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Article

Water–Rock Interactions across Volcanic Aquifers of the Lece Andesite Complex (Southern Serbia): Geochemistry and Environmental Impact

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Abstract: The study of aquifers of the Lece andesite complex (LAC) and its surroundings yielded a new procedural stepwise analysis that allowed the assessment of the origin of elements, particularly in areas affected by both anthropogenic and natural influences. The methodology uses the mineralogical composition of the rocks, including the elements available in rocks and groundwater. This study analyzes the element ratios B/Cl^-, Na^+/Ca^{2+}, Ca^{2+}/Mg^{2+}, HCO_3^-/Cl^-, and $Na^+/Na^+ + Cl^-$; the correlations are coupled with a statistical analysis. In addition to reevaluating the already published water content, we provide an important new dataset. The results show that the main source of the water contamination with the elements B, F, U, As, Cu, Fe, Zn, Co, and Ni is the processes occurring at the contact between the groundwaters and non-altered/altered (propylitized) andesite rocks. This is also observed in the waters extracted from crystalline schists. The results may help develop an efficient use and assessment of the qualitative water potential of the LAC reservoirs. Similarly, the results highlight the applicability of the groundwaters, facilitating their regional research and use, further encouraging new initiatives for the preservation and protection of human and animal health.

Keywords: (thermo)mineral aquifers; andesites; Djavolja varoš; Fluor; boron; trace elements; natural pollution; enrichment factor

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1. Introduction

The quality of water and level of contamination by toxic elements or potentially toxic elements (PTEs) depend on possible anthropogenic and natural sources. Many human activities such as industrial activities, agricultural activities, mining, traffic, and urbanization/urban land use; wastewater leakage and waste material infiltration processes; and industrial influence may contaminate water with toxic/potentially toxic elements: Al, As, Cd, Co, Cr, Cu, Fe, Mn, Hg, Ni, Pb, and Zn. Besides the listed sources, thermal waters connected to power plants can be a source of pollution with the element Fluor, whereas eventual pollution with boron may originate from a variety of laundry products [1,2]. The vulnerability of a groundwater aquifer and its pollution risks in the anthropogenic environment may increase due to natural conditions (i.e., geological factors, suitable hydrogeological conditions, and products of water–rock interaction).

Water–rock interaction often triggers both congruent and incongruent dissolution processes that cause partial solubilization of primary minerals, eventually enhancing the formation of secondary minerals [3]. Accordingly, the chemical composition of groundwater is influenced by the geological structure and available minerals embedded into the surrounding rocks, as well as conditions such as the presence of gas phases, fluid pH, and subsurface temperature. In addition to geochemical properties, the geochemistry of groundwater is strongly dependent on subsurface hydrogeological conditions, in particular the velocity of the subsurface water flow, the type of faults and fractures, depth of reservoirs. Also, it depends on the factors that control the water inflow from the near-surface media [4,5]. Geochemical reactions such as dissolution/precipitation of solids, cation exchange/adsorption, and complexation can frequently provide a significant contribution to the variation in the elemental concentrations in the groundwaters.

The investigated area is the Lece andesite complex (hereinafter LAC), which is emplaced within the western realm of the gneissic basement unit or the Serbo-Macedonian Unit. The LAC occurs along the Tethyan active margin, and the Jurassic–Cretaceous members belong to the composite Vardar Zone (southern Serbia) [6–8]. Besides exposing the unaltered volcanic-type system (andesite) and its pyroclastic equivalents, the massif includes segments of hydrothermally altered (mostly propylitized rocks). The LAC is characterized by several registered, currently explored hydrothermal ore-bearing mining areas: Djavolja Varoš, Lece, Tulare, and Sijarinska Banja. These mineralizations are associated with several generations of veins: pyrite–quartz–pyrite–quartz–carbonate secondary pyrite–chalcopyrite veins and brown carbonate veins [9]. These occurrences may represent the source of the contamination of the groundwaters with toxic elements. On the other hand, the LAC massif contains the area that belongs to the National Park Radan, which is inhabited by rural households with individual farming activities. In addition, the Prolom Banja, Tulare, and Sijarinska Banja spas are the prominent spas exploited in the investigated area [10]. Therefore, possible sources of anthropogenic contamination, i.e., potentially risky activities, are associated with agricultural (farming) and ongoing tourism.

The origin and geochemistry of the groundwaters occurring across the Serbo-Macedonian Unit and surrounding area were the focal points of several reports [5,11–18]. The analyzed water samples have exceeded the concentrations recorded for the elements B, F, Li, Rb, and Sr, as well as for REEs, including Th and U. In some areas (Sijarinska Banja, Tulare, Prolom), the activity concentrations (BqL^{-1}) of ^{222}Rn and ^{226}Ra are documented [17]. The highest concentration of Rn is depicted in the thermal groundwater samples collected from Sijarinska Banja and Viča, Suva Česma, marking an eastern extension of the Tulare fault. This water-bearing regional fault structure passes near the Banjska Reka and the Toplica fault zone. Water resource management for volcanic complexes is a challenge with increasing water demands (for irrigation, drinking water, etc.) or overexploitation of rivers or aquifers. Vitecoqu et al. [18] suggested that a multidisciplinary study of the waters in volcanic (andesitic-type) rocks should be provided for better characterization of the hydrogeological functioning of aquifers and to better evaluate groundwater resources. That can be very important in areas with metallic mineralizations occurring in hydrothermally altered andesites. Water–rock interaction and the water composition in and around volcanic aquifers, in particular in andesitic systems, have been the main topic of a number of studies [3,19–23]. However, this approach is often neglected. In the previous study [24], some issues revolving around the Lece andesitic complex are addressed; in the present study, we continue with these investigations.

In this paper, we provide an update on the chemical content of the groundwaters formed in the volcanic aquifers of the Lece complex (LAC) and its immediate surroundings. In addition to the reevaluation of the already published water content, we provide an important new set of hydrogeochemistry data (collected from the boreholes and springs). The chemical composition, in particular that of subsurface geothermal waters, has often been the crucial factor for a definition of the origin, usage, balneological valorization, and geothermal potential [5]. In the initial stage of the study, constraints on the tectonic and hydrogeological setting of the volcanic aquifers belonging to the LAC are provided [24]. By following up on this recent composite LAC study, here we present a new conceptual model, allowing groundwater observations, further defining the sources of the elements that can potentially have an environmental impact. This study provides a kind of procedural stepwise analysis that can be used in studies related to similar groundwater areas potentially affected by both anthropogenic and natural influences (contamination with toxic elements). To define and separate the anthropogenic impact, it is very important to put constraints on the ongoing natural processes, including the sources of the elements recorded in the fluids. The results are a function of the following assumptions: (i) Many elements are hosted in minerals of the volcanic rocks and can be emitted in the water or fluid-type environment accounting for the protracted water–rock interaction. We also considered (ii) that the presence of higher concentrations of these leached elements from the altered rock could impose the risks of contamination of the local environment. Accordingly, the objective of this hydrogeochemical LAC study is to put constraints that are useful in defining the origin of the toxic elements on the new methodology and to differentiate the anthropogenic sources of the contamination from natural sources in the areas where both sources exist. That includes (1) the application of available hydrogeological and mineralogical constraints, for which the main purpose is to identify the nature and the intensity of a water–rock interaction, and (2) the analysis of the processes of chemical alteration of rock-related minerals and (iii) the concentrations of elements in the groundwater (main components (cations/anions), minor and trace elements). Moreover, we put constraints on (3) the possible pollution effects induced the by presence of different concentrations of the toxic elements in the regional reservoirs (hydrogeochemistry and the level of potential contamination). That further allows the classification of the waters that belong to a group of those that are "impossible to use". We also provide (4) observations on the potentials of the water resources associated with the LAC, extrapolating an action plan that encourages the preservation of the local natural ecosystem.

2. Geological and Hydrogeological Setting of the LAC Complex and Surroundings

The Lece-Radan calc-alkaline ore-bearing volcanic complex or Lece district [8,25,26] is located within a complex tectonic assembly of southern Serbia (Figure 1a). A number of volcanic bodies crosscut the area of Central Serbia, in which plutonic rocks belong to considerably large magmatic provinces of the Cenozoic age [27–29]. The Lece-Radan magmatic assemblage is emplaced into the former lithospheric-scale crustal suture, comprising the Vardar Zone s.s. and Serbo-Macedonian Unit [6,7]. A number of NNW–SSE fault lineaments mark a segment of former lithospheric-scale contact [30,31], whereas a number of the post-accretionary or younger E–W-directed Neogene faults crosscut the investigated area of the LAC [32]. The LAC rock assembly comprises the gneiss–marble-bearing crystalline Serbo-Macedonian Unit. The East Vardar Zone comprises Jurassic ophiolites and mélanges, overlaying Tithonian limestone [33]. Mesozoic succession includes the Lower Cretaceous "paraflysch" [34] overlain by the Upper Cretaceous turbidities of the Sava Suture Zone [35]. These rocks are largely pierced by the Lece-Radan magmatic complex (LAC), which is of the Oligo-Miocene age [36–38]. The widespread Miocene relaxation of the thickened lithosphere permitted the intrusion of a large number of magmatic bodies. The post-orogenic extensional stage allowed the inception of a number of extensional faults, which further contributed to the formation of the metamorphic and magmatic-type (thermal) aquifers.

From the hydrogeological point of view, the LAC exhumed in southern Serbia belongs to water-permeable solid rocks with a number of fractured-type reservoirs [39,40]. In this research, two types of aquifers are observed. Shallow aquifers, formed in the near-surface zone of fractured rocks, fill in and drain out reservoirs by gravitational forces. These fluid-bearing pools are positioned above the level of the surface flows (the level of draining bases), and they drain throughout the sources that are occurring most often at local barriers, whether they are of lithological or tectonic origin. For example, aquifers can be in contact with volcanic rocks, crystalline schists, or unaltered rocks with hydrothermally altered volcanics [40]. Another type of aquifer (aquifer controlled by tectonically active faults, underlying shallow near-surface levels, positioned deep inside and along the perimeter of the massif) is under stable hydraulic pressure [5,11–16,24,39,40].

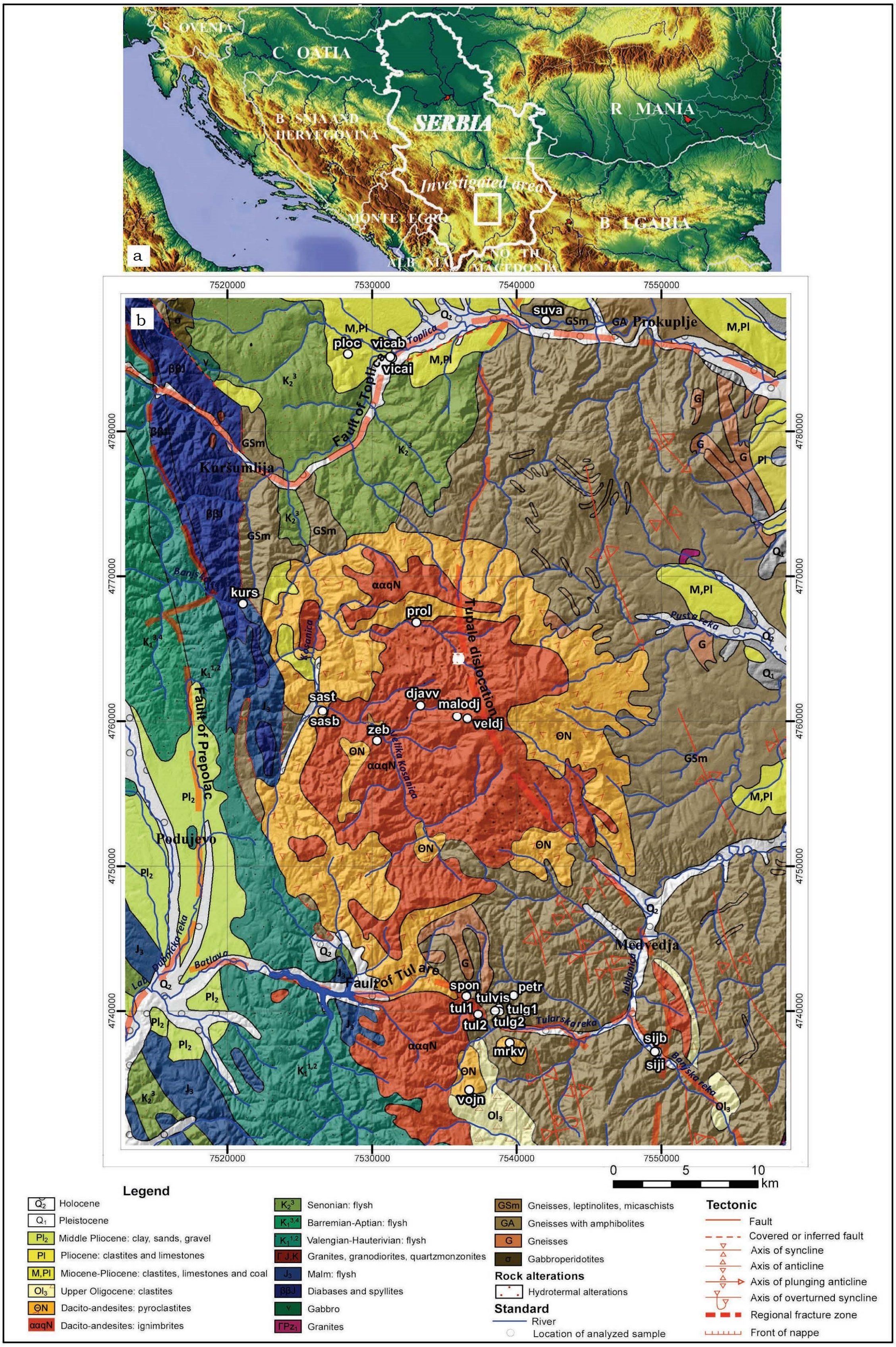
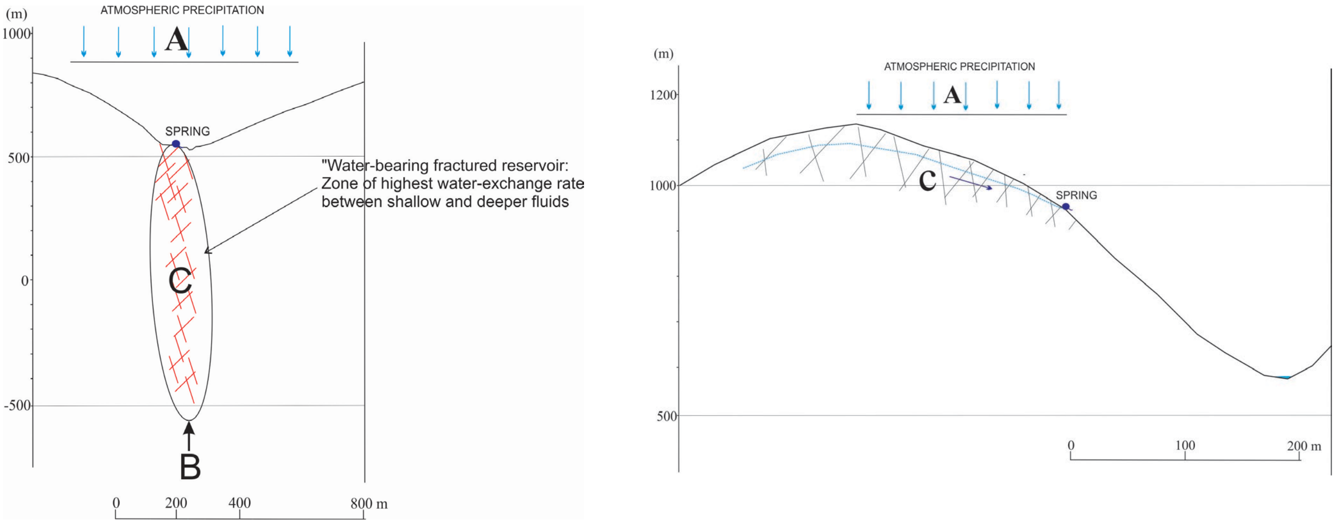


Figure 1. (**a**) The position of the LAC in Serbia; (**b**) geological map of the LAC massif with localities (modified after Geological Map of SFRY, 1:100,000) [41].

In such circumstances, the composition of investigated groundwaters that belong to the investigated LAC could be formed in the two following scenarios (Figure 2):

(1) In aquifers that are controlled by deep tectonic structures, a certain amount of elements (such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} or minor/trace elements: F, B, Fe, Li, Rb, etc.) are transported from deeper reservoir sections after the process of decomposition of minerals from the water-bearing rocks or reservoirs (Figure 2a, labeled as "C"). The processes of decomposition of minerals in the aquifer are stimulated primarily by the presence of gases CO_2, H_2S, etc., that migrate from deeper crustal levels up towards more shallow zones (Figure 2a, labeled as "B").

(2) In shallow aquifers, a certain amount of elements may arrive after a downward percolation of atmospheric water together with gases O_2, CO_2, He, Ne, Ar, etc. (Figure 2b, marked as "A") [42]. Gaseous components, carried by atmospheric water, can interact with minerals constituting the reservoir rocks (Figure 2b, labeled as "C"). Thus, further, these aggressive components (O_2, CO_2, newly formed H_3O^{+}, etc.) in most shallow aquifers often lead to the oxidation processes of sulfides, hydrolysis of aluminosilicate/silicates, carbonates, etc. In deeper aquifers, however, the aggressive components of atmospheric water are not present (depleted already in the shallower areas, long before the waters reach deep-settled reservoirs). The finite chemical composition of the groundwaters, distributed across all aquifers, is associated spatially with the reservoirs themselves (Figure 2a,b labeled as "C").



(**a**) (**b**)

Figure 2. The hydrochemical model of groundwater formation: (**a**) in aquifers with deep water flow (fault zone) and (**b**) in aquifers associated with near-surface fractures.

Therefore, the mineral composition of investigated water-bearing reservoir rocks can represent the most relevant source of elements. The processes between exposed (contact) minerals and circulating groundwaters (in the aquatic subsurface environment) control the final content of elements in the fluid. Accordingly, the initial stage of this composite study is a definition of the lithological assemblages distributed across the investigated subsurface reservoir areas and their mineralogical composition (particularly those being in contact with groundwaters). In such a manner, it is possible to explain the processes of the distribution of the elements in the LAC subsurface water-bearing environments.

Lithology, Mineralogy, and Geochemistry of Rocks and Associated Aquifers

In most of the external LAC realm, the high-grade crystalline schists (gneiss) of the Serbo-Macedonian Unit abut the LAC volcanic body (Figure 1b). The emplacement of the magmatic body along the former compressional suture assembly and a successor regional extension yielded a complex geological framework, which allowed the formation of a large number of aquifers. The LAC comprises an unaltered (central) segment of volcanic rocks of the Miocene age, originating together with its pyroclastic equivalents. The main minerals embedded into the investigated volcanic rocks are plagioclases (andesine), hornblende, and augite [43,44]. Biotite and chlorite are subordinately presented, and accessory minerals are apatite, magnetite, and zircon (Table 1). There are a number of crystalline gneiss varieties; the most common are the fine-grained biotitic gneisses, leptinolites, and mica-schists, as well as leukogneiss, amphiboles, and amphibolites [36–38,45,46]. The main minerals of lithological units belonging to the Serbo-Macedonian Unit are quartz, plagioclase (oligoclase-andesine), biotite, muscovite, hornblende, feldspar, apatite, sphene, garnet, disten, staurolite, rutile, zircon, sphen, sillimanite. The LAC massif also includes a number the rock segments that are hydrothermally altered and propylitzed, thus involving a wide range of mineralogical spectra. The presence of sulfides is typical for the propylitization zones, pyrite, and chalcopyrite, and sphalerite, galenite, marcasite, enargite, tetrahedrite, pyrite, chalcopyrite, gold, antimonite, covelin, hematite, ankerite, siderite, and quartz are documented in hydrothermally altered rocks (Table 1).

Table 1. Mineral composition of volcanic complex of Lece and main, minor, and trace elements [38–40,47–49]. Legend: Na-group of alkaline elements having significant positive correlation; Fe group of alkaline, siderophile, and chalcophile elements having a significant positive correlation; $\boxed{\mathbf{F}}$—typical volcanic elements positively correlated with a number of elements.

Minerals		**Composition**	**Major and Trace Elements**	**Goldshmit Classification of the Elements**
		Minerals of Vulcano Complex		
Main	Plagioclase	$Na\text{-}CaAlSi_3O_8$	K, Ba, Sr, Fe	Lithophile: Li, **F, B**, Na, Mg, Al, Si, P, Cl, K, Ca, Ti, **V**, Cr, Mn, Br, Rb, Sr, Zr, Y, Nb, Cs, Ba, Hf, Th, U Chalcophile: S, Cu, Zn, Ga, Ge, As, Se, Ag, Cd, In, Sb, Hg, Tl, Pb, Bi Siderophile: Fe, Co, Ni, Mo, Pd, Ir, Au
	Hornblende	$NaCa_2(MgFeAl)_5SiAl_8O_{22}(OH)_2$	**F**, **Cl**, REE	
	Augite	$Ca(MgFeAl)(SiAl)_2O_6$	Ti, Mn, Na	
Minor	Biothite	$K(MgFe)_3(AlSi_3O_{10})(OH)_2$	Na, Rb, Cs, **F**, Nb	
	Chlorite	$(MgFeAl)_6(AlSi)_4O_{10}(OH)_8$	Ni, Cr, Li	
Accesorry	Apatite	$Ca_5(PO_4)_3(\mathbf{FCl}OH)_2$	Fe, Sr, Al, U, Th, REE, W, Nb	
	Magnetite	$Fe_2O_3\ (FeFe_2O_4)$	Mg, Mn, Al, Ti, **V**, Cr	
	Zirkon	$ZrSiO_4$	Hf, Th, U, Y, REE	
Sulphides (propilitized zone)	Pyrite	FeS_2	Co, Ni, Au, Ag, Cu, Sb, Tl, As	
	Chalcopyrite	$CuFeS_2$	Ag, Au, As, Bi, Ge, Ga	
Minerals of ore mineralization and hydrothermal alterated rocks	Sphalerite	$ZnFeS$	Cd, In, Ga, Hg	
	Galena	PbS	Ag, Cu, Bi, Fe, Sb, As, Mo, Se	
	Marcasite	FeS_2	Ni, Co, Bi, Cu, As, Sb, Tl	
	Enargit	Cu_3AsS_4	Sb, Fe, Zn, Pb, Ag	
	Tetrahedrite	$Cu_{12}Sb_4S_{13}$	As, Fe, Ag, Hg	
	Pyrite	FeS_2	Co, Ni, Au, Ag, Cu, Sb, Tl, As, Se	
	Chalcoopyrite	$CuFeS_2$	Ag, Au, As, Bi, Ge, Ga	
	Gold	Au	Fe, Cu, Ag, Pd, Ir, Bi	
	Antimonite	Sb_2S_3	As, Pb, Ag, Cu, Au	
	Covelin	CuS	Fe, Se, Ag, Pb	
	Hematite	Fe_2O_3	Ti, Al	
	Ankerite	$Ca(MgFe)CO_3$	Mn	
	Siderite	$FeCO_3$	Mn, Ca, Mg, Zn	
	Quartz	SiO_2	Al, Na, Mg, Ti	
	Tourmaline	$Na(Mg,Ca,Fe)Al_6(BO_3)_3Si_6O_{18}(OH,F)_4$	Mn, K, Ti, Li, **F, B**	

Table 1. *Cont.*

Minerals		Composition	Major and Trace Elements	Goldshmit Classification of the Elements
		Minerals of cristaline shists		
Main	Quartz	SiO_2	Al, Na, Mg, Ti	Lithophile: Li, **F, B**, Na, Mg, Al, Si, P, Cl, K, Ca, Ti, Cr, Mn, Rb, Sr, Zr, Nb, Cs, Ba, Hf, Ta, W, Th, U Chalcophile Pb Siderophile: Fe
	Plagioclase	$Na\text{-}CaAlSi_3O_8$	K, Ba, Sr, Fe	
	Biothite	$K(MgFe)_3(AlSi_3O_{10})(OH)_2$	Na, Rb, Cs, F	
	Muscovite	$KAl_3Si_3O_{10}(OH,F)_2$	Na, Mg, Fe, Li, Cr	
Minor	Hornblende	$NaCa_2(MgFeAl)_5Si\,Al_8O_{22}(OH)_2$	**F, Cl**, REE	
	Microcline	$KAlSi_3O_8$	Cs, Li, Rb, Pb, Na . . .	
	Apatite	$Ca_5(PO_4)_3(FClOH)_2$	Fe, Sr, Al, U, Th, REE	
	Sphene	$CaTiSiO_5$	Fe, Nb, Ta, TR . . .	
	Distended	Al_2SiO_5	Fe, Cr, Na, K	
	Staurolite	$FeAl_5Si_2O_{12}(OH)$	Mg, Mn	
	Rutile	TiO_2	Fe, Nb, Ta, W, Sn. . .	
	Zircon	$ZrSiO_4$	Hf, Th, U, REE	
	Silimanit	Al_2SiO_5	Fe, Al, Si	
	Tourmaline	$Na(Mg,Ca,Fe)Al_6(BO_3)_3Si_6O_{18}(OH,F)_4$	Mn, K, Ti, Li, **B, F**	
		Minerals of marble in the cristaline shists		
Main	Kalcit	$CaCO_3$	Ni, Mn, Co, Fe, Sr	Lithophile: Li, **F, B**, Na, Mg, Al, Si, Cl, K, Ca, Ti, **V**, Cr, Mn, Rb, Sr, Nb, Cs, Ba, Ta Chalcophile: Zn, Pb Siderophile: Fe, Co, Ni
	Dolomit	$CaMg(CO_3)_2$	Mn, Co, Zn, Sr	
	Kvarc	SiO_2	Al, Na, Mg, Ti	
Minor	Mikroklin	$KAlSi_3O_8$	Cs, Li, Rb, Pb, Na	
	Plagioklas	$Na\text{-}CaAlSi_3O_8$	K, Ba, Sr, Fe	
	Amphiiboles	$(Na, K\ ili\ Ca)_{0–1}(Ca, Fe, Mg, Mn, Li\ ili\ Na)_2(Li, Cr, Fe, Mn\ ili\ Ti)_5(Si, Al\ ili\ Ti)_8O_{22}(OH,F,Cl)_2$	Mn, K, Na, Cr, Li, Fe,	
	Sphene	$CaTiSiO_5$	Fe, Nb, Ta, REE. . .	
	Coysit	$CaAl_3Si_3O_{12}(OH)$	Fe, **V**	
	Diopside	$CaMgSi_2O_6$	Al, Fe, Cr, Mn, **V**	
	Chlorite	$(MgFeAl)_6(AlSi)_4O_{10}(OH)_8$	Ni, Cr, Li	
	Tourmaline	$Na(Mg,Ca,Fe)Al_6(BO_3)_3Si_6O_{18}(OH,F)_4$	Mn, K, Ti, Li, **F, B**	

The complex regional geology of the investigated area with the localities of the groundwater samples is depicted in Figure 1b. A number of faults are presented as well. As can be seen from Figure 1b, the investigated area contains the exposed intermediate or basic-type igneous rocks, which are the principal reservoir and the groundwater sampling locations: Tul1, Tul2, Prol, Zeb, Malodj, Veldj, Sast, Sasb, Vojn, and Mrkv (dacito-andesites/pyroclastics); Djavv (altered andesites); Kurs (diabase/spilites). Siji, Sijb, Petr, Tulg1, Tulg2, Tulvis, Spon (gneiss/amphiboles), and Suva (gneisses/leptinolite/mica schist) are placed in the area of metamorphic rocks, whereas Vica1, Vica2, and Ploc are placed in the area of sedimentary rocks (clastites, marble, and coal). However, the data taken from the geological map (Figure 1b) sometimes are not in accordance with data collected from different studies and experiences. Here, we should emphasize that it is very important to establish a database including geological/hydrogeological and mineralogical data of the investigated area. This is especially important in the case of ecological and environmental studies of anthropogenic sources of contamination by toxic elements or PTEs.

The connection between the reservoir lithology and the associated aquifers is as follows: The groundwater outlet referred to as the "Suva fontana" (the sample "Suva") is in a documented connection with the underlying marbles. The outcropping marble is in association with calcite and dolomite (predominantly dolomite), very often containing quartz, microcline, plagioclases, amphibole, sphen, coysit, diopside, and chlorite [48,49]. The geology of the Viča aquifer (the samples "Vicb" and "Vici") emanates from the Upper Cretaceous sediments that transgressively overlie the recrystallized basement schists of the Serbo-Macedonian Unit. The Upper Cretaceous rocks present different sedimentary sequences, having three subsequences including turbidites [34,37,38]. The mineral waters of the Kursumlijska Banja Spa (the sample "Kurs") emanate from the Lower Cretaceous sediments and a number of the Jurassic sedimentary, igneous, and metamorphic rocks (ophiolite mélange) [33]. Stratigraphically, the entire Lower Cretaceous sequence has been developed, represented by microconglometric–arenitic, alevrolite–limestone, arrhenitic–alevrolite, and arrhenitic–limestone sequences lying over the basal breccia (complete "paraflysch") [34,50]. The Lower Cretaceous "paraflysch" sequences are in a tectonic relationship with the older Jurassic rocks (hiatus) [34]. The ophiolites are embedded into a very fine-grained, alevrolite-based matrix, having a small amount of a sandy component. The matrix often contains fragments of solid rocks, consisting of strongly silicified limestones, diabase, and Upper Jurassic limestone [33]. The mineral waters of Prolom Banja originate from several water-permeable fracture zones that are embedded into the LAC [15]. Therefore, groundwaters of the spring "Prol" emanate from andesites. The groundwater of the area "Đavolja Varos" (Djavv) emanates from propylite or from a large segment of metamorphically transformed volcanic rocks (Figure 1b). The "Đavolja Varos" as a fracture-type reservoir has observed hydrochemical zonality induced by the lithological and mineralogical composition of the volcanic rocks exposed to some degree of dissolution. Thus, dissolution of the surrounding media is observed within a deeper groundwater flow, occurring within reduction-type conditions [12]. The Pločnik ("Ploc") spring is placed in the Mesozoic sediments which overlie the crystalline schists, and may also contain smaller inclusions of marble. This spring marks the regional fault structure.

The samples "Tulvis", "Tulg1", "Tulg2", "Petr", "Spon", and "Mrkv" represent the investigated groundwater springs with chemical compositions that could be the result of an interaction with volcanic and crystalline schist-associated minerals (Figure 1b). The samples "Zeb", "Vojn", "Sast", "Malodj", and "Veldj" are in the area of the unaltered and hydrothermally altered volcanic rocks, dacite–andesite, and pyroclastite.

The analysis of the content of the trace elements extracted from the LAC has shown that this ore-bearing region is characterized by a higher content of Pb, Zn, Cu, Mn, Ag, As, Au, Bi, Cd, Hg, S, Sb, Se, Te, Tl, and W [44]. A particularly high content stands out from the crustal segment that is outcropping near the ore fields Tulare and "Đavolja Varoš". The content values of Cr, Ni, and Co in the volcanic rocks of the LAC are mostly lower than the reference average content in the Earth's crust. The same was concluded in the case of the content of the elements Ba, Be, Cs, Ga, Ge, Hf, In, Li, Mg, Mn, Nb, P, Rb, Re, Sc, Sr, Ta, Th, Ti, U, V, and Zr in the volcanic rocks of the LAC [44]. The geochemical analysis confirmed the presence of a number of rare earth elements: La, Ce, Tb, Y, Y, Yb, and Lu. The content of heavy elements from the rare earth group (Y, Yb, and Lu) is lower than the average values in correlative igneous rocks. The content values of the light rare earth element group (LREE—La, Ce) are mostly lower than the average values of the content depicted from analog andesite rocks [44].

3. Water–Rock Interaction—Chemical Weathering

The concentration of the elements in the natural groundwaters (isolated from anthropogenic influence) largely depends on the geological–geochemical properties of the investigated area, as well as on the conditions that allow the elements to be present in mobile forms. The rather rich mineralogical content of the investigated rocks (Table 1) allows the assumption that the presence of a large number of elements should be expected in the groundwater environment. That stands in particular for deeper groundwater circulations (flowing along and across the crosscutting fault zones). The lithological members as the hosts of the circulating waters can represent an important source of different minerals, including the presence of lithophile, siderophile, and chalcophile elements that occur in minerals (Table 1). Many of the listed minerals (Table 1) are not soluble in hot or cold water. Nevertheless, the reactions responsible for the chemical alteration of the rocks and the mobilization of the trace elements and main components (cations and anions) are hydrolysis and oxidation [50,51]. A single way of their immobilization from the crystalline structure of alumosilicates is the chemical alteration enhanced by CO_2 (reaction hydrolysis induced by $CO_2 + H_2O <=> H_2CO_3$—unstable carbonic acid) with higher temperatures (Equation (1)) [20]:

$$2(\mathrm{Na, K, Rb})\ \mathrm{AlSi_3O_8} + 2\mathrm{CO_2} + 11\mathrm{H_2O} \rightarrow 2\ (\mathrm{Na, K, Rb})^- + \mathrm{Al_2Si_2O_5(OH)_4} + 4\mathrm{H_4SiO_4} + 2\mathrm{HCO_3}^- \quad (1)$$

or the reaction of hydration (Equation (2)):

$$\mathrm{K_2\ (MgFe)_3\ [Al\ Si_3\ O_{10}](F,OH)_2} + \mathrm{H_2O} \rightarrow \mathrm{(MgFe)_3\ [Al\ Si_3\ O_{10}\ (F,OH)_2]_n{\cdot}H_2O} + 2\mathrm{F}^- + 2\mathrm{K}^+ \quad (2)$$

After the decomposition of minerals such as plagioclase, hornblende, augite, biotite, chlorite, and tourmaline, the elements listed in Table 1 can become mobile. However, the presence and concentrations of the elements in groundwaters are the result of the balances controlled by the following conditions: Eh, pH, nature of the elements, solubility of the newly born compounds, and presence of hydrogeochemical barriers. In summary, concentrations depend on the following reactions: desorption–adsorption/cation exchange, oxidation–reduction, hydrolysis, precipitation, and complexation processes. Additionally, accounting for the presumed mixing of the investigated groundwater with atmospheric equivalents (Figure 2a,b, labeled as "A"), the mixing process may cause the dilution of groundwaters. That further induces a decrease in the concentrations of a group of elements or concentrates with another (supplied from the atmospheric/surface waters).

Some minerals such as apatite (the source of F and Sr; Table 1) are exposed to hydrolysis under lower temperature conditions:

$$\mathrm{Ca_5\ (PO_4)_3\ F} + 3\mathrm{H_2O} \rightarrow 5\mathrm{Ca}^{2+} + 3\mathrm{HPO_4}^{2-} + \mathrm{F}^- + 3\mathrm{OH}^- \quad (3)$$

The emission of the elements can be induced by the presence of acids. The process of oxidation of sulfides forms strong acids like H_2SO_4 according to Equation (4). Therefore, in addition to the presence of weakly diluted H_2CO_3 acid, other stronger acids could be present in the subsurface system as well.

$$2\mathrm{FeS_2} + 7\mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 2\mathrm{Fe}^{2+} + 4\mathrm{SO_4}^{2-} + 4\mathrm{H}^+ \quad (4)$$

The newly formed sulfuric acid reacts with the minerals in the zone of propylitized rocks, enhancing the chemical denudation of rock. Therefore, silicate minerals (e.g., tourmaline) or sulfide minerals can be decomposed, further allowing the release of the entire cluster of elements.

4. Materials and Methods

This study includes 23 thermal and non-thermal groundwater samples collected from 14 springs of the following designations: Suva, Vici, Siji, Ploc, Djavv, Tulvis, Petr, Vojn, Spon, Zeb, Sast, Malodj, Veldj, Mrkv. Sampling included 9 wells (Vicb, Kurs, Sijb, Tul1, Tul2, Prol, Tulg1, Tulg2, Sasb). The water samples were collected during 2019 and sampled in two different (PET) bottles: (i) filled with water with the purpose of measuring the concentration of cations, anions, halogen elements, Si, and B; (ii) filled with water acidified with HNO_3 acid (1:1) to pH 2 to measure minor and trace elements. The chemical analyses of the waters were performed by using the following methods:

(1) The concentrations of the main components, namely cations (Na^+, Ca^{2+}, K^+, Mg^{2+}) and SiO_2 were measured by atomic absorption spectrophotometry, flammable technique (AASF) (PERKIN ELMER 6500, Perkin-Elmer, Norwalk, CT, USA);

(2) The concentration of anions was measured by using the volumetric method (HCO_3^- and Cl^-) and UV/VIS spectrophotometry (PERKIN ELMER λ 15, Perkin-Elmer, USA-PO_4^{3-}, and SO_4^{2-});

(3) The concentrations of minor and trace elements (Al, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Li, Mn, Mo, Ni, Pb, Rb, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, V, W, Y, Zn, Zr, U, Ce, Dy, Er, Eu, Gd, Ho, In, La, Lu, Nb, Nd, Pr, Re, Sc, Sm, Tb, Tl, Tm, Yb, and Hg) were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7700, Agilent Technologies, Inc, Santa Clara, CA, USA);

(4) The concentration of boron was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Spectro Blue, Kleve, Germany);

(5) The concentration of bromides and iodides was analyzed by ion chromatography (IC) (Dionex 1600), and the concentration of fluorides was analyzed by potentiometry with an ion-selective electrode (ISE) Consort);

(6) pH and temperature (T) were measured in situ by using a multi-component instrument (Ejkelkamp, Giesbeek, The Netherlands).

The statistical analyses, including descriptive statistics, Pearson's correlations, cluster analysis (CA), and principal component analysis (PCA), were carried out using SPSS 21 for Windows. The Piper diagram and Gibbs diagram were prepared using Grabner and Windows Excel programs, respectively.

5. Results

In addition to the mineralogy of the aquifer rocks and the composition related to the main components and the minor and trace elements, the second part of the study is the characterization of the groundwater composition. The resulting concentrations of the main components (cations, anions) and the minor and trace elements are above a detection limit (hereafter DL) for listed techniques (Table 2a,b).

Table 3 represents the descriptive statistics (average, standard deviation, minimum, maximum, median) of the chemical constituents, namely the main components (mgL^{-1}) and minor components, identified across the entire set of sampled groundwaters (B, Si as SiO_2, and F in mgL^{-1}; Rb, Cs, Ba, and Sr in µgL^{-1}). Also, Table 3 presents descriptive statistics of chemical constituents in two separate groups of water samples: (1) group of samples of water with deep circulation; (2) group of samples of water with shallow circulation.

Previously defined rock types, minerals, and processes reflect the type of groundwater, the groundwater's physicochemical and chemical properties, and the presence of trace elements (Table 2a,b, Tables 3 and 4).

Outlined by the Piper diagram (Figure 3), the groundwaters are grouped into five types: HCO_3-Na, HCO_3-Cl-Na, HCO_3-Mg-Ca, HCO_3-Ca, and SO_4-Cl-Mg type.

The data presented in Table 4 show that the investigated groundwaters have been formed within porous volcanic rocks, often hydrothermally altered with clusters of abundant mineralization. Thus, the groundwaters can be subdivided into two main groups: (1) deeper reservoirs controlled by hydraulic pressure, mainly controlled by the sub-vertical regional-scale faults, and (2) shallow aquifers with a changeable groundwater level, frequently documented within near-surface compartments (prone to direct percolation of atmospheric water). As explained earlier, the investigated groundwaters are circulating across faulted and fractured volcanic rocks, gneiss, and other crystalline schists, which can further affect their chemical composition (Table 4).

The results (Tables 3 and 4) show that deeper aquifers can be characterized as a group of thermal mineral waters (above 15 °C and mineralization above 1000 mgL^{-1}, e.g., 1307–5257 mgL^{-1}). The dominant presence of the main components (anions and cations, $\geq$20 meq %) clustered the samples of this groundwater into a HCO_3-Na type, except for the sample Ploc (HCO_3-Cl-Na type and T = 12 °C). This type of groundwater can be an indicator of higher values of F [52]. The presence of Fe and Mn (Tul2 and Sijb) may indicate a reduction type of water environment [53]. Thermal waters extracted from reservoirs accommodated within the rocks of volcanic complexes are characterized by a higher content of Si, F^-, B, H_2S, etc. [4]. Therefore, extremely high values of F^- and B (as well as H_2S) such as those in Ploc suggest the volcanogenic origin and the presence of volcanic rocks in the deepest sections.

Table 2. (**a**) The concentrations of the main components (anions and cations) and minor elements (mgL^{-1}). (**b**) The concentrations of the trace elements (μgL^{-1}).

(**a**)

Sample	**Ca**	**Mg**	**Na**	**K**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**	**F^-**	**SiO_2**	**B**	**TDS**	**PO_4^{3-}**
Suva	43.0	24.0	984	45.0	2782	118	12.0	8.30	42.0	27.7	2675	<0.010
Vicab	15.0	6.00	1048	38.0	2757	122	<0.50	37.5	31.4	1.500	2662	<0.010
Vicai	38.6	17.0	272	19.4	887	37.2	9.50	6.10	19.5	36.9	865	<0.010
Kurs	21.3	30.0	725	41.0	2196	23.0	<0.50	5.25	69.3	18.2	2032	<0.010
Sijb	25.4	16.0	1139	67.0	3001	103	10.0	3.32	77.2	11.0	2915	0.011
Siji	23.4	16.0	1110	66.0	3013	99.0	9.00	3.14	73.0	11.2	2952	0.016
Tul1	130	54.0	892	26.0	2678	181	81.0	4.10	60.5	25.0	2786	0.042
Tul2	107	47.0	1215	65.0	3392	244	80.0	3.75	87.5	31.1	3561	0.024
Prol	4.60	<0.10	44.0	0.20	125	3.00	<0.50	0.77	30.2	0.140	147	0.021
Ploc	22.0	43.0	516	7.00	1336	223	13.0	31.0	9.00	39.4	1530	-
Djavv	3.40	70.0	4.00	0.50	0.50	53.0	226	2.42	99.5	0.290	357	0.029
Tulvis	89.8	27.1	12.2	0.90	433	6.70	1.80	0.28	14.8	0.035	371	0.012
Tulg1	84.2	26.0	13.6	6.60	412	12.4	2.10	<0.10	19.9	0.062	372	0.483
Tulg2	68.1	20.5	10.0	0.30	320	11.7	2.00	0.36	13.5	0.036	287	0.025
Petr	37.7	10.0	7.40	2.60	165	10.6	2.50	0.52	17.3	0.023	175	0.038
Mrkv	50.1	5.80	7.30	0.40	195	6.40	1.30	0.28	18.2	0.015	189	0.056
Vojn	40.9	9.60	6.00	1.00	177	8.90	1.00	0.22	17.5	0.015	174	0.044
Spon	79.0	29.4	7.60	3.20	378	16.0	3.60	0.30	5.60	0.133	334	<0.010
Zeb	67.3	24.4	10.7	1.70	348	7.10	0.90	<0.10	23.1	0.022	310	0.059
Sast	40.7	8.50	6.90	4.40	183	9.00	<0.50	0.36	46.8	0.032	210	0.422
Malodj	11.2	3.00	5.00	0.70	51.9	6.30	1.50	0.24	24.0	0.008	79.0	0.046
Veldj	12.0	2.70	4.10	0.20	61.0	4.20	1.00	0.27	24.8	0.006	82.0	<0.010
Sasb	76.2	49.3	22.5	3.00	511	12.4	8.60	0.25	29.1	0.270	459	<0.010

(**b**)

Sample	**Al**	**Fe**	**Mn**	**Rb**	**Li**	**Ba**	**Sr**	**Cs**	**Ge**	**Be**	**Cr**	**Sc**	**V**	**U**	**Cu**	**As**	**Zn**	**Te**
Suva	<20.0	26.9	84.4	164	1352	113	1018	104	100	1.60	7.50	3.90	<0.50	0.13	12.5	<2.1	<6.2	<1.0
Vicab	<20.0	78.9	111	127	805	308	751	39.2	138	3.00	8.60	3.30	<0.50	<0.13	15.0	<2.1	<6.2	<1.0
Vicai	<20.0	18.5	0.80	39.8	250	87.4	461	10.2	36.1	0.51	10.7	2.10	<0.50	1.30	3.40	<2.1	<6.2	<1.0
Kurs	<20.0	46.1	11.7	188	3116	254	1155	198	48.8	0.41	8.90	6.30	<0.50	<0.13	9.80	<2.1	<6.2	<1.0
Sijb	<20.0	1139	15.2	250	1262	413	2932	107	17.9	2.20	9.90	5.70	<0.50	<0.13	24.2	11.7	<6.2	1.1
Siji	<20.0	104	21.9	253	1317	206	2882	103	17.0	1.50	10.9	5.80	0.57	<0.13	19.5	4.5	<6.2	1.2
Tul1	44.9	579	341	191	1501	19.1	3794	486	30.6	2.00	8.20	4.10	0.95	2.70	30.3	<2.1	<6.2	<1.0
Tul2	<20.0	1554	35.8	286	2156	45.8	5450	530	44.3	2.50	13.9	5.90	<0.50	0.45	26.9	5.4	<6.2	1.9
Prol	<20.0	19.5	0.80	0.52	3.70	<3.40	48.5	0.79	2.50	<0.18	3.30	2.70	9.60	2.30	<3.50	5.7	<6.2	<1.0
Ploc	130	251	16.7	19,5	95.6	128	612	1.10	242	<0.18	4.80	1.00	<0.50	<0.13	5.00	<2.1	<6.2	<1.0
Djavv	36,911	19,675	3080	2.60	98.7	<3.40	166	<0.50	6.80	9.10	30.7	94.9	10.4	54.6	1322	4.1	2358	<1.0
Tulvis	<20.0	22.4	0.80	1.60	4.10	72.3	857	0.74	<0.50	<0.18	1.90	1.50	1.50	15.5	<3.50	<2.1	38.5	1.1
Tulg1	<20.0	64.7	64.1	0.60	2.30	159	789	<0.50	<0.50	<0.18	2.30	1.70	3.70	8.20	<3.50	<2.1	<6.2	1.0
Tulg2	25.8	184	65.0	0.54	<0.50	146	482	<0.50	<0.50	<0.18	2.10	1.30	<0.50	2.90	<3.50	<2.1	13.4	<1.0
Petr	30.2	537	33.6	1.00	7.20	85.4	127	<0.50	<0.50	<0.18	2.20	1.60	0.59	0.17	3.50	<2.1	<6.2	<1.0
Mrkv	46.3	68.0	2.20	1.10	1.70	10.0	285	1.50	<0.50	<0.18	2.00	1.70	2.60	7.20	<3.50	12.6	<6.2	<1.0
Vojn	<20.0	20.1	0.80	1.40	4.80	212	394	0.78	<0.50	<0.18	1.80	1.50	<0.50	1.80	<3.50	3.2	<6.2	<1.0
Spon	<20.0	23.8	0.80	0.73	11.6	58.8	220	0.25	<0.50	<0.18	2.30	0,78	<0.50	1.70	8.00	<2.1	9.4	<1.0
Zeb	118	140	10.5	6.20	3.70	83.6	642	0.59	<0.50	<0.18	1.80	1.70	1.90	7.60	4.10	<2.1	<6.2	<1.0
Sast	647	707	4.10	21.4	3.70	64.2	244	1.53	<0.50	<0.18	2.80	2.90	4.40	3.80	<3.50	5.4	9.3	<1.0
Malodj	26.6	64.0	1.70	2.30	<0.50	11.0	115	<0.50	<0.50	<0.18	<1.70	1.08	1.10	<0.13	<3.50	<2.1	<6.2	<1.0
Veldj	35.7	28.6	0.80	0.59	<0.50	<3.40	104	<0.50	<0.50	<0.18	<1.70	1.70	3.00	0.21	<3.50	<2.1	<6.2	1.2
Sasb	<20.0	47.3	12.5	12. 8	20.9	72.7	1429	8.30	<0.50	<0.18	2.30	2.60	<0.50	7.12	<3.50	24.2	8.1	<1.0

Table 3. The descriptive statistics of main components and minor elements (F, Si, B mgL^{-1}; Rb, Li, Ba, Sr μgL^{-1}) in: group 1–water with deep circulation; group 2–water with shallow circulation, and all groundwater samples (total).

	Ca	**Mg**	**Na**	**K**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**	**F^-**	**SiO_2**	**B**	**Rb**	**Li**	**Ba**	**Sr**
								Group 1						
average	42.9	25.3	794	37.4	2217	115	21.4	10.3	49.9	20.2	151	1185	158	1910
stdev	41.6	17.9	397	24.3	1073	81.7	31.5	12.8	27.0	14.0	102	967	134	1764
								Group 2						
average	50.5	22.0	9.10	2.00	248	12.7	19.4	0.46	27.2	0.07	4.10	12.3	75.3	450
stdev	29.0	19.6	5.10	1.90	162	12.5	62.1	0.60	23.8	0.09	6.20	26.6	64.9	389
								total						
average	47.2	23.4	353	17.3	1104	57.3	20.3	4.73	37.1	8.82	68.3	523	111	1085
stdev	33.5	18.1	460	23.2	1190	72.7	49.0	9.43	26.6	13.3	97.4	840	105	1350
min	3.00	<0.10	4.00	0.20	0,50	3.00	<0.50	<0.10	5.60	0.006	0.52	0.25	1.70	48.5
max	130	70.0	1215	67.0	3392	244	226	37.5	99.5	39.4	286	3116	413	5450
median	41.0	21.0	22.5	3.20	412	12.4	2.00	0.52	24.8	0.14	6.20	11.6	83.6	612
CV	0.71	0.77	1.30	1.34	1.08	1.27	2.42	2.00	0.72	1.50	1.43	1.61	0.94	1.24

Table 4. Type of aquifer, lithological units, and groundwater and physical–chemical characteristics.

Aquifer	Samples	Lithological Units	Type	pH	TDS (mgL^{-1})	T (°C)
Controlled by deep-settled large regional-scale faults; deep water flow	Suv, Vicb, Vici, Kurs, Sijb, Siji, Tul1, Tul2	Andesites, marble, crystalline schists	HCO_3-Na	6.30–7.23	865–3561	20.5–78.0
	Ploc		HCO_3-Cl-Na	7.50	1530	12
Controlled by smaller-scale faults; deep water flow	Prol	Andesites	HCO_3-Na	8.90	147	34
Controlled by near-surface zones; shallow water flow	Djavv	Propylitized, hydrothermally altered andesites	SO_4-Cl-Mg	2.40	357	13
Controlled by near-surface zones; shallow water flow	Tulvis, Tulg1, Sast Tulg2, Petr Zeb, Spon, Malodj, Veldj, Sasb Vojn	andesites–gneiss, gneiss; andesites; volcano sediments	HCO_3-Ca-Mg	6.48–7.06	79–459	10.5–13.2
	Mrkv	andesites–schists	HCO_3-Ca			

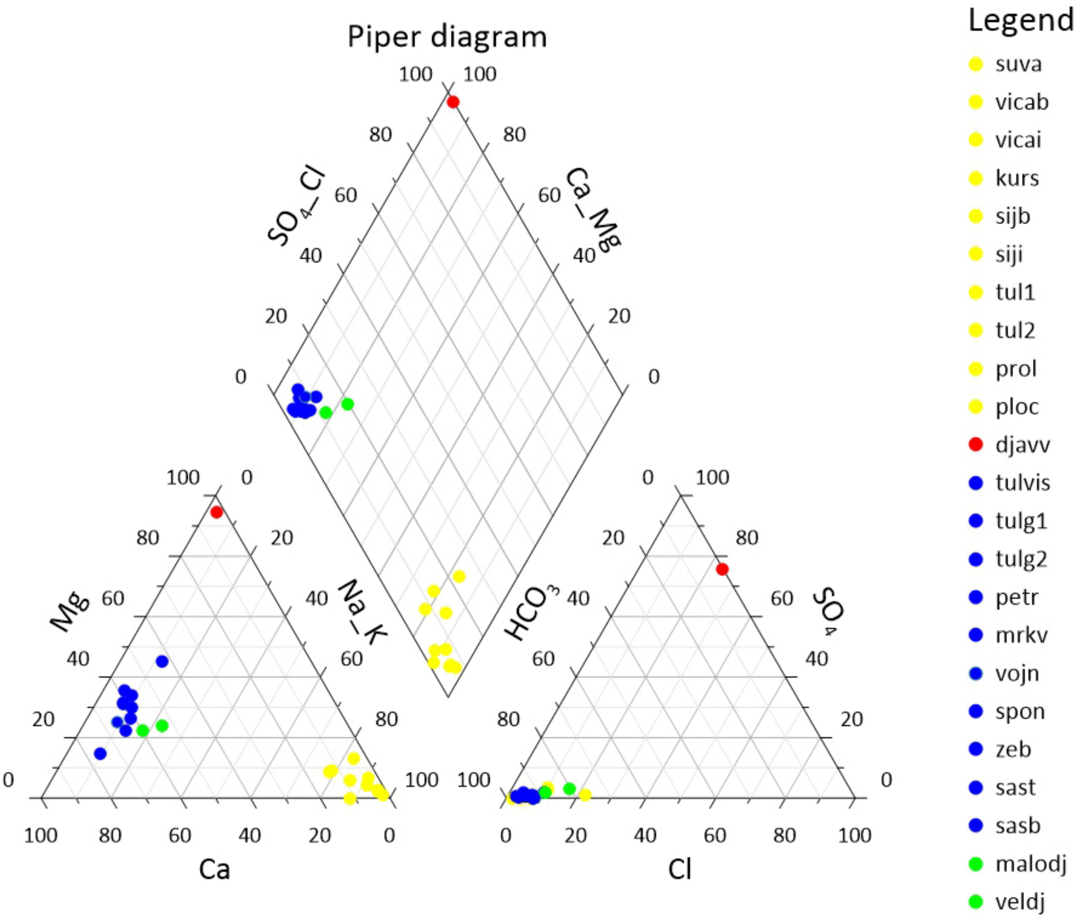


Figure 3. Piper diagram of groundwater of volcanic aquifers of the Lece complex and surroundings.

The investigated groundwaters having a shallow circulation zone are placed across near-surface aquifers and migrate across the intensively faulted and fractured zones. Such fracture zones are spread across the volcanic complex, and the associated fluids are characterized as HCO_3-Ca and HCO_3-Ca-Mg waters (Figure 3). These groundwater samples can also be classified as cold or non-thermal waters (T < 15 °C), having a lower mineralization (of 105–716 mgL^{-1}). The concentrations of the minor elements (F, B, Rb, Li, Si) and main components, except Ca^{2+} and Mg^{2+}, are lower compared to the averages for thermal water from deeper circulation and are similar to the BG values. The same conclusion was reported by Jayawardana et al. (2016) [54]. The average values of concentrations of Ca^{2+} and Mg^{2+} in both groups of groundwaters (Table 3) do not differ significantly. However, the different concentration of Na^+ (and K^+) indicates the presence of cation exchange processes where Ca^{2+} takes the place of Na^+ (as a consequence of the presence of clay minerals) [20]. Along with Na, the other positive charged ions Cs^+, Rb^+, and Li^+ can be emitted in the water environment [55]. Into this group of waters falls a water sample from Djavv, representing the groundwater of SO_4-Cl-Mg type. Waters of this type are distributed in the shallow zones of the near-surface altered rocks [13]. Similarly, studies by Cuccuru et al. (2020) and Paternoster et al. (2017) [3,56] reported two main types of thermo-mineral water-flow systems that have recently been documented within the volcanic rocks belonging to the Tertiary basins of Sardinia (andesite to granite-hosted groundwater).

The waters exhibit a wide range of pH values. The highest value is in the sample “Prol” (alkaline), which is the consequence of the presence of soluble carbonates, e.g., the Na^+ and $CO_3{}^{2-}$ (4 mgL^{-1}) forms. Alkaline waters with a high pH (9.5), lower TDS, and dominant presence of Na were registered by Michard (1990) [57] in waters circulating within volcanic complexes (granites). The lowest pH value of 2.40 is recorded in the water sample of “Djavv”. That is a consequence of the interaction between thermal water and propylitized rocks and the oxidation of sulfides (Equation (4)). At the same time, the oxidation of sulfides is the main reason for a detected concentration of Fe (197 mgL^{-1}) and $SO_4{}^{2-}$ (226 mgL^{-1}) being yielded (Table 2a,b). Furthermore, a higher concentration of Fe occurs together with a higher concentration of Mn. This relationship develops because of the release of the adsorbed Mn^{2+} during the reduction of Fe^{3+} [3,53] or dilution of Fe-Mn oxi-hydroxides in acidic conditions (lower pH).

In addition to the main components (mgL^{-1}) in waters circulating in and around the LAC, the (minor) elements having a higher abundance are B, Si (as SiO_2), and F^- in mgL^{-1} and Rb, Cs, Ba, and Sr (in μgL^{-1}, Table 3). A coefficient of variation (CV, Table 3) that is above 0.70 (70%) [58] indicates a higher variability of the main and the listed minor components. The presented average values of the main components and the minor elements (Table 3) are above the values of the typical concentration of these elements in the bottled waters of Serbia [59] (here taken as the background (BG) values) and the waters produced in Europe [60]. Reinman and Birke (2010) reported that some waters of Europe, with the group of elements such as B, Be, Br, Cs, F, Ge, Li, Rb, Te, and Zr ruling out the presence of shallow fresh groundwater, exhibit unusually high concentrations that are typical for a “mineral water”. After an experiment with hydrothermal fluids and their interaction with andesites, Yudiantoro et al. (2021) [61] concluded that hot water springs contain higher average values of Li (1.14 mgL^{-1}), Cl^- (529 mgL^{-1}), Si (2662 mgL^{-1}, and B (14.1 mgL^{-1}). Besides the observed lithophile elements (B, Rb, Sr, Ba, Li, Si, and F), the water–rock interaction increases the concentrations of other trace elements such as lithophile and chalcophile elements and Fe (Table 2b). The highest values are observed in thermal groundwater samples that originate from deeper circulation zones. Furthermore, as the result of reactions, the existing conditions within propylized andesites (Djavv) are leaching of elements such as U, Cu, Fe Zn, Co, and Ni (Table 2b). The results are in accordance with the study of water–volcanic rock (U-bearing granite) interaction [62]. The water of the area is poorly mineralized, with a lower pH (about 4), and contaminated with Fe (up to 1849 mgL^{-1}), Mn (up to 777 mgL^{-1}), Cu (up to 5.4 μgL^{-1}), As (up to 14.7 μgL^{-1}), and U (up to 66.2 μgL^{-1}).

REEs and other trace elements are occasionally presented in the thermal water with deep circulation (Supplementary Materials Table S1). As the representation of water from a shallow aquifer, the sample Sast shows interesting content because of the appearance of the elements La, Nd, Ce, Zr, and Y that originate from andesite (hornblende) [63]. Other elements such as Br, Cd, Be, Co, Ge, Ga, Se, Ta, In, Nb, REE, Ti, Zr, Bi, Hf, Mo, Ni, and Hg are not detected (<DL) in cold/non-thermal groundwaters; thus, they are omitted in Table 2b.

6. Discussion

6.1. Water–Rock Interaction—Hydrogeochemistry of Water

6.1.1. Main Composition

The hydrogeochemistry of water and the presence of trace elements depend on the type of rocks and chemical reactions, as well as on the intensity of water–rock contact/interaction. The LAC area carries two main groups of groundwaters and five water types: (1) thermal waters from a deep fluid flow system (under hydraulic pressure) of HCO_3-Na and HCO_3-Cl-Na types; (2) groundwaters that arrive from a shallow fluid flow system (a) in aquifers lying in non-altered rocks—HCO_3-Mg-Ca and HCO_3-Ca types; (b) groundwater that is formed within hydrothermally altered rocks belonging to a SO_4-Cl-Mg type.

In general, water–rock interactions (in granite effusive, schists, etc.) show the pattern of a transformation of water composition affected by the temperature and duration of interactions in order: HCO_3-Ca, Na -> HCO_3-Na, Ca, and HCO_3, SO_4-Na -> SO_4-Na. The results of the transformation are in the form of mature thermal waters within the volcanic complex, which should be of the SO_4-Na type [11]. However, this is not the case for the carbonated waters in the investigated area, because these originate from the zones of younger magmatism (Miocene magmatic reactivation). Pantić et al. [15] concluded that the groundwater flowing across magmatic and metamorphic media in the Serbian–Macedonian crystalline core (where LAC belongs) is mainly of the HCO_3-Na type. It can be formed as a product of the hydrolysis of aluminosilicates (e.g., Na-feldspars or Ca-feldspars according to reaction Equation (1)) occurring at higher temperatures [4]. Accordingly, the hydrogeochemical composition of thermal water enriched with Na^+ is a consequence of (1) contact with rocks of the area rich in Na and (2) exchange of Ca^{2+} from the waters with Na^+. In such cases, the other conditions can be a rather slow exchange of waters across the subsurface system, a longer time of water–rock contact, commonly the prevalence of redox conditions, and a lower influence of incoming atmospheric water. On top of that, the pH values range from slightly acidic to alkaline-type (Table 4) [12,64]. The formation of a HCO_3-Cl-Na water type was unraveled in the research of Pasvanoğlu and Çelik, in waters of the volcanic rocks occurring as a consequence of these two processes [20]. Additionally, Cl^- ions are typically the indicators of existing deep-water circulations [61]. A HCO_3-Ca type of water exists not only in waters originating from rocks rich in carbonates but also in waters originating from aluminosilicates with abundant Ca (e.g., Ca-feldspars). After that, the Ca^{2+}-Na^+ cation exchange transforms it to the HCO_3-Na type. In the study conducted by Jeong et al. (2019) [21], the authors concluded that the presence of the HCO_3–Na type differs from local groundwaters (HCO_3—Ca type) or thermal waters occurring in granite and gneiss areas of South Korea. Such a presence is the consequence of the initial transformation of the HCO_3-Ca type. As explained earlier, the SO_4-Cl-Mg type of water is the consequence of the interaction between circulating thermal waters and propylitized rocks, as well as the oxidation of sulfides including the decomposition of aluminosilicates induced by strong acid.

Parameters such as the TDS, the ratio of the percentage of meq cations $Na^+ + K^+/(Na^+ + K^+ + Ca^{2+})$, and the percentage meq anions $Cl^-/(Cl^-+HCO_3^-)$ can be taken into consideration for the construction of the Gibbs diagram. The Gibbs diagram (Figure 4) depicts which types of groundwaters have a dominant role in the processes of supplying the reservoirs. Even though Ploc, Djavv, and Prol are nitrogen-type waters and the aquifers are influenced by surface water [11,24], the resulting diagram shows that the influence of atmospheric water (rainfall) or surface water is insignificant in both types of aquifers (shallow and deep). That further implies a significant influence of the composition and mineralization of groundwaters, as these processes are hosted longer within the aquifers during water–rock interaction, diminishing the influence of atmospheric/surface water.

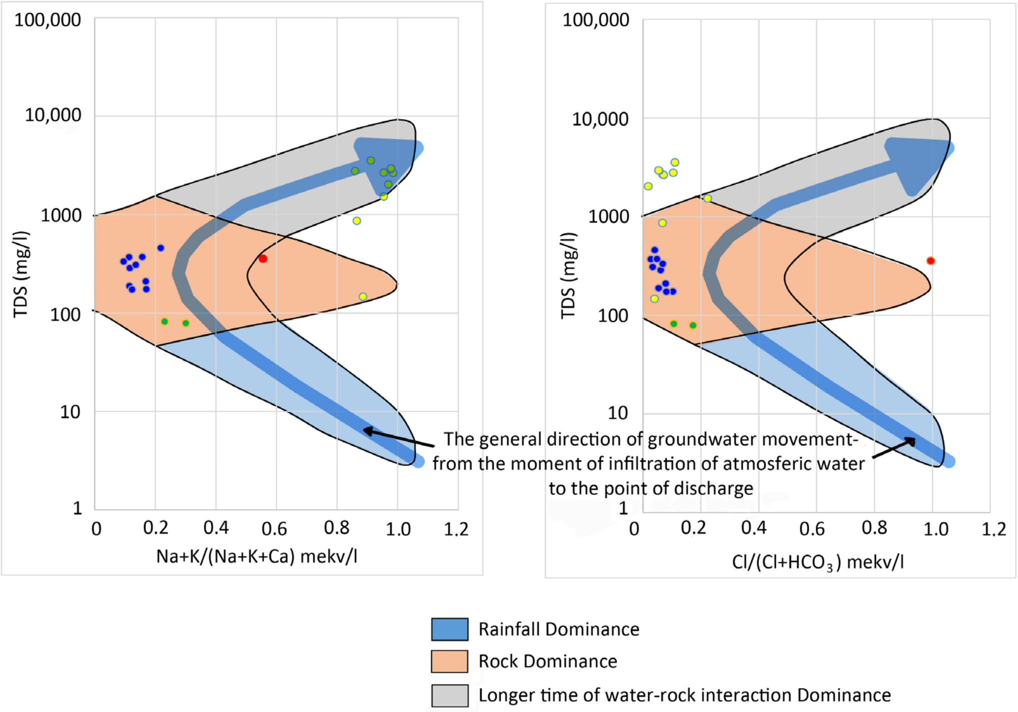


Figure 4. Gibbs diagram of groundwater samples (modified).

6.1.2. Trace Elements

As we explained earlier, REEs occur occasionally in thermal water, as well as in the samples of shallow aquifers Djavv and Sast (Supplementary Materials Table S1). Todorović (2020) [65] concluded that interaction within fractured aquifers in Paleozoic schists and marbles led to the enrichment of water with heavy rare earth elements (HREEs). Her study refers to the samples Vic (Toplice fault zone) Tul, and Sija (external zone of Lece complex). The HREE enrichment and Ce anomaly (increasing values) are indicators of higher temperature, redox conditions, the presence of long-term circulation, and slower processes of rock dissolution. In this study, enrichment with HREEs by comparison to LREEs is observed in the sample Djavv. This can be the indicator of the presence of the HREEs, which become mobile during water–rock interaction, in rocks and the conditions suitable for the formation of the ion complexes. Here, a positive Eu anomaly confirms the same. On the other hand, in this study, the water of the Sast is characterized as enriched with LREEs over HREEs, further confirming the water's contact with more acidic igneous rocks [65]. The negative anomaly of Ce in this sample suggests the presence of an oxidative environment. In a study, the thermal and cold springs of volcanic complexes [66] with low pH values and high concentrations of sulfate exhibited a very high REE content (0.64 to 3.15 mgL^{-1}). The authors confirm that pH and non-equilibrium complete dissolution with leaching of cations from rocks are the main factors controlling REE concentrations in investigated thermal and acidic cold springs. The results of the concentrations of REEs in similar conditions (Djavv) are lower than those detected in the study of Shakery et al. (2015) [66].

As we mentioned above, elements such as Br, Cd, Be, Co, Ge, Ga Se, Ta, In, Nb, rare earth elements (REEs), Ti, Zr, Bi, Hf, Mo, Ni, and Hg are not detected (<DL) in cold/non-thermal groundwaters. In addition, the calculation of the correlation coefficients between these elements or the statistical analysis (later in the text) of data is missing. In the following paragraphs, the occurrence of some of the listed trace elements (Supplementary Materials Table S1) that are detected in a few relevant samples will be discussed.

Niobium is detected in Vicab, occurring as a consequence of decomposition, which comes, for example, from biotite embedded in the local schists (Table 1). Tungsten is detected in the samples Vicab, Suva, and Vojn. It is an element often detected in pegmatites, granites, and contact-metamorphic rock sections. Furthermore, the high-temperature hydrothermal veins are mapped in granites and schists as well as in minerals such as fluorite, apatite, molybdenite, and wolframite [67]. As shown in Table 1, the presence of the minerals in the area of the Lece volcanic complex is not detected, except for apatite (a mineral of andesite rock). Nevertheless, the water–rock interaction in schists can be the source of detected W, in particular in thermal waters, such as Vica and Suva.

Iodine is found in a lower concentration in most of the rock assemblages because of its incompatibility relative to the most rock-forming (silicate) minerals. Iodine is detected in higher concentrations in sulfide minerals, organic matter, and iron oxides. Even though I^- is relatively concentrated in mineral veins (rich in sulfide minerals) and hydrothermal solutions [68], it is not detected in the sample Djavv. The presence of iodide is detected in the thermal waters of Kurs, Tul1, Tul2, Suva, and Ploc (Table 2b).

The highest Ge content is usually associated with geothermal aquifers, i.e., groundwater fluid flow through a reactive silicate-rich bedrock. Previous geochemical studies revealed an increased Ge content in mineral waters of the Sudetes and the Bieszczady mountains, Southern Poland. Here, the two main types of CO_2-rich waters and thermal SO_4-HCO_3 waters with F, H_2S, and Rn are enriched with Ge (relative to the crustal composition) [69]. Similarly, in the investigated area of the LAC, Ge is detected in the investigated thermal waters (with deep water flow) and in Djavv. In cold waters extracted from the shallow aquifers, Ge is absent.

Significant correlations between U and Mg, $SO_4{}^{2-}$, Al, Fe, Mn, Be, Cr, V, and Sc (Supplementary Materials Table S2) and the absence of correlation with PO_4 suggest the chemical composition appears to be a function of the processes including acidic decomposition of aluminosilicates as well as sulfide oxidation (Table 1). As we explained, during the chemical alteration of rock minerals, the already available trace elements like Be, Li, Rb, and Th, which are detected in the feldspars and quartz-rich rocks, become mobile [70]. Additionally, U is very soluble in water in the form of the hexavalent uranyl cationic complex $(U^{6+}O_2)^{2+}$. Thus, in the sample with the highest concentration of 54.9 μgL^{-1} (Djavv), we expect that it is complexed with $SO_4{}^{2-}$ anions. Uranium, Ra, and Rn in waters frequently originate from granites, gneisses, sandstone, clays, etc. Thus, a value equivalent to the MAC of 15 μgL^{-1} (WHO, 2004) [71] is recorded for the sample Tulvis or the waters placed within crystalline schist. This further confirms the water interactions with volcanic rock occurring in the shallower aquifers. Additionally, values of U lower than the MAC are detected in other waters of the shallow aquifers (Mrkv, Tulg, and Zeb; Table 2b).

As a summary, the widest range of the elements is detected in the thermal groundwater sample from the well Vicab, and the waters from Djavv. Even though the sample Vicab is placed in the area of marbles, clastites, and coal (Figure 1b), the results show intensive groundwater–volcanic rock interactions. Therefore, this composition corroborates the decomposition of the silicates and sulfide minerals in these reservoirs. Moreover, the presence of the detected trace elements is in line with the conditions that support a mobile form of the elements.

6.2. The Intensity of Water–Rock Interactions and Pearson's Correlation

The following text discusses the observed (chosen) ratios between the concentrations of the elements (Table 5) and Pearson´s correlation coefficient (Supplementary Materials Table S2). The main goal is to define the conditions and intensity of the water–rock interactions, as well as the origin of the elements. The chosen correlation (Table 5) mostly represents the ratio of the main components and a conservative element such as Cl. The highest values of Cl^- ions are related to increasing mineralization and depth of the water circulation in reservoir rocks [20,65]. Being such an indicator, the concentration of Cl^- ions is chosen for the calculation of the enrichment factor (EF) that is discussed in the last paragraphs.

Table 5. The ratio between the concentrations of cations and anions.

		Ca^{2+}/Mg^{2+}	Na^+/Ca^{2+}	HCO_3^-/Cl^-	B/Cl^-	$Na^+/Na^+ + Cl^-$
Group 1	Suva	1.79	22.9	23.5	0.235	0.89
	Vicab	2.50	69.9	22.6	0.012	0.90
	Vicai	2.27	7.05	23.8	0.992	0.88
	Kurs	0.70	34.5	95.5	0.791	0.97
	Sijb	1.56	45.6	29.1	0.107	0.92
	Siji	1.44	48.3	30.4	0.113	0.92
	Tul1	2.41	6.86	14.8	0.138	0.83
	Tul2	2.28	11.4	13.9	0.127	0.83
	Prol	-	8.80	41.7	0.047	0.94
	Ploc	0.51	23.5	5.99	0.177	0.70
Group 2	Djavv	0.04	1.33	0.01	0.005	0.07
	Tulvis	3.19	0.14	61.9	0.005	0.63
	Tulg1	3.23	0.17	34.3	0.005	0.54
	Tulg2	3.24	0.15	26.7	0.003	0.45
	Petr	3.80	0.19	15.0	0.002	0.40
	Mrkv	8.50	0.14	30.5	0.002	0.53
	Vojn	4.27	0.15	19.7	0.002	0.40
	Spon	2.72	0.10	23.6	0.008	0.32
	Zeb	2.79	0.16	49.7	0.003	0.61
	Sast	4.82	0.17	20.3	0.004	0.43
	Malodj	3.67	0.45	8.25	0.001	0.44
	Veldj	4.44	0.33	14.5	0.001	0.49
	Sasb	1.55	0.30	41.2	0.022	0.64

The highest value of the Ca^{2+}/Mg^{2+} ratio marks a minor presence of the Mg-bearing minerals in rocks in contact with water around geothermal fields [54]. The results (Table 5) show the presence of Mg-bearing minerals or the presence of Mg as a minor element in the igneous rocks (diabase) and nonalterated andesite of Kurs and Djavv, respectively. In the sample Prol, Mg is not detected (<0.10 mgL^{-1}). The highest ratio of Ca/Mg is registered in the sample Mrkv (labeled as HCO_3-Ca type of water, Table 4) in the aquifer formed at the contact between andesites and schists. That confirms rather the absence of Mg in the minerals than the processes of cation exchange. Namely, the ratio $Na^+/Na^+\text{-}Cl^- > 0.5$ (as well as the ratio $SiO_2/Na^+ + K^+\text{-}Cl^- < 1$) indicates the presence of ion exchange of Ca^{2+} and Mg^{2+} (from water) with Na^+. That refers exactly to the water migrating from deeper circulation zones (0.70–0.97). The other parameter ratio $SiO_2/Na^+ + K^+\text{-}Cl^- < 1$ across all samples of water from deeper circulation (group 1) confirms that. On the other hand, the values $SiO_2/Na^+ + K^+\text{-}Cl^- < 1$ in the samples of the shallow aquifer (especially Tulvis, Tulg, Mrkv, Sasb, Zeb) do not support the presence of this process. This further implies that the $Na^+/Na^+ + K^+$ values below 0.7 in this study (Table 5) should be rejected.

As HCO_3^-/Cl^- has higher values, the intensity of the process of decomposition of rocks (minerals) is higher; consequently, the values of TDS are higher [20]. Most of the groundwater of the investigated area has a dominant presence of HCO_3^- over Cl^- and SO_4^{2-} except for the sample Djavv. According to the classification of the HCO_3^-/Cl^- ratio [20] (Table 5), the waters having a ratio of $HCO_3^-/Cl^- > 10$ are mostly HCO_3^--rich mineral waters, whereas waters having a ratio of $HCO_3/Cl^- < 1$ are interpreted as Cl^--rich (Djavv). Furthermore, a higher HCO_3^-/Cl^- ratio in the cold groundwaters (e.g., Zeb, Tulvis) reflects a shorter flow path and a faster water cycle, whereas a lower HCO_3^-/Cl^- ratio suggests that the thermal waters of the LAC have a longer subsurface flow path and represent a deep circulation water equivalent (Tul1 and Tul2) [20,54].

The Na^+/Ca^{2+} ratio has a range from 6.86 to 69.8 (group 1, Table 5), being the opposite of the range 1.57–20.0 (group 2), which supports a dominant ongoing supply from deeper fluid flow zones characterized by intense water circulation. Furthermore, B and Cl^- are conservative elements and the B/Cl^- ratio is used to indicate a common reservoir source or initial processes of dissolution of deep rock as well [72]. Once in the mineral waters, the Cl concentrations increase (occasionally as a function of depth), and a decrease in the B/Cl^- ratio can be observed. On top of that, in carbonated waters from the zones of younger magmatism (likely a Miocene magmatic reactivation), this ratio increases sharply [73]. The B/Cl^- ratio across the shallow aquifers reaches a value of 0.001–0.022, whereas the range of the ratio of deeper aquifers is 0.012–0.992. These highest values initially suggest the presence of processes of dissolution of minerals with the contact of waters from deeper circulation. The difference between the B/Cl^- ratios in Vicai and Vicab (maximum and minimum values, group 1, Table 5) suggests different depths and reservoirs of these waters. On the other hand, a Cl^-/B ratio ranging from 10–30 is indicative of water directly extracted from andesite rocks [20]. Therefore, the value of 21.4 observed in the sample Prol suggests that the chemical content is rather typically a result of the andesite host (rock)–water interaction. Indeed, Prolom water is the only fluid formed in the andesite rocks or the center of the volcanic LAC andesite complex [24].

The values of Pearson's coefficient (Figure 5, Supplementary Materials Table S2) indicate the relationship between the main components and the minor elements. The relationship suggests a significant level of the correlation ($r \geq 0.60$, $\alpha = 0.01/0.05$) between Na and K, HCO_3, Cl^-, SiO_2, B, Rb, Li, Sr, and Ba; K and HCO_3^-, Cl^-, SiO_2, B, Rb, Li, Sr, and Ba; HCO_3^- and Cl^-, B, Rb, Li, Sr, and Cs; TDS and Na, K, HCO_3^-, Cl^-, SiO_2, B, Rb, Li, and Sr; and SiO_2 and Rb, Li, and Sr. A significant correlation between the components, particularly between SiO_2 and HCO_3^-, may suggest a chemical alteration of aluminosilicates (feldspars, plagioclase, micas, hornblende, augite, etc.). The alteration is according to Equation (1), further attributed as one of the sources of ion HCO_3^- and lithophile elements. Similarly, the authors Jayawardana et al. (2016) and Okan et al. (2017) concluded the same in their studies [54,72].

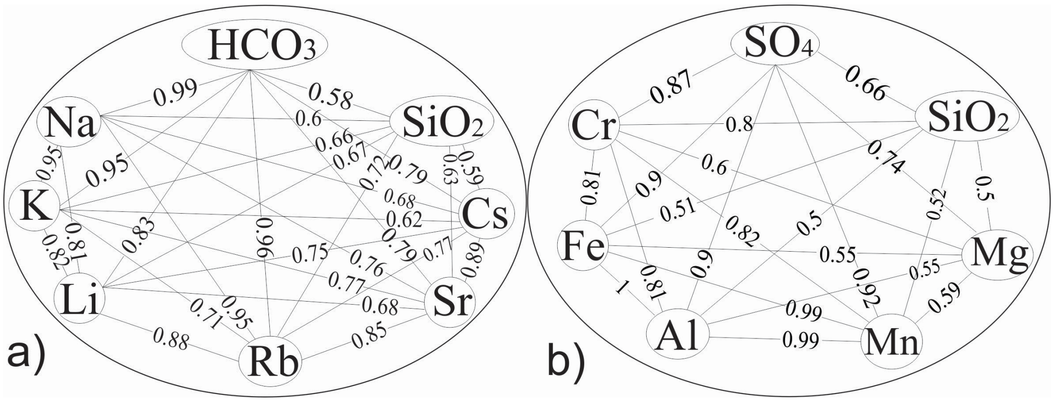


Figure 5. Pearson's correlations between (**a**) lithophile elements and (**b**) lithophile, siderophile, and chalcophile elements.

It is known that the group of volcanogenic elements/gases includes Cl, F, B, etc./CO_2 and H_2S [74–76]. These elements here have a significant correlation with some other elements (Supplementary Materials Table S2). Therefore, the same origin is confirmed by applying the Pearson's coefficient: Cl with F (0.66), B (0.75), Rb (0.68), Li (0.52), Sr (0.72), Cs (0.70), Cr (0.91), Fe (0.92), Al (0.90), and V (0.82); F with Na (0,46), HCO_3^- (0.42), and B (0.40); B with Na (0.61), K (0.51), HCO_3^- (0.61), Rb (0.53), Li (0.63), Sr (0.50), and Cs (0.54); V with Cr (0.996), SO_4^{2-} (0.52), Al (0.66), Fe (0.65), and Mn (0.64). In the carbonated waters that occur in the areas of LAC-related magmatism, the paragenesis of B, K, and Cl^- has been observed [73]. These correlations suggest that the composition of waters originates from the aquifer directly formed in the volcanic massif, or from the aquifer lying within or near the contact with the surrounding rocks. That further means the emplacement of the Miocene volcanic body has a wider effect, being intruded into a wider area of the abutting crystalline schists. Moreover, the proof is the fact that during drilling in Kuršumlija Banja and Sijarinska Banja spas, discharged waters originated from the zone of volcanic veins [77,78]. This fact further corroborates that the composition of the water from the deeper aquifers within the LAC-surrounding metamorphic rocks is influenced by a dominant water–rock interaction with the minerals belonging mainly to the surrounding volcanites.

The concentrations of Li, Rb, and Cs are noticeably higher in the thermal waters than in the cold waters, being released mainly from feldspars and some clay minerals [20]. In this study, in addition to a higher correlativity with Si, Na, K, HCO_3^-, etc. (Supplementary Materials Table S2), the lithophile elements Rb, Cs, and Li are well correlated with each other. Such correlativity shows the main mode of their origin (defined in Equation (1)). To define the intensity of water–rock interaction, the Li-Rb-Cs diagram is used (Figure 6). In addition, it can show whether the concentration of these three elements in the water is similar to that in their parental rock (andesite, dacite, or gneiss).

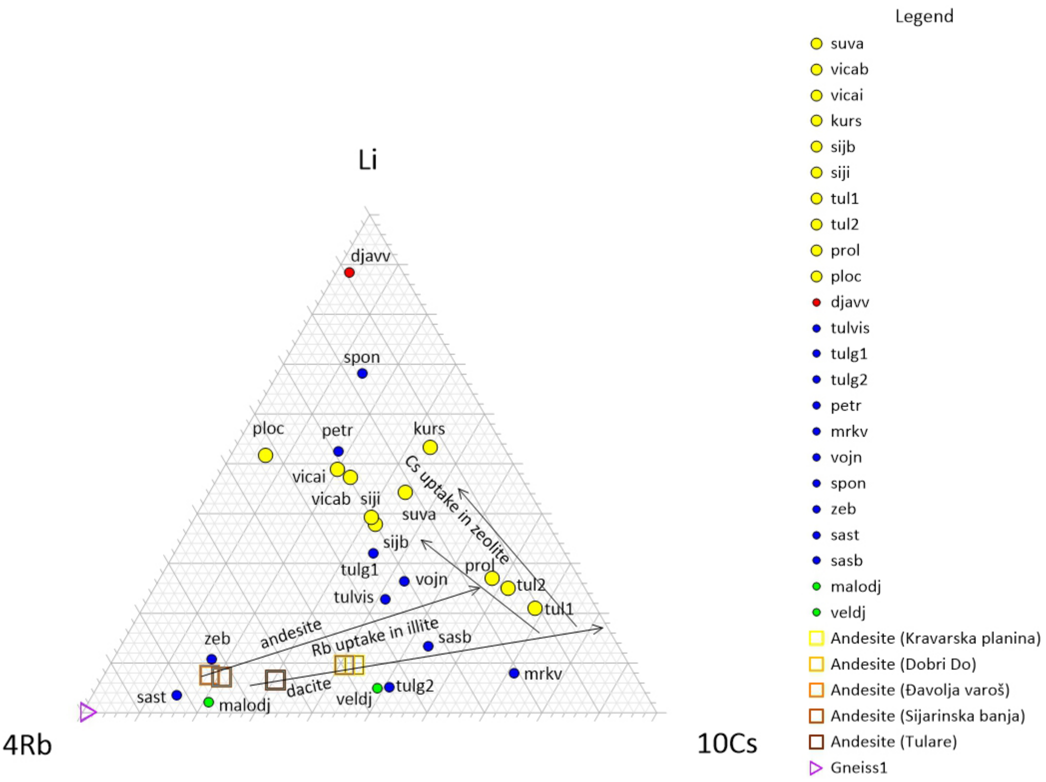


Figure 6. Li-Rb-Cs diagram.

The relative concentrations of Li, Rb, and Cs in the investigated water samples show their different dispersions from the parent rocks, mostly in the groundwater samples of deeper water flow, and the intensive rock–water interaction. The highest difference is observed in the sample Djavv, indicating the influence of altered rock–water interaction. Generally, after the decomposition of minerals that consist of these elements, the concentration in water depends on their nature. Thus, Li^+ and Rb^+ can be exchanged with K^+ in clay minerals, i.e., the K-containing alteration products [79]. Sometimes in the processes of adsorption of secondary formed minerals, Li stays in the water after the immobilization from the rocks [20], whereas Cs as an element with a higher ion radius is adsorbed at the surface [72]. Therefore, one of the reasons for such dispersion can be the series of secondary processes affecting their concentration after the water–rock interaction (presence of hydrogeochemical barriers). The water samples with a composition close to that of the parental rocks (andesites of Sijarinska and Tulare) are Sast, Zeb, and Malodj, and those for dacite/andesite (Dajvolja Varos, Dobri Do, Kravarska Planina; Figure 6) are Veldj and Tulg2. These are mostly waters from the shallow aquifers, and the results depicted in the diagram confirm the influence of water–andesite rock interaction. On the other hand, the influence of gneisses on the composition of water is minor.

7. Water–Rock Interactions and Statistical Analysis

The statistical analyses CA and PCA are used in this section to define the influence of the investigated water–rock interactions. The main idea is the use of statistical analysis as a tool that is capable of verifying the hypothesis that the main components originate from the minerals listed in Table 1. At the same time, the results are useful for observing the origin and association of the elements, particularly the trace elements.

7.1. Cluster Analysis

Hierarchical CA (Q mode, Peason method) was carried out by using the concentration of the main components (anions, cations) and the minor elements represented in Table 3.

The results of the CA are shown in a dendrogram (Figure 7). In the dendrogram, clusters are subdivided into four groups, which represent the four types of groundwaters: (I) a group that contains 11 samples (numbered 5–20), (II) a group that contains 9 samples (numbered 16–23), (III) a group that contains 2 samples (21 and 22), and (IV) a group having a single sample (11, Djavv). The first group includes the thermal waters, which originate from a deeper zone of fluid circulation (in the following order: Sijb, Siji, Vicab, Suva, Kurs, Tul1, Tul2, Vicai, Ploc, Prol) as well as Sast (shallow aquifer). The second group includes the samples originating from the shallow zone of water circulation (in order: Mrkv, Vojn, Petr, Tulg1, Tulg2, Zeb, Tulvis, Spon, and Sasb). The third group includes groundwaters also originating from the shallow zone of fluid circulation (Malodj and Veldj). The fourth group represented in the dendrogram (Figure 7) is the water sample originating from a shallow aquifer zone but extracted from propylitized andesite rocks. The grouping trend has a reasonable distribution that is in connection with the difference in the element concentrations depicted between the thermal and the colder non-thermal waters ($HCO_3{}^-$, $SO_4{}^{2-}$, Na, F^-, B, Si, TDS). Moreover, the proof of the contact with volcanic rocks designates the Sast water in the deep circulation sample group. The cluster grouping of the samples Malodj and Veldj (21, 22, Figure 7) is at the closest distance to cluster 4 (Djavv). These water samples were taken at a very short distance from each other, in the proximity of the “Djavolja Varos” area (Djavv). However, the waters originate from the aquifer of unaltered volcanic rocks, in the hypsometrically prominent areas (>1000 m). The lowest TDS values (79 mgL^{-1} and 82 mgL^{-1}) indicate a shorter time and lower intensity of water–rock interaction. These differences make the water samples separate in the dendrogram.

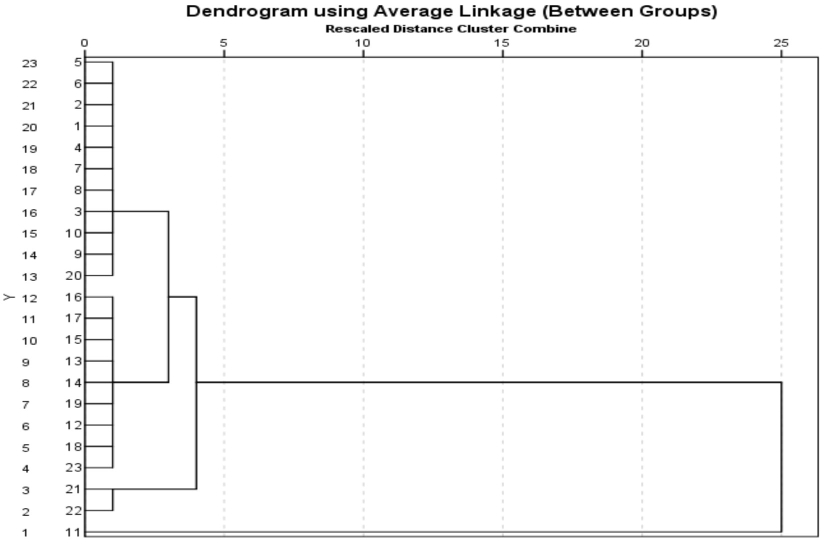


Figure 7. Hierarchical dendrogram of the samples.

7.2. PCA

The results of the PCA (represented as a factor matrix after the Varimax rotation) are given in the following three tables: Tables 6–8. The PCA has been applied separately, taking into account the following: (1) main components (anions and cations) and minor elements (PCA1, Table 6); (2) main components, minor elements, and trace elements (concentrations >DL; PCA2, Table 7); and (3) trace elements (PCA3, Table 8).

Table 6. PCA1.

Element	PC1	PC2	PC3	PC4
Ca				0.969
Mg		0.830		
Na	0.942			
K	0.985			
HCO_3^-	0.941			
Cl^-	0.599		0.647	
SO_4^{2-}		0.974		
F^-			0.883	
SiO_2	0.675	0.664		
B			0.632	
TDS	0.928			

Table 7. PCA2.

Element	PC1	PC2	PC3
Ca			0.933
Mg		0.655	0.648
K	0.957		
Na	0.965		
B	0.644		
Al		0.988	
Fe		0.989	
Mn		0.991	
Li	0.906		
Rb	0.976		
Cs	0.737		0.561

Table 8. PCA3.

Element	PC1	PC2	PC3
Fe	0.990		
Mn	0.987		
Rb		0.902	
Li		0.850	
Ba			0.953
Sr		0.936	
Cs		0.960	
Cr	0.865		
Sc	0.996		
V	0.651		
U	0.927		
Cu	0.992		

(1) According to Kaiser's criterion (eigenvalues > 1), the four main components (PCs) could be identified: PC1 explains 42.4% of the total variance and includes Na, K, HCO_3^-, Cl^-, SiO_2, and TDS. As explained by using the mineralogical composition of the rocks, the reactions (Equations (1) and (2)) and Pearson's correlation coefficient

show that the majority of the elements originate from the aluminosilicates. As more intensive water–rock interaction is present, more silicates will be decomposed. As a consequence, more HCO_3^- ions, $K^{+,}$ and Na^+ will be generated, and a higher concentration of the ions will be present in the water environment (higher TDS values). PC2 explains 20.2% of the variance and includes Mg, SO_4^{2-}, and SiO_2. Sulfates that are formed in the rocks containing sulfides after the oxidation process (Equation (4)) occur in the area of hydrothermally altered rocks (Djavv). As explained earlier, more H_2SO_4 enhanced the decomposition of silicates, and Mg originates from nearby silicates of the andesite complex (Table 1). An evident strong positive correlation between elements Mg, Fe, and Mn (Table 6) confirms the previous observation. PC3 explains 18.2% of the total variance and includes the following elements: Cl, F, and B. These elements can be mobilized after the decomposition of minerals such as biotite and thurmaline. PC4 explains 12.4% of the total variance and includes Ca. The results in Table 1 show that Ca as a lithophile element is a component of many silicate minerals and carbonates. A significant correlation can be observed between the elements represented in carbonates, such as Sr, and Mg, suggesting that the origin of Ca is from the carbonates as well.

(2) PCA2: The results of the statistical analysis (Table 7) are given as the three main components: PC1 (44,9% of the total variance), PC2 (30,6% of the total variance), and PC3 (13,5% of the total variance). The grouping confirms the previous conclusions of the same origin of the elements: PC1 includes elements of the same origin that occur in the carbonated thermal waters: K, Na, B, Rb, and Cs. PC2 includes Mg, Al, Fe, and Mn, whereas PC3 includes Ca, Mg, and Cs. Combined, such a grouping suggests that Ca and Mg also originate from silicates and carbonates, represented by a marble sequence occurring in the schists (Table 1). Cs is a lithophile element that is capable of exchange with K in feldspars and micas, occurring in the thermal groundwaters, which are positioned near the contact with the felsic igneous rocks [15]. As explained earlier, the coefficient of the correlation with a higher significance (between Cs and main components and minor elements, Table 6) suggests the same origin, or an origin from the nearby silicates of andesites and schists. The grouping with Ca and Mg which originate from the major minerals of marble can be connected with the decomposition of minor minerals embedded in the marble fractions of the schists (for example microcline; Table 1).

(3) PCA3 refers to the trace elements detected in the sampled groundwaters. The three extracted PCs are as follows: PC1, representing 51,4% of the total variance: Fe, Mn, Cr, Sc, V, U, and Cu; PC2, representing 31,6% of the total variance: Rb, Li, Sr, and Cs; PC3, representing 9,1% of the total variance: Ba. The grouping of PC1 could indicate the origin (e.g., elements in minerals, apatites, magnetite) and the conditions that are reflected in the concentrations. Additionally, the processes can be related to the main element or Fe and its behavior. It is a well-known fact that Fe, Cr, and V are associated with a number of minerals [80]. On the other hand, Mn and Fe have the same behavior according to the conditions (Eh, pH) that were explained earlier. The concentration of Cu increases only in the sample Djavv. In that manner, Cu represents a valid indicator of the decomposition of sulfide minerals. The grouping in PC2 has been already explained. Barium is not well correlated with elements such as Sr and Ca (Table 8). The correlation coefficient between K, Rb, Na, HCO_3^-, and TDS (0.3–0.6) suggests a connection with the components originating from silicates (e.g., plagioclases, Table 1). However, the separation of Ba from other elements can be interpreted as a possible consequence of the barriers and the conditions that have an impact on the decrease in its concentration.

The PCA results (Tables 6–8) along with the Pearson´s correlations (Figure 5) summarize the two main groups of the elements/components: (1) HCO_3^-—Na—K—Li—Rb—Sr—Cs—SiO_2 as lithophile elements and (2) the SO_4^{2-}—Cl^-—Cr—Fe—Al—Mn—Mg—SiO_2 group of lithophile, lithophile/siderophile elements (Fe, Mn I Cr), as well as S (as SO_4^{2-}), an element that is associated with chalcophile elements. From the geological point of view, the main components and minor elements of the first group are present in the minerals in the aquifers of the LAC and its surroundings (metamorphic rocks—crystalline schists; labeled in Table 1). As the opposite, the other named group of the elements is presented in the volcanic rocks of the LAC and its surroundings, as well as the altered volcanic rocks (labeled in Table 1).

8. Environmental Impact and Applicability of Groundwaters

The concentration level of the toxic elements and PTEs in the waters and the physicochemical characteristics (e.g., T, pH, TDS) would be the criteria for assessing their environmental impact and applicability, which can be defined by using the enrichment factor (EF), MAC, and BG values.

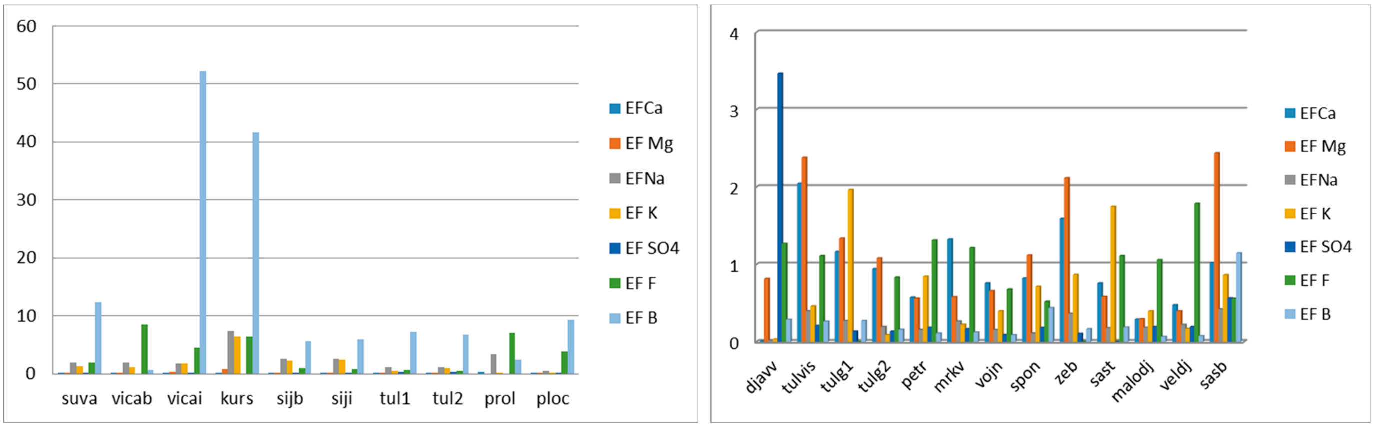
8.1. Enrichment Factor

The enrichment factor (EF) has been used in several studies as an assessment of the anthropogenic influence on the level of contamination of sediments and soils by toxic elements [81] or enrichment of groundwater with toxic elements [55,82,83]. The elements used for normalization ("denominator") in these studies are different (such as Co, Li, Al, Fe, and Sc). In this study, the EF values for the detected trace elements and F and B were calculated to (a) assess the ecological risk and identify the anomalous concentrations in the groundwater (Sc is taken as the denominator) and (b) define the origin of the water in the aquifers (Cl is taken as the denominator). The reference background (BG) values taken into account are the median concentrations of the elements in bottled water in Serbia [59]. These waters originate from different sources, i.e., types of rocks, across Serbia. The justification for using Sc and Cl as "denominators" is as follows: these elements have a good positive correlation with Al and Si, the main constituents of alumosilicates (Supplementary Materials Table S2); there is no industrial use of Sc/Cl in the area, and therefore there is no anthropogenic emission, so they behave conservatively during chemical weathering [55].

8.1.1. Enrichment Factor as an Indicator of the Source of the Water Systems

To define the origin of waters, values of EF ≤ 1 indicate that the contribution is the same as the reference, whereas EF > 1 indicates an external enrichment [64]. The highest EF values for the elements suggest a special contribution of the origin (natural or anthropogenic). Therefore, values of EF > 1 of Na, K, B, and F in the water of deeper aquifers and some waters from shallow aquifers (Figure 8) indicate an external contribution of enrichment with the elements, i.e., intensive water–volcanic rock interactions. The same results were reported by Hernandez Morales et al. (2017) [64].

The highest EF for SO_4^{2-} in the sample Djavv confirms the processes of decomposition of sulfide minerals. The values of EF for SiO_2 are greater than 1 in the samples Sast, Malodj, and Veldj, so the processes highlight the decomposition of rocks of the aquifer bearing andesites/dacite. The water sample Tulvis is enriched with Ca^{2+} and Mg^{2+} cations, suggesting a water–rock interaction in the shallower aquifer embedded into the crystalline schists and volcanic rocks (confirmed by the presence of U earlier).



(**a**) (**b**)

Figure 8. EF for the main components, F, and B as an indicator of the source of the water system in (**a**) deep aquifers and (**b**) shallow aquifers.

8.1.2. Enrichment Factor as a Risk Assessment

The results of the calculated EF values show that there is no enrichment (EF < 1) in the water of the shallow or deeper aquifers with Be, Ba, Rb, Sr, Li, SiO_2, and As. The exception is a severe enrichment with Vicb with Be and a minor enrichment with As (Mrkv and Sast). The EF for Cu only in the sample Djavv indicates moderate enrichment, whereas the values are EF $\leq$ 1 in other samples. Moderate enrichment with Cr is registered in the samples Vicai and Ploc. The EF values for Al show a very severe enrichment (Djavv) and similar severe enrichment (Ploc). In groundwaters of the shallow aquifer, the EF values suggest a moderate to very severe enrichment with Al (Veldj < Malodj < Zeb < Sast). Enrichment with Ge is registered in samples Vicai, Vicab, Suva, and Ploc (moderately severe–severe), whereas moderately severe enrichment with Cs is registered in samples Tul1 and Tul2. The samples Kurs and Suva are moderately enriched with this element.

Regardless of the most abandoned elements (Table 3), it can be noticed that the waters Vicab and Ploc are moderately to severely enriched with F. The EF values in other samples are lower than 1 (no enrichment) or show minor enrichment (Vicai). The EF values for B in the same samples indicate a severe to very severe enrichment. Moderate enrichment with B is registered in Tul1, Tul2, and Suva. Enrichment with Fe is registered in all samples of the investigated area, and the highest values are registered in Tul2, Ploc, and Djavv.

Here, it should be emphasized that the EF values for U in the already mentioned samples of the shallow aquifers (Tulvis, Tulg1, Mrkv, and Zeb) are in the range of 2–7, indicating an enrichment with U.

The observed EF values indicate that the groundwaters of the deeper aquifers of the volcanic complex and in altered andesite rocks, i.e., Vicab, Ploc, Prol, Tul1, Tul2, and Djavv, are more enriched with a wider range of the minor and trace elements. As we explained, the presence of CO_2 (making unstable H_2CO_3) coupled with a higher temperature of groundwaters will promote the leaching of trace elements due to the chemical reactions and alteration of minerals. On the other hand, oxidation of sulfides in the altered rocks of the LAC emanating the range of toxic elements has importance as well. However, the usage of the groundwater and the level of contamination can be assessed by comparing the values of the concentration of the toxic elements with the BG and MAC values.

8.1.3. Contamination Level

As we explained earlier, two main groups of waters are observed across the investigated area: group 1—thermal groundwaters with deeper circulations; group 2—cold groundwaters with shallow circulations. The concentrations of the toxic elements in these waters are not the same, and these waters differ in applicability.

Diagrams show the average values of B, F, and SiO_2 (Figure 9a) and the average values of the minor and trace elements (Figure 9a,b) detected in the groundwaters with deeper groundwater flow ("group 1") and shallow water flow ("group 2"), including the specific sample Djavv.

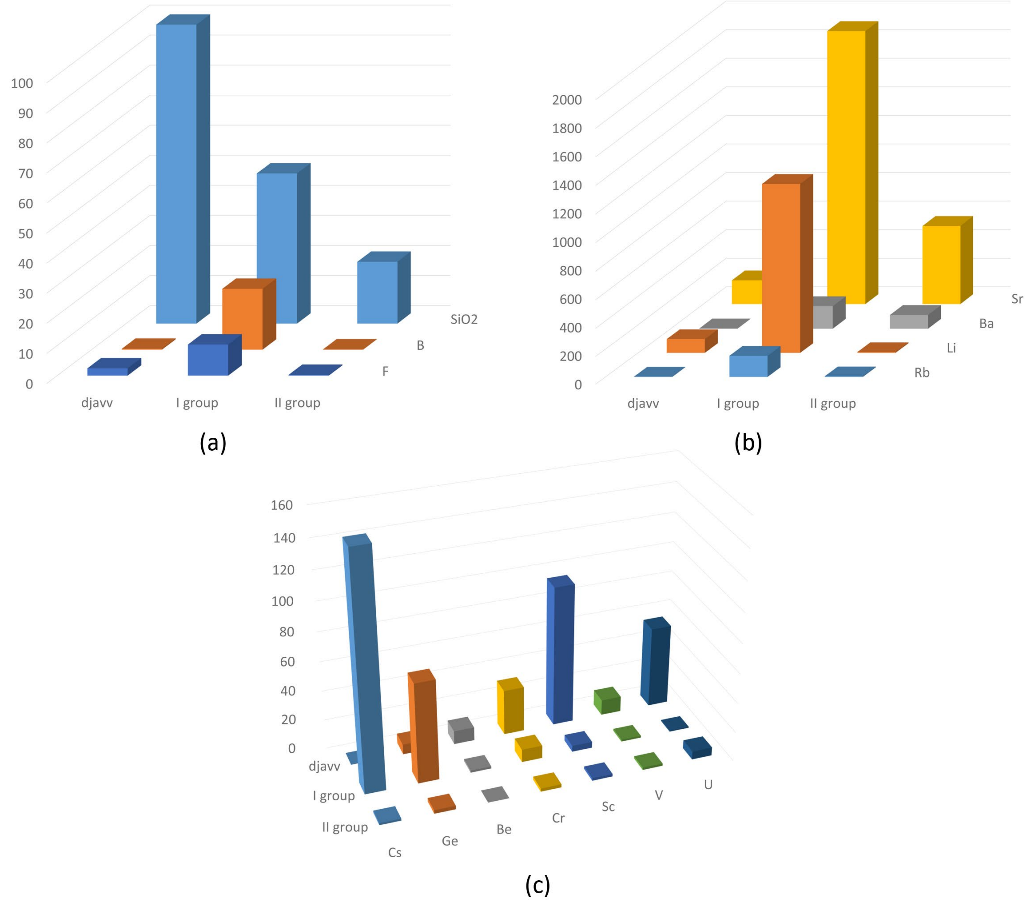


Figure 9. Concentrations of (**a**) F^-, B, and SiO_2; (**b**) minor elements; and (**c**) trace elements in groundwaters (group 1, deep water flow; group 2, shallow water flow and Djavv).

The highest values of the B and F elements are registered in the thermal waters (group 1) (Figure 9a). The values are above the MAC according to the proposal of the WHO (0.50 mgL^{-1} and 1.5 mgL^{-1}). The average concentration of Al is higher than the value of 0.01 mgL^{-1} (in both groups), whereas the concentrations of Fe, Mn, Ba, Cr, and U are lower than the MAC (0.30 mgL^{-1}, 0.40 mgL^{-1}, 0.70 mgL^{-1}, 0.05 mgL^{-1}, and 0.015 mgL^{-1}, respectively). Furthermore, the average values of the elements Cs, Cr, Be, Sc, V, and U (besides B, Si, Rb, Sr, F, Ba, and Li, Figure 9b) are higher than the values of the typical concentrations of these elements in bottled waters of Serbia and Europe [59,60] but lower than the defined MAC.

In summary, such thermal groundwater may present a source of environmental contamination by the elements F and B. Exposure to fluoride in concentrations higher than the MAC value in drinking waters may often induce dental fluorosis. That is particularly usual in the regions of natural sources like volcanic complexes with these elements (e.g., Vranjska Banja) [84]. Boron is an essential trace element that is required for normal plant growth. However, the concentration range between deficiency and toxicity has a rather narrow span. The usage of surface water and groundwater with higher concentrations of boron for drinking and irrigation purposes could pose a potential health risk [85]. Accounting for the cumulative effects in soils and plant uptake, the presence of higher concentrations can damage wheat grains [86]. Furthermore, the presence of B can be an indicator of the ongoing exploration of boron ores [80]. On the other hand, thermal waters with a higher temperature that are exchanged directly in the environment in soils or surface water can be a contaminant in some way. Thus, these waters (except Ploc water, which is cold water) can be used for heating, heat pumps, local agriculture (greenhouses), industrial processes, etc. Additionally, thermal waters containing higher concentrations of SiO_2 (above 50 mgL^{-1}), Sr (above 10 mgL^{-1}), B (above 5 mgL^{-1}), and F^- (more than 2 mgL^{-1}) along with Fe and Rn can be useful for medical purposes [87,88]. The latter elements are present in the higher-temperature waters in the areas of Sijarinska Banja (Siji, Sijb), Kuršumlijska Banja (Kurs), Tulare (Tul1, Tul2), and Viča (Vici, Vicb). These waters have mostly been used for balneotherapy and recreational purposes [87,88]. Prolom Banja Spa (Prol) water is used as bottled mineral water (because of its higher pH value and lower mineralization).

Turning now to the groundwater of the shallow aquifers, there are three different levels of quality and contamination depending on the type of rock and the intensity of water–rock contact/interaction:

(1) The subsurface conditions existing in the propylized andesites (Djavv) promote the leaching of the following elements: U and F (Figure 9a,c) and Cu, Fe Zn, Co, and Ni (Table 2b). Groundwaters with a detected elevated concentration of the latter elements, in combination with the pH values of 2.4, represent a serious source of the contamination of the local environment.

(2) The samples Malodj and Veldj, as water in contact with minerals of unaltered volcanic rocks, in hypsometrically prominent areas (>1000 m above sea level), and with shortened time of the water–rock contact, are of good drinking quality (Table 2a,b).

(3) The waters originating from the aquifer at the contact near the unaltered volcanic rocks (with the TDS value between 189 and 459 mgl^{-1}, As up to 24.2 μgL^{-1}, Zn up to 38.5 μgL^{-1}, F^- up to 520 μgL^{-1}, Fe up to 537 μgL^{-1}, Al up to 647 μgL^{-1}, Cu up to 8.0 μgL^{-1}, and U up to 15.5 μgL^{-1}) can contain some elements above the MDK for drinking water. In the sample Mrkv, the concentration of As is registered to be above the MAC of 0.01 mgL^{-1}. Arsenic is a well-known toxic element [53], and its presence imposes some limits to the eventual applicability of groundwater for drinking purposes. In the sample Tulvis, the maximal value of radioactive element U was registered, approaching the MAC value of 15.0 μgL^{-1}. Thus, some samples can be used for drinking conditionally with regular control.

9. Conclusions

To define the anthropogenic impact on the environment of an area, it is very important to define the natural processes and sources. For that reason, this study provides a methodology that can be useful for (i) observing and defining the sources of the toxic elements or PTEs, (ii) defining the water potential, (iii) developing a mitigation strategy to protect health and the environment from contamination, and (iv) developing plans for the construction of local water supply systems. It can be a procedure pattern, or template, in particular for studies that are related to groundwater areas where both anthropogenic and natural influences could affect the contamination with toxic elements.

The methodology presented in this (hydrogeo)chemical study uses the mineralogical composition of the rocks of the LAC. That includes the simultaneously observed lithophile, chalcophile, and siderophile elements in the rocks and main, minor, and trace elements in the groundwater; the element/ion ratio Cl^-/B, Na^+/Ca^{2+}, Ca^{2+}/Mg^{2+}, HCO_3^-/Cl^-, $Na^+/Na^+ + Cl^-$, and SiO_2/Na^++K^+-Cl; and correlations coupled with a statistical analysis of data.

The conceptual model refers to the following five stages along with results:

I. Observation of the tectonic and hydrogeological setting of the volcanic aquifers belonging to the LAC. For these purposes, in a previous study, we initially provided this information.

II. Observation of the possible anthropogenic sources of contamination with toxic elements.

The investigated area belongs to the National Park Radan. Rural households, hotels, and small livestock plants can be a source of local contamination of groundwater by emanating water with B, Zn, Co, etc.

III. Simultaneous observation of the lithological/mineralogical compositions of the rocks and data of main, minor, and trace elements in the rocks and the water samples is conducted to determine the chemical processes and the conditions that are responsible for the mobility of the elements (especially toxic) and thus their possible natural origin.

The investigated area of the Miocene volcanic rock complex of Lece (LAC) presents volcanic rocks, namely altered and non-hydrothermally altered andesites, and surrounding crystalline schists embedded into the volcanic rocks. Such a complex and varied mineral composition of volcanic rocks and metamorphic rocks (crystalline schists and gneisses) caused the formation of groundwater with very diverse compositions and potentials for use. By observing the concentrations of the main components and the minor and trace elements, we conclude that there are two significant types of chemical reactions: oxidation and hydrolysis (induced by unstable carbonic acid). The presence of the elevated concentrations of the lithophile elements B, F, Li, Sr, Rb, and Cs (particularly in groundwaters with deeper circulations) indicates an intensive water–rock interaction and decomposition of aluminosilicates in the first place (plagioclase, biotite, hornblende, muscovite, etc). The presence of other trace elements, Cr, Be, Sc, V, U, etc., corroborates the chemical reactions occurring between minerals (aluminosilicates, apatite, carbonates of marble fraction, etc.). In the most contaminated water sample, Djavv registered the presence of chalcophile and siderophile elements (Cu, Fe, Mn, Zn, Ni, Co, Cd) and a higher concentration of H_3O^+ and SO_4^{2-} ions/lithophile elements: Ga, Ce, Re, In, Th, Nb, U, and REEs. That corroborates the processes of the leaching of the elements after the decomposition (oxidation) of sulfide minerals and silicate mineral rocks (here induced by a strong acid effect). The radioactive element U is found in concentrations above BG values in the researched waters (in more than 60% of the samples, in the concentrations range of 1.3–54.6 μgL^{-1}). Its presence confirms that the water of shallow aquifers can also be in contact with minerals of volcanic rocks.

IV. After the observation of the chemical composition of water/rock correlations between the elements, grouping is performed to evaluate the origin of waters in different reservoir systems, as well as the origin of the toxic elements therein. We also used it to identify the intensity of water–rock interaction.

In the LAC area, two main groups of groundwaters and five water types are documented: (1) group of thermal waters from deep fluid flow system (under hydraulic pressure) of HCO_3-Na and HCO_3-Cl-Na types; (2) group of groundwaters arriving from a shallow fluid flow system (a) in aquifers in non-altered rocks of HCO_3-Mg-Ca and HCO_3-Ca types. This group includes Malodj and Veldj water with low TDS values and low concentrations of minor and trace elements (<DL), suggesting a short duration of water–rock interaction. (b) Groundwater that is formed in the altered rocks belongs to the SO_4-Cl-Mg type. Besides the long-term contract of circulation of water within deep zones of the aquifer, the processes of cation exchange of Ca^{2+} and Mg^{2+} from water with Na^+ (from minerals such as clays) are responsible for the presence of the HCO_3-Na water type. This study confirmed the presence of Fe and its behavioral influence on the concentration of some elements (Mn, V, Cr, U, etc.). In addition, we implied the possible existence of other barriers that are responsible for the balanced concentrations of elements such as Rb^+, Cs^+, $Li^{+,}$ and Ba^{2+}. Furthermore, the significant influence of the composition and mineralization of groundwater processes during the water–rock interaction diminished the influence of atmospheric surface water. The PCA results along with Pearson´s correlations summarize two main groups of elements: (1) HCO_3—Na—K—Li—Rb—Sr—Cs—SiO_2 and (2) SO_4—Cl—Cr—Fe—Al—Mn—Mg—SiO_2. The main component and minor elements of the first group are present in the minerals in the aquifers of the LAC and its surroundings (metamorphic rocks—crystalline schists). As the opposite, the other group of elements is presented in the volcanic rocks of the LAC and surroundings, as well as altered volcanic rocks. The presence and significant correlations of the minor and trace elements with

elements of typically volcanic origin (Cl, F, B, and V, 20% 0.4–0.5; 80% 0.5–0.996) led to a possible conclusion: the compositions of analyzed waters were dominantly formed by the interaction with minerals of volcanic rocks. Apart from Prolom water, which is formed in the volcanic complex itself, this phenomenon occurs in the water from the schists, in the immediate and closer periphery of the complex. The content of elements of volcanic origin in these waters from the rim of the LAC indicates the presence of volcanic rocks within the schists, i.e., its much wider distribution.

V. Observation of the concentration level of the depicted toxic elements and environmental impact; applicability of the waters and their potential.

The quality and the contamination level of groundwater (of the deep and shallow aquifers) and its applicability depend on the type of rocks and the intensity of water–rock contact/interaction. Thus, in the groundwaters with deep circulation (long term of water–rock interaction), the presence of B, F, and As (Sijb) is registered in concentrations above the MAC values for drinking water. The presence of F and B along with Rn, Si, Sr, etc., and gases (CO_2, H_2S) in mineral and thermal waters with deep circulation (except for Ploc, which is cold) emphasizes medical, balneological, and sports–recreational potential. Today, in this regard, these waters are used in famous spas (Sijarinska, Kuršumlijska, and Prolom spas). Prolom Banja Spa (Prol) water is used as bottled mineral water (because of its higher pH value and lower mineralization). The applicability of other shallow aquifer groundwater systems would be described as follows: Water originating from an aquifer of unaltered volcanic rocks with a shortened time of contact with rocks (Malodj and Veldj) is of good drinking quality. Other waters originating from an aquifer of unaltered volcanic rocks can contain elements above the MDK for drinking water (As, U, Al, and Fe). Thus, some samples (Tulvis, Tulg1, Tulg2, Petr, Mrkv, Vojn, Spon, Zeb, Sast, Sasb) can be used for drinking conditionally with regular control. Finally, the presence of chalcophile and siderophile elements, including H_3O^+, in Djavv water, indicates that this water is a source of contamination of the environment. Therefore, waters originating from aquifers with minerals of hydrothermally altered (propylitized) rocks cannot be used for any purpose.

In summary, the presence of F, B, U, As, Cu, Fe Zn, Co, and Ni in the groundwaters of the investigated LAC area is not of anthropogenic origin. The main source of the contamination is the processes of water interacting with the altered andesites (with the presence of mineralizations), as well as long-term contact with the groundwater within the volcanic aquifers of the andesite Lece complex. The intensity of the contamination of the environment can be increased by ongoing mining activities in the zone of propylitization. Therefore, a strategic plan for further mining activities should be made carefully.

The presented method can be useful in defining the origin of toxic elements, particularly in similar areas. It is useful for differentiating the anthropogenic sources of contamination from the natural ones in areas where both sources exist. The implementation of the concluding remarks should be an attempt to develop a mitigation strategy, prevent the pollution of other aquifer zones, and move water supply systems away. These results of future research would enable a more rational and efficient assessment of the qualitative water potential of the LAC and the applicability of water, plausible planning of regional research and its use, and encouragement of new initiatives for the preservation and protection of human and animal health.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15203653/s1. Table S1. Minor and trace elements in groundwater and Goldshmit classification of elements; Table S2. Pearson's coefficient.

Author Contributions: M.P.S.: conceptualization, formal analysis, methodology, supervision, validation, visualization, writing—original draft. G.M.: conceptualization, project administration, formal analysis, methodology, supervision, validation, visualization, writing—original draft. D.S.: visualization, writing. S.S.: supervision, statistical analysis, validation. I.J.: formal analysis. M.M. and N.O.: visualization, formal analysis. All authors have read and agreed to the published version of the manuscript.

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