurrent increase in the supply of such sediments in the eastern part of the Ioannina polje. Thus, the quality of soil in this NW–SE trending zone is definitely improved, mainly because of the supply of calcium carbonate from the aforementioned karst structure, resulting in the development of good quality soil for agricultural use and, consequently, in the development of karst ecosystem.
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1. Introduction

The long-term development of global socio-economic systems requires the sustainable use of natural resources (Brundtland, 1987; Tóth et al., 2007). According to Tóth et al. (2007) a variety of landscapes, land use traditions, social environments, scientific schools, languages and many other factors, generated a diversity of definitions and understandings of the concept of "soil quality" in Europe. Complex approaches to describe soil (and land) quality through the multifunctional nature of soil (and land) appeared in the second half of the 20th century worldwide, giving the frame for a possible common scientific understanding of the problem. One of the first widely accepted definitions was published by the Food and Agriculture Organisation of the United Nations (F.A.O., 1976) describing land quality as "*a complex attribute of land, which acts in a distinct manner in its influence on the suitability of land for a specific kind of use*".

Soil chemistry has traditionally focused on the chemical reactions in soil that affect plant growth and nutrition (Sparks, 2003). However, at the beginning of 1970s, and certainly in the 1990s, as concerns increased about inorganic and organic contaminants in water and soil and their impact on plant, animal, and human health, the emphasis of soil chemistry is now on environmental soil chemistry (Kabata-Pendias and Pendias, 2001; Reimann et al., 2014a,b). According to Sparks (2003) environmental soil chemistry is the study of chemical reactions between soil and environmentally important plant nutrients, radionuclides, metals, metalloids, and organic chemicals. Soil is a significant link in the food chain as it provides major and trace elements and compounds not only to plants, but to water, animals and people directly or indirectly (Demetriades et al., 2010; Johnson et al., 2011; Kabata-Pendias and Mukherjee, 2007; Kabata-Pendias and Pendias, 2001; Urushibara-Yoshino, 1993). The quality of soil is mainly linked to its mineral composition and the concentration of chemical

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elements and compounds therein (Papadopoulou and Vryniotis, 2007; Papadopoulou-Vrynioti et al., 2013a; 2014; Polyzopoulos, 1976; Sposito, 1983).

The term 'karst ecosystem' is defined as the environment with its living element and the factors that affect it (Neuendorf et al., 2011; Skilodimou et al., 2013). According to Yuan (2001), the karst ecosystem is explained as the ecosystem that is restrained by karst environment, especially, by karst geological setting and how the karst environment affects life (Papadopoulou-Vrynioti et al., 2013b, c; Vreča et al., 2001), and also the reaction of life support systems to the karst environment. The presence of karst rocks affects directly the karst ecosystem (Jianhua et al., 2007; Pfeffer, 2010; Tepsongkroh, 2000), due to its hydrogeological regime (Mertzanis et al., 2005a, b, 2011), which is completely different from other ecosystems in the same climatic zone. Karstic rocks, especially limestone and dolomite, through dissolution, supply soil with the necessary nutrients to improve its quality.

In most regions of Hellas, because of the widespread distribution of limestone and dolomite, soil has high contents of calcite and, consequently calcium, one of the main nutrients for the healthy growth of plants. At several places in Hellas, dolines and poljes (e.g., Kopais plain) occur, and they are suitable for agriculture because of their fertile soil (Papadopoulou-Vrynioti, 1990, 1999, 2004).

This paper's purpose is to examine the quality of soil in the plain to the NW of Ioannina, in relation to the occurrence of karstic rocks in the greater area, and the development of good quality soil for agricultural use and for karst ecosystem (Barany-Kevei, 2000; Jianhua et al., 2007). For this purpose, the concentrations in soil of the following parameters are examined, i.e., $CaCO_3$, water-soluble Ca^{2+}, bicarbonate (HCO_3^-), exchangeable cations (Ca^{2+}, Mg^{2+}), and the values of pH and CEC.

2. Study area

The area under study is situated to the NW of the city of Ioannina in Epirus of north-western Hellas, and is part of the Ioannina karstic basin (Fig. 1). It is an elongated area of 80 km^2 between the mountain range of Mitsikeli to the NE, the intermontane plateau range to the W, the plains of the Protopappas and Petsalion villages to the NW, and the city and lake of Ioannina to the SE towards where the majority of the drainage flows. The altitude of the plain part of the study area, where the soil geochemical survey was carried out (Vryniotis, 2010), varies from 465 m in the area of Lapsista, to 520 m in the SW edges of the area of Rodotopion and the mountain of Marmaras to the west. The Ioannina plain is interrupted by a series of NW–SE trending limestone hills of small extent (Fig. 1), reaching an altitude of up to 758 m, which divide the plain area in two separate zones with the same trend; these limestone hills, because of their small area extent do not appear to affect much the chemical composition of soil in the study area. The eastern part of the plain, directly to the NW of the Ioannina lake basin, has the largest area.

The precipitation as well as temperature variation throughout the year are major factors that affect the physico-chemical processes in the water–soil–fauna–flora system. The climate of the study area is continental, and according to the records of the Hellenic National Meteorological Service, it has an average annual precipitation of

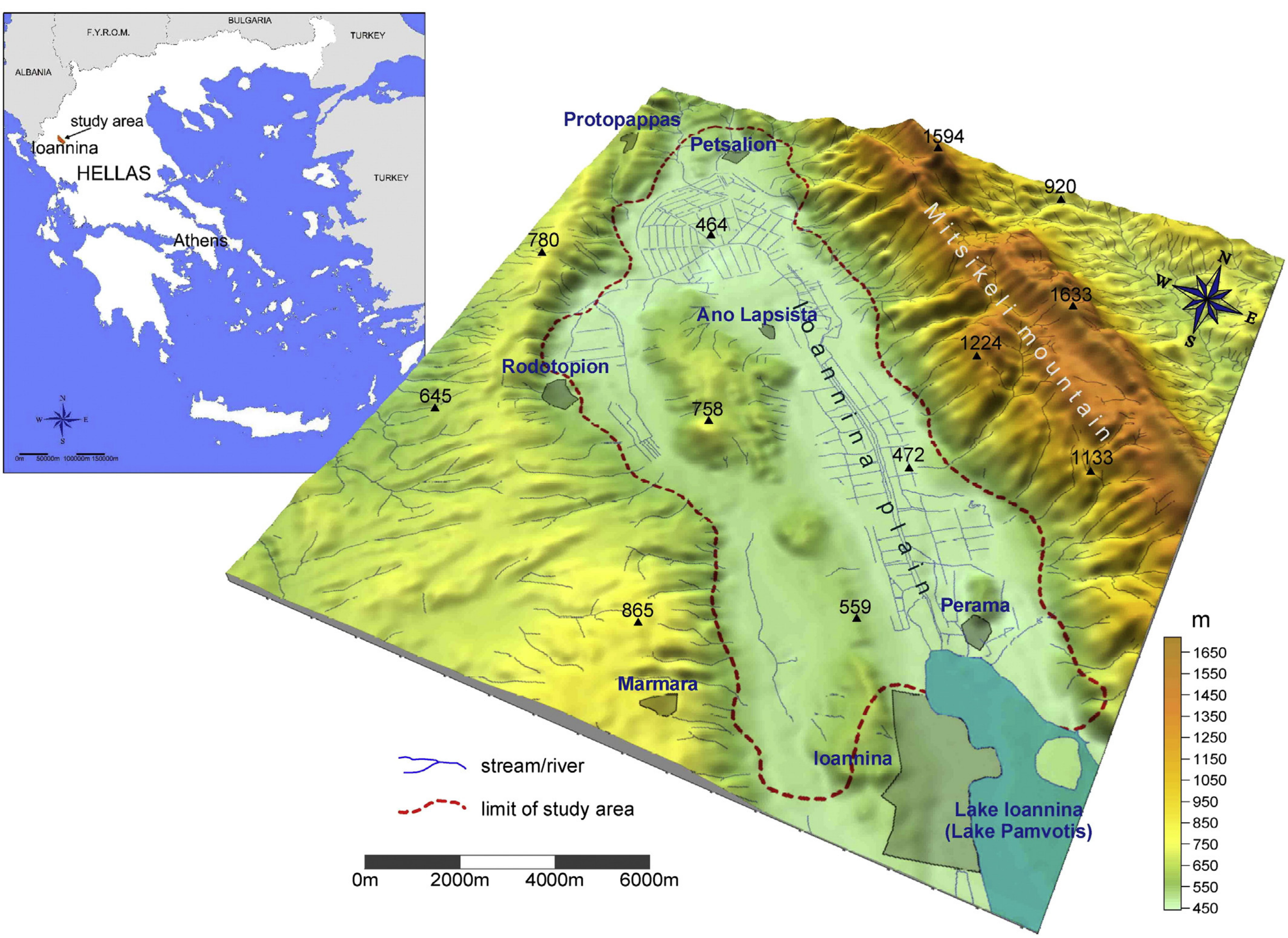

Fig. 1. Location map and three-dimensional terrain map of the study area, Ioannina plain, Hellas.

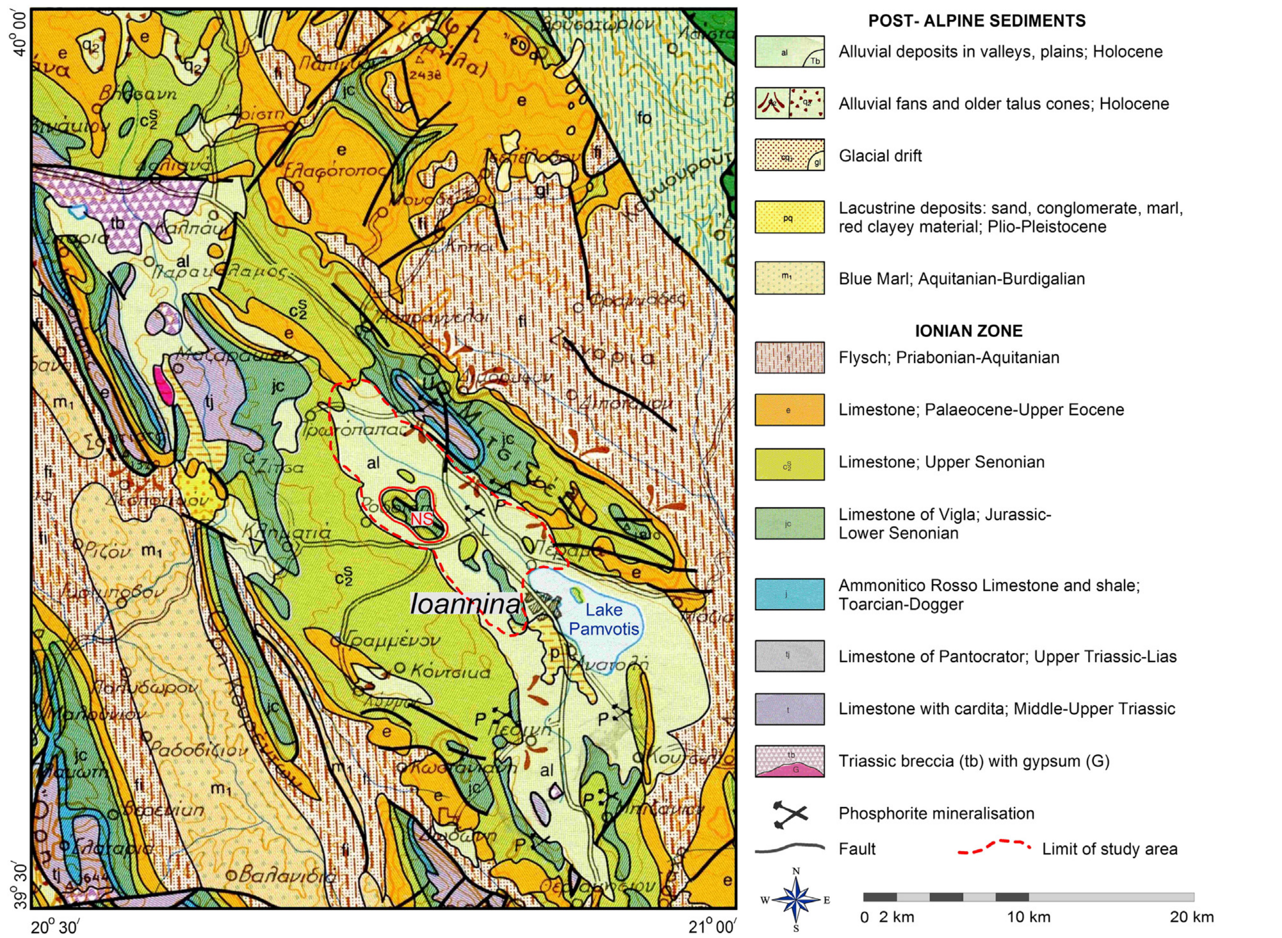

Fig. 2. Simplified Geological lithological map of the study area, Ioannina plain, Hellas (extract from the 1:500,000 Geological map of Hellas; Bornovas and Rondogianni-Tsiambaou, 1983).

1181 mm, with December having the highest monthly average at 174.9 mm, and the lowest in July at 32 mm. The average annual temperature is 14.3 °C, with an average winter and summer temperatures of 10.1 °C and 30.9 °C, respectively; the maximum recorded summer temperature is 42.4 °C, and the lowest winter is −13 °C.

2.1. Geological setting

The geological formations in the greater area, which are the supply source of the Ioannina plain in alluvial deposits, belong to the Ionian zone (Bornovas and Rondogianni-Tsiambaou, 1983; Perrier et al., 1967). The Ionian zone is the westernmost tectonic zone of Hellas and belongs to the wider Adriatic–Ionian geotectonic zone. The Alpine sediments of this zone, begin with Lower to Middle Triassic evaporite deposits (>2000 m thick), known only from boreholes. At the surface they are exposed as diapiric gypsum and evaporite solution-collapse breccias (known as Triassic breccias) derived from the transformation of the initial subsurface evaporite, mainly after their diapiric injections during the Ionian orogeny (Karakitsios and Pomoni-Papaioannou, 1998; Karakitsios and Rigakis, 2007) (Fig. 2).

Evaporite solution collapse breccias with gypsum bodies are found on the surface at many parts of the greater region, mainly in the south and west of the study area. Triassic evaporite deposits are followed, through the Middle-Upper Triassic (Ladinian–Rhaetian) Foustapidima limestone, by the Lower Jurassic shallow water Pantokrator limestone, more than 1000 m thick. The overlying pelagic Siniais limestone corresponds to the beginning of the Ionian Basin formation. Distensional tectonics, associated with the opening of the Tethys Ocean, combined with the halokinesis of the Ionian evaporitic base, resulted in the formation of several small structurally-controlled sub-basins with half-graben geometry (Karakitsios, 1992, 1995). This is evidenced by facies and thickness variations in the Middle Liassic to Malm deposits (Siniais limestone, Ammonitico Rosso or Lower Posidonia Beds, Limestone with Filaments, Upper Posidonia Beds), and by the direction of synsedimentary tectonic features (slumps, faults). Prismatic synsedimentary wedges in these sub-basins vary in thickness along an E–W direction and underline the facies distribution. Unconformities are located on top of tilted blocks and the Ammonitico Rosso and Lower Posidonia Beds are located in the deeper parts of the half-grabens.

The deposition of the pelagic Vigla limestone (Berriasian–Turonian) all over the Ionian zone marks the end of the internal differentiation that characterised the area during the Middle Lias–Malm interval. The Senonian to Eocene limestone, which rests on the Vigla limestone, corresponds to calciturbidite comprising limestone fragments, derived from the adjacent Gavrovo platform to the east, and the Apulian platform to the west, with calcareous cement containing pelagic fauna. Flysch sedimentation in the main part of the Ionian zone began at the Eocene–Oligocene boundary (Priabonian–Aquitanian), and is characterised by some conformable transitional marly limestone beds overlying the upper Eocene limestone.

Major orogenic movements occurred at the end of the early Miocene (Burdigalian), with the inversion of the Ionian Basin succession (Karakitsios, 1995). The structures, inherited from the Jurassic extensional phase, were reactivated during the compressional phase of orogenesis with westward and eastward displacements. This tectonic style was facilitated by diapiric movements involving the basal evaporitic salt intervals (Karakitsios, 1995, 2013).

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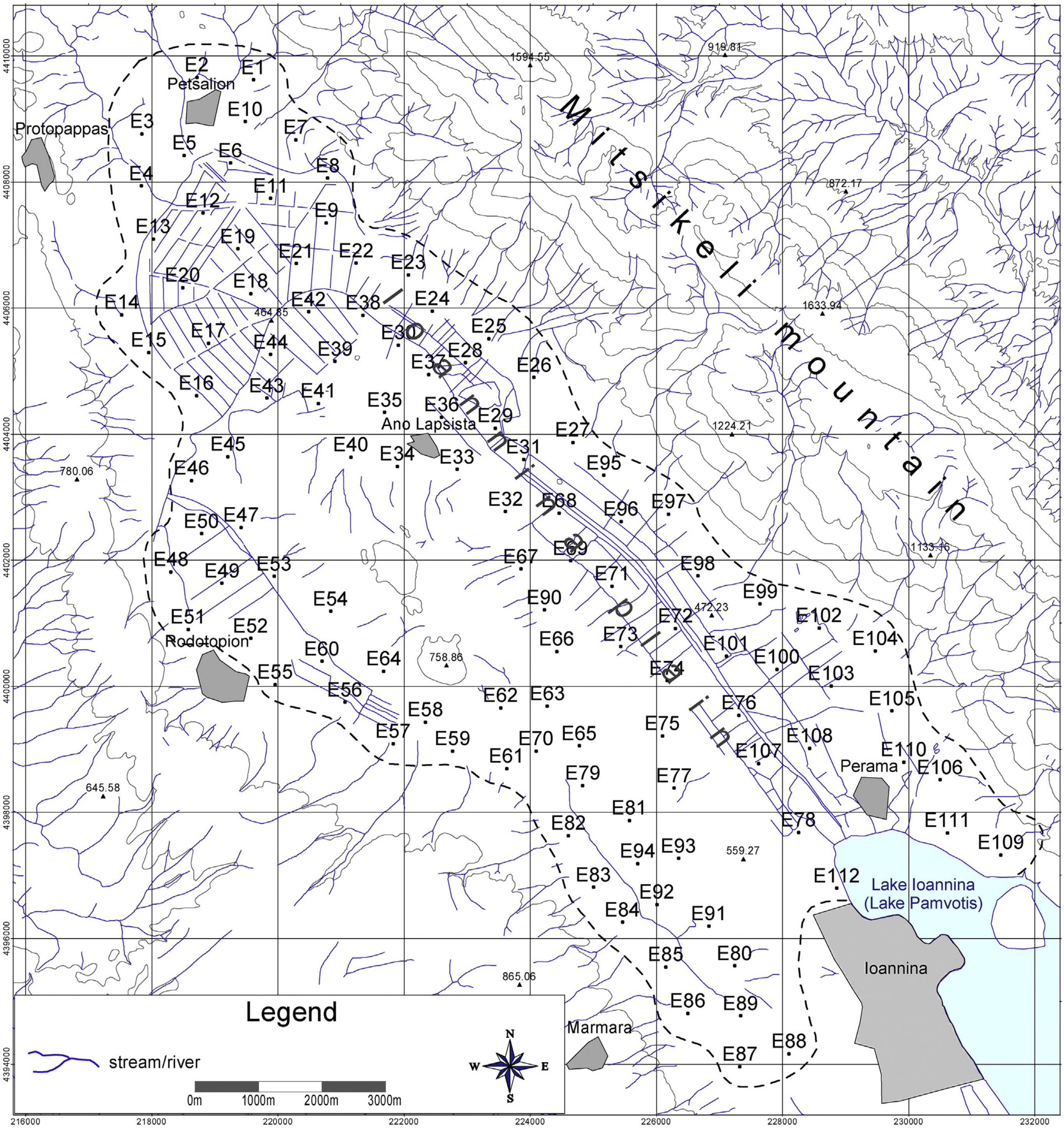

Fig. 3. Map showing soil sampling locations of the study area, Ioannina plain, Hellas.

As far as the post-alpine sediments are concerned, there are some blue marl formations from the late Miocene in the south and west of the study area, as well as some lacustrine sandy-clay formed in the Pliocene (Karakitsios, 1994,1998, 2005; Karakitsios and Gournellos, 1999).

The Quaternary sediment deposits cover the greatest part of the plain. Their composition depends mostly on the type of rock formations in the supply area, the transport distance from the source area, etc. To the west and south, there are many old siliceous deposits, consisting of angular fragments of flint and terra rossa, derived from the decalcification of limestone areas. In the SW and N, terra rossa occurs in various areas. In the NE and SW, there are old and recent scree cones. There also occur recent lacustrine and fluvial deposits, including alluvial deposits, and to the north and east, and some glacial scree deposits.

Tectonically, the area is characterised by a series of anticlines and synclines, as well as faults, all of a NW–SE orientation (Karakitsios, 1992, 1995). The geomorphological conditions of the study area, as will be mentioned in detail in the next section, have been affected severely by these large scale tectonic formations that prevail in the greater area.

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Table 1.
Summary statistics of soil samples (N = 112) collected from the Ioannina basin, NW Hellas.

Parameter	Units	Extraction method	Minimum	Median	Maximum
CEC	meq/kg		77	175	409
pH			4.95	6.62	7.75
$CaCO_3$	%	Total	0.05	0.9	59
Ca^{2+}	mg/kg	Exchangeable	882	2786	7615
Mg^{2+}	mg/kg		67	172	1290
Ca^{2+}	mg/kg	Water extractable	13.6	87.4	394
HCO_3^-	mg/kg		31.9	123	690

2.2. The Ioannina karstic basin

Limestone of varying age is the major rock for the development of karst characteristics of the Ioannina basin. Apart from the karstic processes, the tectonic regime played a significant role in the development of the basin, since the whole area is situated in a syncline (Karakitsios, 1994; Karakitsios and Gournellos, 1999). The Ioannina basin meets all the criteria to be characterised as a "polje" of the Dinaric Karst system (Katsikis, 1981). In fact, it is a closed, concave structure, with a flat base floor, consisting of Quaternary loose deposits, interrupted by residual small extent limestone hills (hum), and it is drained by

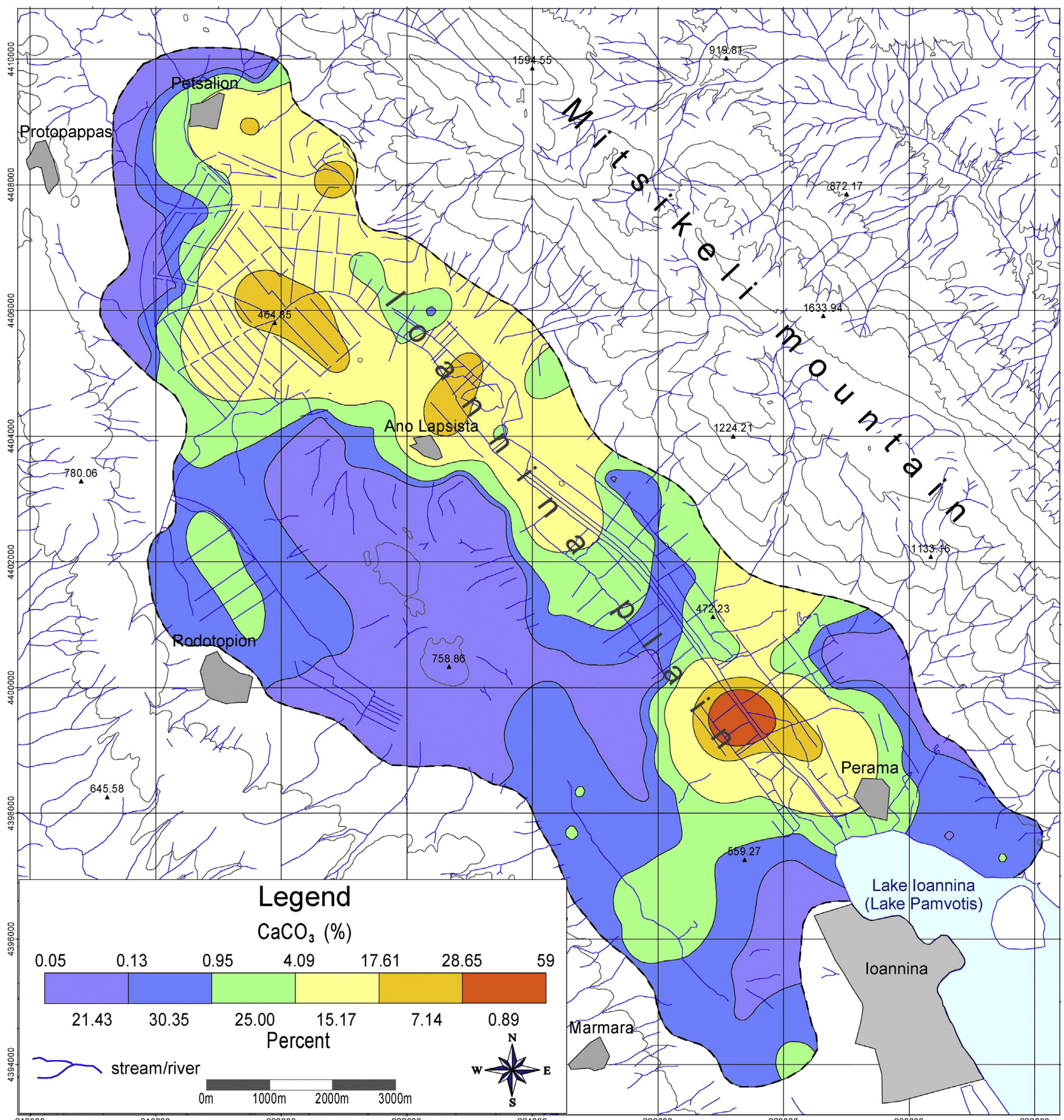

Fig. 4. Map showing the spatial distribution of calcium carbonate ($CaCO_3$) in surface soil, Ioannina plain, Hellas.

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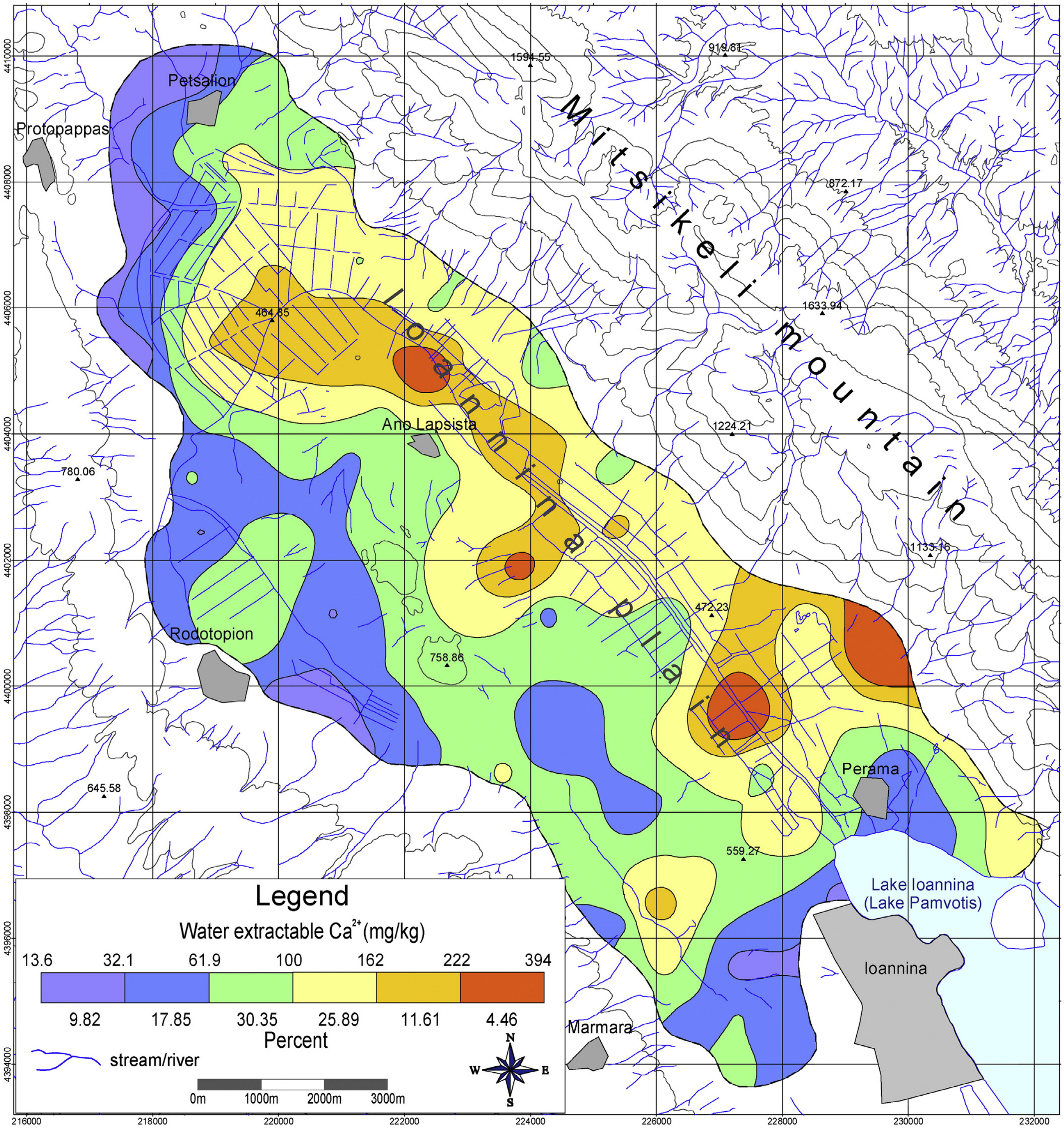

Fig. 5. Map showing the spatial distribution of water extractable Ca^{2+} content in surface soil, Ioannina plain, Hellas.

three underground 'sinkhole systems'. The base of this polje is mainly a system of flat alluvial cones covered by impermeable alluvial sediments primarily derived from the flysch outcrops of the area of Driskos, and not so much from the insoluble detritus that remains after the dissolution of the karstic rocks. This can be attributed to the size of the polje. In large-scale karst formations, such as the case in question, where the polje is about 35 km long and varies in width from 3 to 10 km, the insoluble material remaining from the karstification is not enough to deposit sediments of considerable thickness. In particular, a great part of this insoluble material is removed by subsurface karstic conduits that have been developed because of tectonic discontinuities (Papadopoulou-Vrynioti, 1990, 2004). However, the deposition of such sediments in the eastern part of the Ioannina polje can be attributed to the inclination of the limestone slopes up to 30° in the western part of Mitsikeli mountain, which is cross-cut by numerous V-shaped valleys (e.g., Lagkadas valley) and small size canyons. The aforementioned inclination increases the transport capacity of the streams and, therefore, the supply of such sediments in the eastern part of the Ioannina polje (Papadopoulou-Vrynioti et al., 2013a).

The volume of surface runoff, as expected, depends on rainfall intensity; after periods of heavy rainfall there is a higher runoff, and is much slower during the period of snow melting (Mertzanis, 1992).

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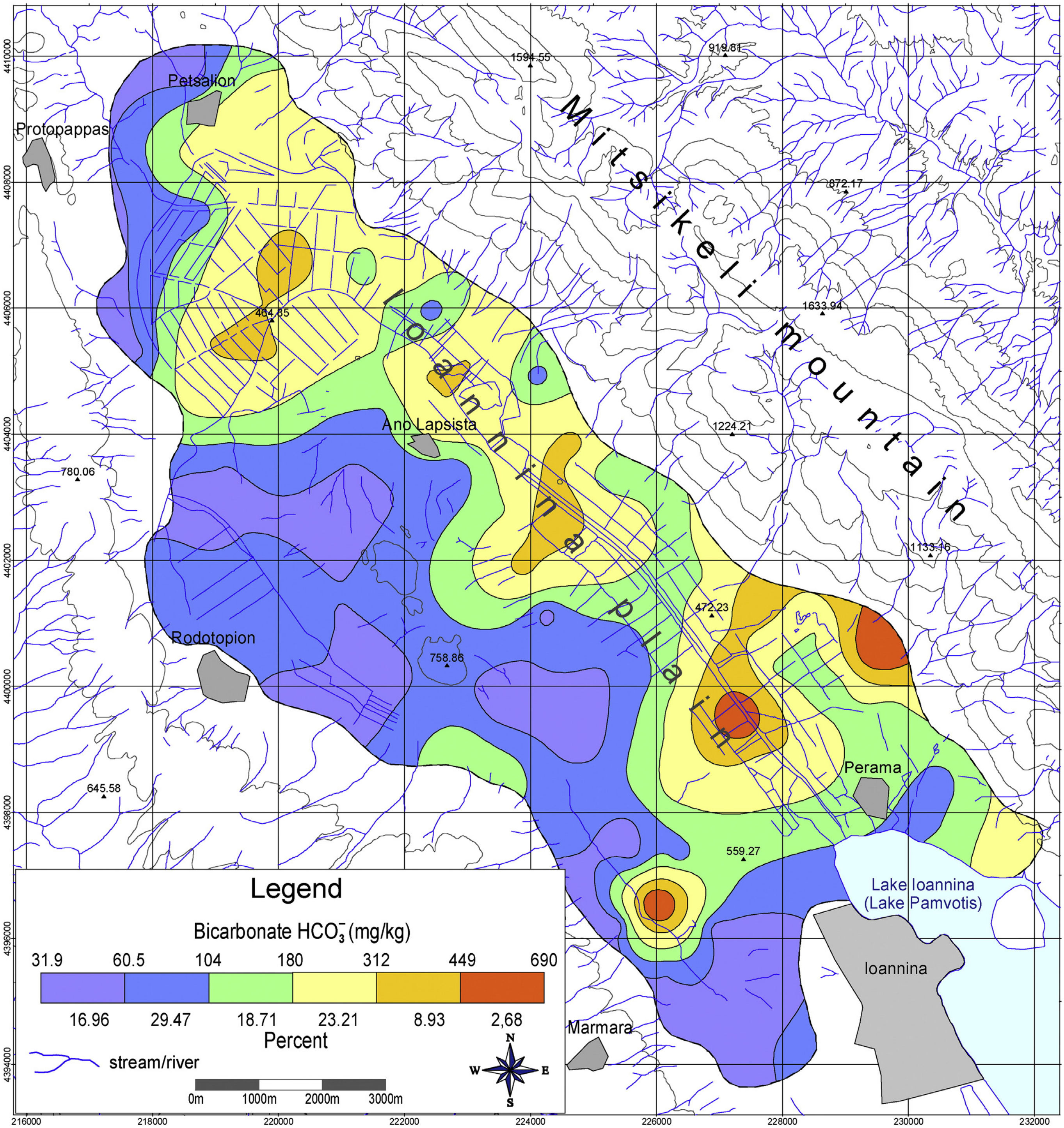

Fig. 6. Map showing the spatial distribution of bicarbonate (HCO_3^-) content in surface soil, Ioannina plain, Hellas.

There is a great variety of transported material, mainly derived from the mechanical erosion due to the action of frost (freeze–thaw process), as well as from karstification, as indicated by the occurrence of terra rossa soil.

3. Methods

3.1. Sampling

The alluvial soil of Ioannina plain that was sampled is mostly loam, silty clay loam, clay and clay loam. The geochemical soil sampling was conducted at a cultivated or potentially cultivated area of about 100 km^2 (Vryniotis, 2010). In total, 112 soil samples were collected from 0 to 30 cm depth at an average density of 1 sample/km^2. The location of soil samples is shown in Fig. 3. At each sampling site, a composite soil sample of about 1.5–2 kg was collected from two suitable points.

3.2. Sample preparation and analysis

All soil samples were air-dried at room temperature (<25 °C) for several days, and after disaggregation in a porcelain mortar they were sieved through a 2 mm nylon screen.

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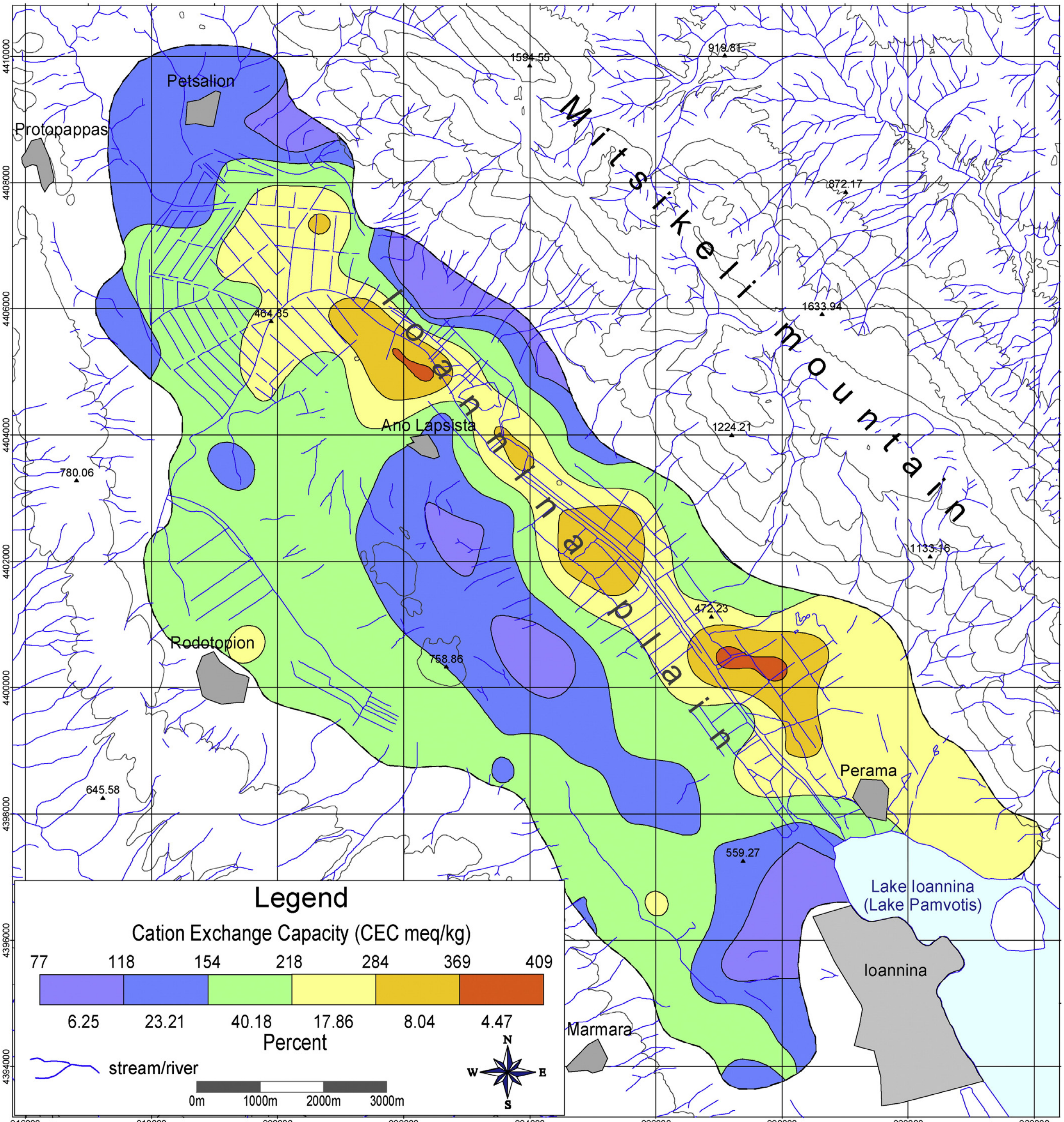

Fig. 7. Map showing the spatial distribution of Cation Exchange Capacity (CEC) values in surface soil, Ioannina plain, Hellas.

The soil samples were analysed for $CaCO_3$, water-soluble Ca^{2+} ions, bicarbonate (HCO_3^-), the exchangeable cations of Ca^{2+} and Mg^{2+}, cation exchange capacity (CEC), and pH (Vryniotis, 2001; Vryniotis and Papadopoulou, 2004). The $CaCO_3$ was measured with a Bernard Calcimeter, which is based on the volumetric analysis of carbon dioxide CO_2 that is liberated during the addition of a solution of 4N HCl acid on a 2 g soil sample aliquot.

The water-soluble Ca^{2+} and bicarbonate (HCO_3^-) ions were determined on a 100-g soil aliquot to which 500 cm^3 of deionised water were added and stirred for 2 h; after filtering the ions were measured by atomic absorption spectrometry (AAS).

The exchangeable Ca^{2+} and Mg^{2+} cations and CEC were measured on a 5-g soil sample aliquot and the addition of 25 cm^3 CH3COONa solution in a 250 cm^3 conical flask; the mixture was stirred for 10 min at 170 revs/min; after stirring, it was centrifuged at 2700 revs/min for 10 min and the supernatant solution was transferred to a 50 cm^3 beaker; the aforementioned procedure was repeated one more time; the solution was then filtered through a

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Whatman 40 micron-size filter in a 50 cm^3 volumetric flask and made up by the addition of sodium acetate (CH_3COONa), and measured by AAS.

The pH was measured by a calibrated pH-meter on a soil paste made with a 100-g soil sample aliquot in a 250 cm^3 beaker, and the addition of deionised water until saturation.

The overall precision estimated on replicate analyses for all measured parameters is better than $\pm 10\%$ at the 95% confidence level.

3.3. Data processing

The analytical data were processed by Golden Software's Surfer and Grapher programs, and software programs developed by the Division of Geochemistry and Environment of the Institute of Geology and Mineral Exploration (Vassiliades, 2010; Vryniotis, 2010). Many statistical parameters were extracted and graphics plotted, e.g., histograms, cumulative-probability distribution curves and frequency charts. After studying all these graphics, and especially the histograms, the geochemical data were split into populations for plotting the spatial distribution maps by Surfer version 8 (http://www.goldensoftware.com/products/surfer).

4. Results and discussion

4.1. Environmental soil chemistry

The dissolution of limestone occurs through a series of physicochemical processes in the presence of the aerial, aqueous and solid phases (Bögli, 1980), and supplies soil with nutrients, which are very important for the improvement of its quality, physicochemical equilibrium and, of course, for the health of soil organisms, and sustainable development of the ecosystem. The dissolution of limestone ($CaCO_3$) can be represented by the following simplified chemical reaction: $CaCO_3 + CO_2 + H_2O \leftrightarrow Ca(HCO_3)_2$, where Ca^{2+}, HCO_3^- and OH^- ions are released. The karstification process introduces $CaCO_3$ in soil, which in the Hellenic soil can exceed at times 70% of its total weight. This is due to the widespread occurrence of limestone (Papadopoulou-Vrynioti, 1999).

Calcium is one of the most important cations in soil. It is found in the form of salts, mainly $CaCO_3$. Plants absorb calcium in the form of Ca^{2+} ions from the soil solution, and its presence assists the absorption of other elements, as well as the synthesis of various proteins (Kabata-Pendias and Pendias, 1984, 2001; Alloway, 1997; Kabata-Pendias and Mukherjee, 2007). It is one of the most important elements in soil when it comes to the healthy growth of plants, and is the main regulator of their behaviour. The presence of calcium in the carbonate form acts as a regulator of pH, the variation of which is between 6.5 and 7.5, the most favourable range for the absorption of major elements by plants (Alexiadis, 1980).

Soil texture, water permeability and storage capacity, are natural properties of soil that are affected by the absorbed exchangeable cations (Kabata-Pendias and Pendias, 1984, 2001). The abundance of exchangeable calcium affects these parameters in a positive way. In Hellas, the widespread distribution of limestone formations, in comparison with other lithologies, has a major effect on the quality of soil and the nourishment of plants.

4.2. $CaCO_3$ content in soil

The $CaCO_3$ values vary from 0.05 to 59%, with a median of 0.9% (Table 1; Fig. 4). The spatial distribution of calcium carbonate (Fig. 4) indicates that a great part of soil (over 60%) has a $CaCO_3$ concentration below 1.5% and, therefore, it is poor in $CaCO_3$. The highest values of $CaCO_3$ (>4.09%) occur at the NE parts of the study area, which are close to the foothills of the Mitsikeli mountain range, and around the main channel of the Ioannina drainage basin. According to Alexiadis (1980) the soil in this area, with a content of $CaCO_3$ > 4.09%, is sufficiently enriched in $CaCO_3$.

4.3. Water extractable Ca^{2+} cations

Calcium is very widely spread in the Earth's upper continental crust, with an estimated abundance of 25,657 mg/kg (Rudnick and Gao, 2003), and by extension in soil; in European residual topsoil total Ca varies from 185 to 340,912 mg/kg, with a median of 6590 mg/kg (De Vos et al., 2006; Salminen et al., 2005), while in agricultural and grazing land soil the total Ca varies from 86 to 378,148 mg/kg (median 8494 mg/kg), and from 50 to 362,803 mg/kg (median 7662 mg/kg), respectively (Reimann et al., 2014c). It is of great value in life support systems, and this can be easily realised as Ca is the main constituent of our bones in the form of $Ca_3(PO_4)_2$ (De Vos et al., 2006; Polyzopoulos, 1976; Reimann et al., 2014a, 2014b, 2014c). Plants, take up calcium in the form of Ca^{2+} cations from the soil solution. The presence of calcium in soil, especially in the carbonate form, is the major regulator of its pH.

In the study area, the concentration of water extractable Ca^{2+} varies from 13.6 to 394 mg/kg, with a median of 87.4 mg/kg of dry sample (Table 1; Fig. 5). Such concentrations are not at satisfactory levels, when the surrounding limestone mountainous region is considered.

The highest values of water extractable Ca^{2+} occur in a NW–SE trending zone near to the foothills of Mitsikeli mountain, with the highest concentrations to the north of Perama. The effects of erosion, transportation and deposition of calcium carbonate detritus from the Mitsikeli mountain through which calcium is transported, are quite evident on this map (Fig. 5), as well as the other maps that will be described below.

4.4. Bicarbonate (HCO_3^-)

Bicarbonate anions are of great importance, since their interaction with calcium or magnesium, forms insoluble compounds with the simultaneous emission of CO_2. The concentration of bicarbonates in the soil samples of the study area varies from 31.9 to 690 mg/kg of dry sample, with a median of 123 mg/kg of dry sample (Table 1; Fig. 6). These values are considered relatively low.

Similar to the extractable Ca^{2+} spatial distribution, the highest HCO_3^- concentrations are observed in a NW–SE trending zone close to the foothills of Mitsikeli mountain.

4.5. Cation Exchange Capacity (CEC)

Clay minerals (inorganic colloids) and humus have the ability to adsorb various cations at exchangeable sites at a given pH. These cations have the ability to be exchanged by other ions present in the aqueous soil solution. The nutrients that are uptaken by plants are retained by soil at such exchangeable sites. This cation exchange ability of soil is of great importance for the physicochemical processes, as well as the nourishment of plants. The quantity of exchangeable cations has an effect on the texture, water permeability, water storing capacity of soil and nutrient retention capacity (Polyzopoulos, 1976).

In the study area, CEC varies from 77 to 409 meq/kg of dry sample, with a median of 175 meq/kg (Table 1; Fig. 7). Since the optimum CEC of productive soil is between 150 and 260 meq/kg, these values are at a satisfactory level to characterise the soil of the Ioannina basin as productive. The three highest classes, with CEC values between 210 and 410 meq/kg, form a NW–SE trending zone close to foothills of the Mitsikeli mountain. There appears to be a good spatial correlation with water extractable Ca^{2+} and $CaCO_3$ (Figs. 4 & 5).

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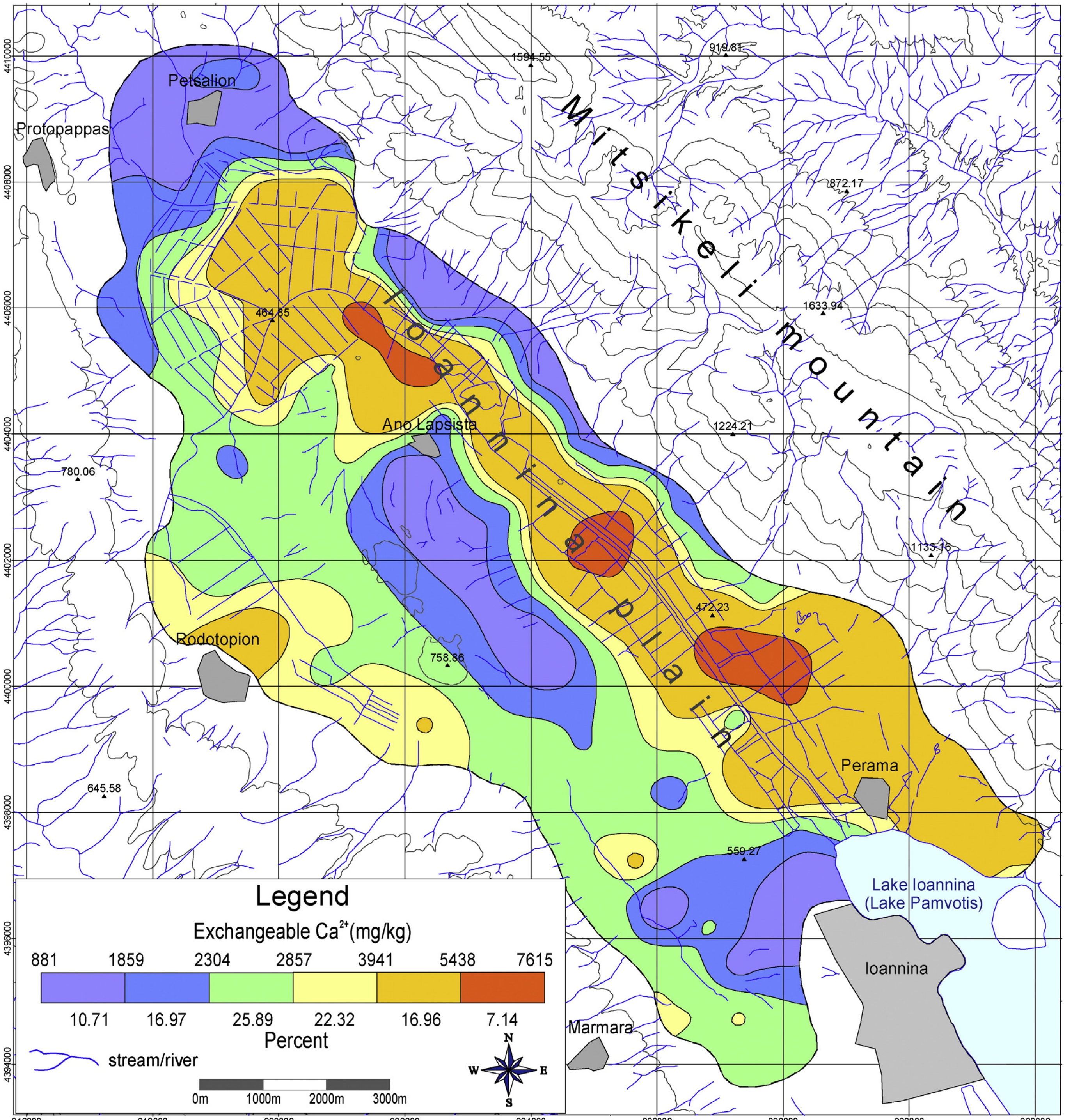

Fig. 8. Map showing the spatial distribution of exchangeable Ca^{2+} content in surface soil, Ioannina plain, Hellas.

4.6. Exchangeable cations of Ca^{2+} and Mg^{2+}

The exchangeable calcium is considered to be one of the most important cations adsorbed by soil, because it plays a major role in soil quality, control of its physico-chemical properties and nourishment of plants. Soil containing calcium carbonate and magnesium, rarely manifests phenomena of deficiency in the supply of cations and adverse physicochemical effects on plants. In general, a Ca:Mg ratio varying from 5:1 to 1:1 favours good soil productivity. In Hellas, since there is an abundance of limestone formations, Ca^{2+} is the dominant among all other exchangeable cations, and it essentially controls soil quality.

In the study area, the exchangeable calcium concentration varies between 882 and 7615 mg/kg of dry soil, with a median of 2786 mg/kg (Table 1; Fig. 8), whereas the exchangeable magnesium concentration is between 67 and 1290 mg/kg of dry soil, with a median of 172 mg/kg (Table 1; Fig. 9). It can be concluded that the soil in the Ioannina basin is generally enriched in exchangeable calcium, whereas it is poor to satisfactory at certain cases with respect to exchangeable magnesium, although this

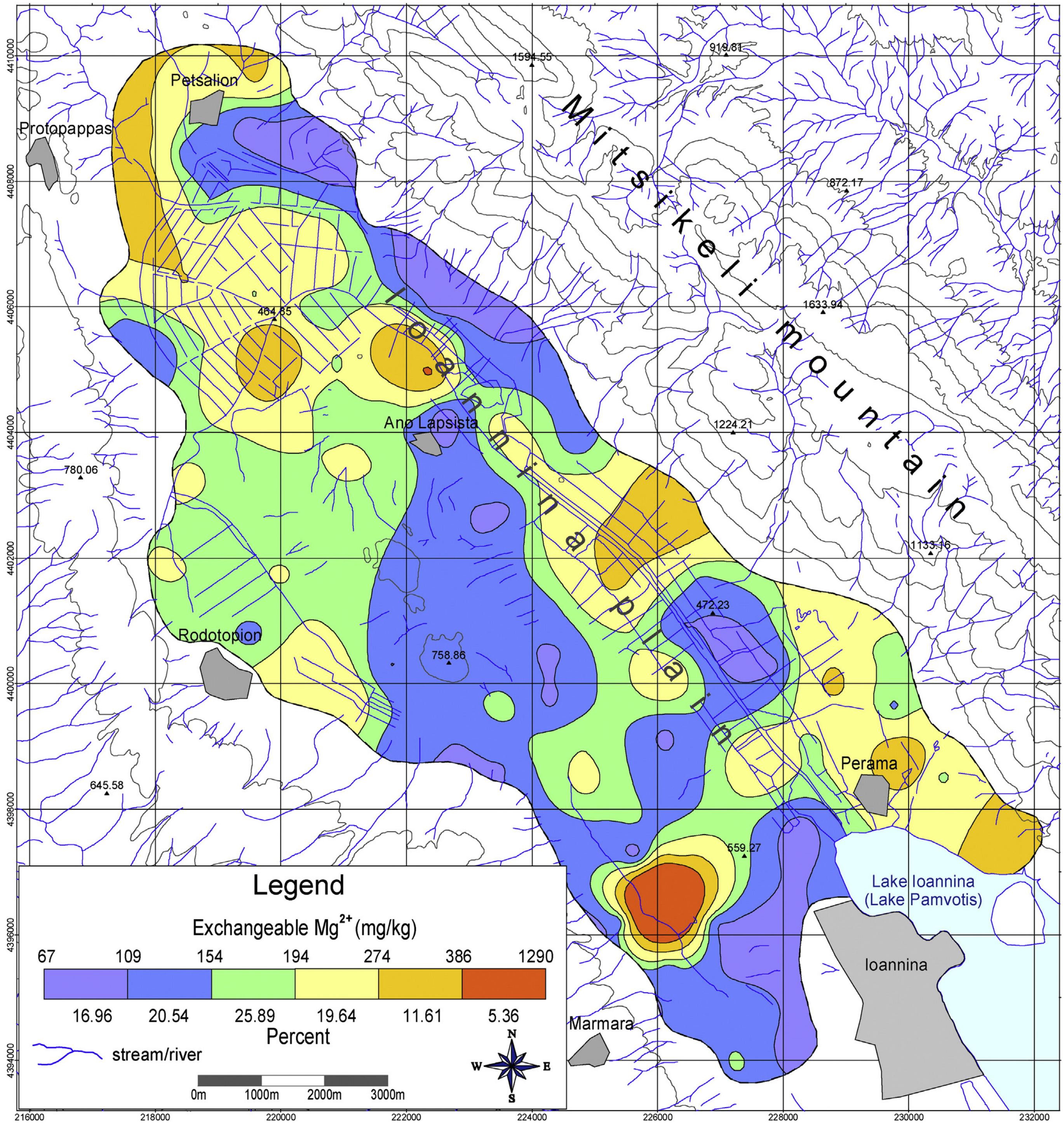

Fig. 9. Map showing the spatial distribution of exchangeable Mg^{2+} content in surface soil, Ioannina plain, Hellas.

does not pose a serious problem in soil productivity, since the lower limit of Mg^{2+} concentration is set at 24.3 mg/kg of dry soil (Alexiadis, 1980).

There is a very good spatial correlation between CEC and exchangeable Ca^{2+} and Mg^{2+}, especially between CEC and Ca^{2+}, and their highest values occur in the same NW–SE trending zone near to the foothills of Mitsikeli mountain.

4.7. pH

A significant key property of soil for the mobility of elements is the pH, and it is an indicator of the general environmental conditions of an area. Soil solutions are characterised as acidic when the pH <7, and alkaline when the pH is >7. When the pH is between 6.5 and 7.3 the absorption of the major elements by plants is favoured (Kabata-Pendias and Pendias, 2001). High concentrations of $CaCO_3$ make soil more alkaline, with the pH varying around 8. At the same time, $CaCO_3$ solubility is greatly dependent on soil pH, and it is actually inversely proportional to it. $CaCO_3$ is rarely found in soil with a pH value lower than 7.

The pH of the study area varies between 4.95 and 7.75, with a median of 6.62 (Table 1; Fig. 10), thus, the soil ranges from acidic to slightly alkaline (U.S. Soil Survey Division Staff, 1993).

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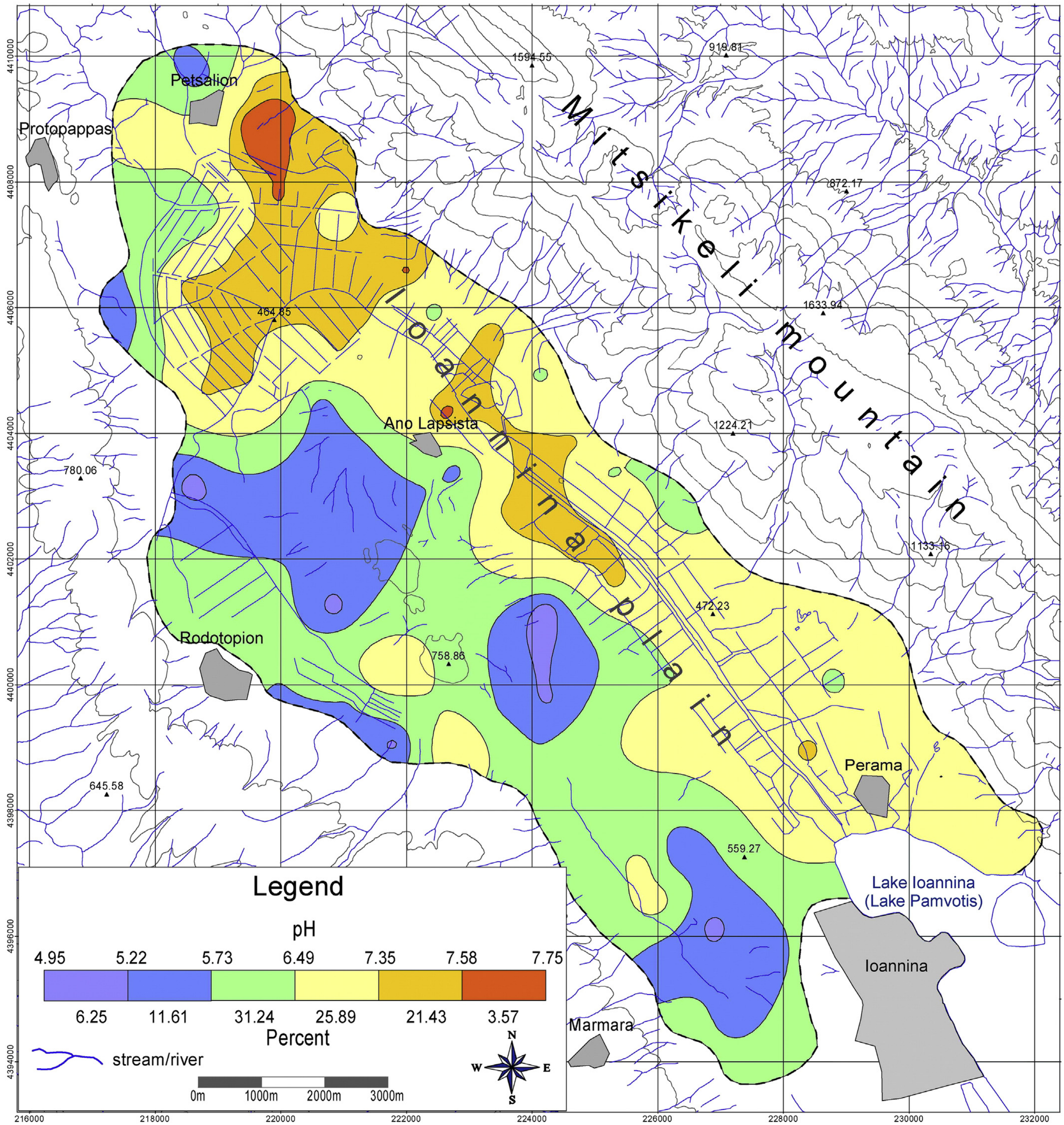

Fig. 10. Map showing the spatial distribution of pH values in soil, Ioannina plain, Hellas.

Fig. 10 shows that the highest soil pH values between 6.5 and 7.75, near-neutral to slightly alkaline soil, occur along the same NW–SE trending zone near to the foothills of Mitsikeli mountain, which is followed by the other parameters, i.e., the concentrations of $CaCO_3$ water-soluble Ca^{2+}, bicarbonate (HCO_3^-), exchangeable cations (Ca^{2+}, Mg^{2+}), and cation exchange capacity.

5. Conclusions

In the study area, the methodology used led us to the following conclusions:

(1) The soil in the NW plain area of the Ioannina basin, covering approximately 60% of the study area, is slightly to moderately enriched in $CaCO_3$. About 23.20% of the sampled soil is adequately enriched in $CaCO_3$ and is suitable for agriculture.
(2) The water extractable Ca^{2+} ions in soil, with a median around 87.4 mg/kg of dry sample, is considered to be at a non-satisfactory level as a soil quality parameter for agricultural use.
(3) The bicarbonate concentration (HCO_3^-) with a median value of 123 mg/kg of dry soil is generally low.
(4) The Cation Exchange Capacity (CEC) with a median of 175 meq/kg is at satisfactory level for productive agricultural soil. There is also

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a very good spatial correlation between CEC and exchangeable Ca^{2+} cations.

(5) The soil is generally enriched in exchangeable Ca^{2+} with a median of 2786 mg/kg.

(6) In general, the soil of the study area with a pH between 4.95 and 7.75 is characterised as acidic to slightly alkaline, and certain areas with a higher pH, ranging from 6.5 to 7.5, are classified as near-neutral and, in general, this is the optimum range for absorption of major elements by plants.

(7) The highest values of $CaCO_3$, water extractable Ca^{2+}, bicarbonate (HCO_3^-), CEC, exchangeable Ca^{2+} cations, and pH are found in a NW–SE trending zone near to the foothills of Mitsikeli mountain. There occurrence in this zone is due to the inclination of the western mountain slopes, up to 30°, which are cross-cut by numerous streams, with a consequent increase in their transport capacity and supply of carbonate sediments to the eastern part of the Ioannina plain.

According to the results of this study, even though the base of the karstic basin of Ioannina is covered with non-soluble alluvial material, derived mainly from the flysch formations of the wider area, the soil near to the foothills of Mitsikeli mountain is enriched in $CaCO_3$, water extractable Ca^{2+} cations, bicarbonate (HCO_3^-) and exchangeable Ca^{2+} cations, with a fairly good CEC values, and near-neutral pH values.

The NW–SE trending zone near to the foothills of Mitsikeli mountain is enriched in the detritus derived from the weathering of limestone, and subsequent fluvial erosion and deposition of the limestone detritus through dissolution supply soil with the necessary nutrients to improve its quality, resulting in the development of good quality soil for agricultural use and consequently in the development of favourable ecosystem. This is a karst ecosystem, because it is mainly developed by processes that occur in the karstic rocks.

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