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Research Article

Boron Isotopes in the Mount Vulture Groundwaters (Southern Italy): Constraints for the Assessment of Natural and Anthropogenic Contaminant Sources

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The Mt. Vulture volcanic aquifer is an important reservoir of effervescent mineral water in southern Italy. This area is included in the Vulture Regional Park and is located on a popular tourist route for its high scenic and ecological value. Unfortunately, signs of anthropogenic impact have recently increased. Among minor elements, boron and its isotopes are considered useful environmental tracers since different anthropogenic and natural sources can be distinguished. In this study, B content and (δ^{11}B) isotope composition were determined in the Mt. Vulture groundwaters. The groundwater chemistry is strongly influenced by input of CO_2-rich volcanic gases, and two different hydrofacies are observed. The first water type (BAW) has bicarbonate alkaline and alkaline-earth composition and relatively low salinity, whereas the second one (HSW) has bicarbonate-sulphate alkaline composition and higher salinity. The HSW are enriched in boron and have low δ^{11}B values (from −9.6‰ to −4.3‰) similar to those measured in the local magmas suggesting that B contents in these waters are influenced by prolonged interaction between local meteoric water and volcanic rocks. As to BAW, a wide variability in B concentrations (from 14 μg/l to 769 μg/l) and B isotope composition (from -16.1‰ to +23‰) has been observed. A possible anthropogenic input is thought to be responsible for such variability. The water samples with high B concentrations and negative δ^{11}B values (−12.2‰ to −16.1‰) are probably influenced by agricultural activities; for water samples characterized by positive δ^{11}B values (from +5.8‰ to +7.9‰) and low B contents, a slight contamination by sewage effluents cannot be excluded. These conclusions are also supported by B/Cl molar ratios ($7.8E-3$ to $1.6E-2$) different from those of the HSW group ($1.1E-2$ to $7.0E-2$). This study highlights that also in the Mt. Vulture volcanic area B isotopes coupled to the B/Cl ratio can be a useful tool for the assessment of natural and anthropogenic contaminant sources.

1. Introduction

The Mt. Vulture basin is one of the most significant aquifer systems of southern Italy. Its groundwater is an important and valuable resource for potable and mineral water supply and agricultural and industrial uses. In the last years, to satisfy the intensifying water demand, groundwater extraction has been gradually increased. However, signs of anthropogenic impact, especially nitrogen contamination, have recently become evident [1]. Assessing the processes controlling groundwater quality is essential for an effective water resource management and protection, especially in the Mt. Vulture area which has an important role for both the local economy and water supply of the whole Basilicata Region. Usually, an isotopic approach can provide information on the type of pollution and on its possible origin. Among minor elements, boron and its isotopes are considered useful environmental tracers for this purpose. Boron is geochemically very mobile and soluble, and in the aqueous environment, it may be as both borate ion ($B(OH)_4^-$) and boric acid (H_3BO_3). Typically, low-saline groundwaters and rivers have low B concentrations (<100 μg/l), whereas saline groundwaters may show high concentrations up to several tens of μg/l [2]. The World Health Organization (WHO)

recommends an upper limit of 500 μg/l in drinking water [3]. The drinking water standard of the European Community [4, 5] and Italian legislation [6] is two times this recommended value. The B dissolved in groundwaters is generally derived by natural sources, related to hydrothermal water sources, weathering of igneous rocks, and leaching from sedimentary deposits of marine and nonmarine origin and seawater intrusion [7, 8]. However, anthropogenic boron input due to manufacturing of glass, ceramics, leather, fertilizers, cosmetics, detergents, etc., as well as municipal wastewater and sewage effluent producing a significant environmental impact, have been demonstrated in surface water and groundwater [8–10]. At lower temperatures, boron can be removed from solution by absorption onto clay minerals and incorporation into secondary minerals [8, 9]. Boron has two natural stable isotopes, ^{11}B and ^{10}B, with abundances of 19.8% and 80.2%, respectively. The boron isotope geochemistry has been used in defining magmatic and hydrothermal processes [11, 12], low-temperature geochemical processes [13], paleo-ocean pH reconstruction [14, 15], and global biogeochemical cycles [16]. In addition, several studies have demonstrated the ability of boron isotopes to detect distinct anthropogenic boron sources in surface water and groundwater systems [17–20]. However, it is not always possible to distinguish agricultural signatures from urban effluents and natural sources only by means of B isotopes because values may overlap. Consequently, other chemical elements or elemental ratios have to be considered along with the B isotope to assess the contaminant sources carefully [20–22]. The B/Cl molar ratio is thought to be a geochemical tracer significantly useful for this purpose. For example, B/Cl values tend to be rather homogeneous for fluids derived from a common reservoir [20, 22], denoting it as a useful tool to discriminate B's origin. With this in mind, the paper focuses on the occurrence and distribution of boron and of its isotopes in the Mt. Vulture groundwaters in order to evaluate B's origin and to distinguish between natural and anthropogenic contaminant sources.

2. Study Area

Mt. Vulture is a Pleistocene stratovolcano composed mainly of pyroclastic deposits and lava flows ranging in composition from foidite, basanites, to phonolites with several intermediate rock types [23, 24]. These products have a strongly silica-undersaturated character with alkaline potassic to ultrapotassic affinities [25]. This volcano is located at the eastern border of the Apennine compressive front, at the western margin of the Apulia foreland (Figure 1). Volcanic activity started at 742 ± 12 ka and continued, interrupted by long-lasting quiescence periods, up to 142 ± 11 ka [26]. In the peripheral sectors of Mt. Vulture, fluviolacustrine deposits of Pliocene and lower Pleistocene age are outcropping (Fiumara di Atella Super-synthem, [27]). The volcanic products lie over Pleistocene gravel and clay, in subhorizontal layers that cover the intensely deformed flysch sediments of Miocene age. The oldest pre-Miocene bedrock units consist principally of deep-sea sediments belonging to units ranging from early Triassic to lower-middle Miocene [28].

The Mount Vulture aquifer, mainly hosted by volcanic rocks, consists of interconnected multilayered aquifer systems, locally confined [29]. The groundwater flow pathways are conditioned by structural hydraulic parameters, anisotropy features of the aquifer, and the existing fracture network [29, 30]. The tectonic discontinuities act as deep preferential groundwater flow and promote the mineralization processes of groundwater occurring within two independent hydrogeological basins, the Monticchio–Atella basin (southern area) and the Melfi–Barile basin (north-eastern area) [31].

The volcano hosts numerous springs and wells emerging at different elevations, especially in the south-eastern and western sectors (Figure 1). The western area of Mt. Vulture is mainly characterized by forests, pastures, and uncultivated fields. Beech forests are widespread at higher altitudes while oak and chestnut trees are found at lower altitudes. Some industrial plants for mineral water extraction are present in a limited area near the Monticchio Bagni site. In the south-eastern area, there are two small villages as well as industrial plants and the agricultural activities are principally related to farming [1].

3. Sampling and Analysis

Waters from 34 springs and operating wells, owned by both companies and private individuals and used for irrigation and drinking water supply, were collected during a single field trip between January and March 2009. The wells have depths between 30 and 250 meters and were drilled into volcanic products (pyroclastic and effusive rocks). The sampling sites were selected based on a previous hydrogeological, hydrogeochemical study [31, 33] and tectonic setting of the investigated area. Waters are mainly located in the Monticchio–Atella basin, fourteen sampling sites in the western sector (Monticchio Bagni area), nineteen in the south-eastern area (near the Atella and Rionero in Vulture village), and only one sample in the north-eastern area of the Melfi–Barile basin. In addition, a single sample of meteoric water, collected at the Monticchio Bagni area in a rain gauge for one month of observation (March 2009), was analyzed.

B concentrations were measured by inductively coupled plasma-mass spectrometry (Element Finnigan) at the Activation Laboratory of Actlabs (Ontario, Canada). The determination of B was performed using the external standard calibration method, employing NIST and SLRS standard reference materials for calibration. The precision of the analytical results, estimated by running triplicate analyses every 10 samples, was 2-5%. The accuracy of the results (±5%) was obtained by analyzing certified reference materials from the Merck Calibration Laboratory. Samples for B isotopic composition were filtered in the field using 0.45 mm filters. Boron isotopic composition was determined by negative-ion thermal-ionization mass spectrometry (N-TIMS), direct loading procedure at the Isotope Science Laboratory of University of Calgary (ISL-UC), following the methods described by Gaillardet [34]. The external reproducibility of $\pm 1\delta$ ($2\sigma_{\text{mean}}$ corresponding to $2s/n^{0.5}$, where $n = 3$ replicate analyses) for the B isotope measurements was

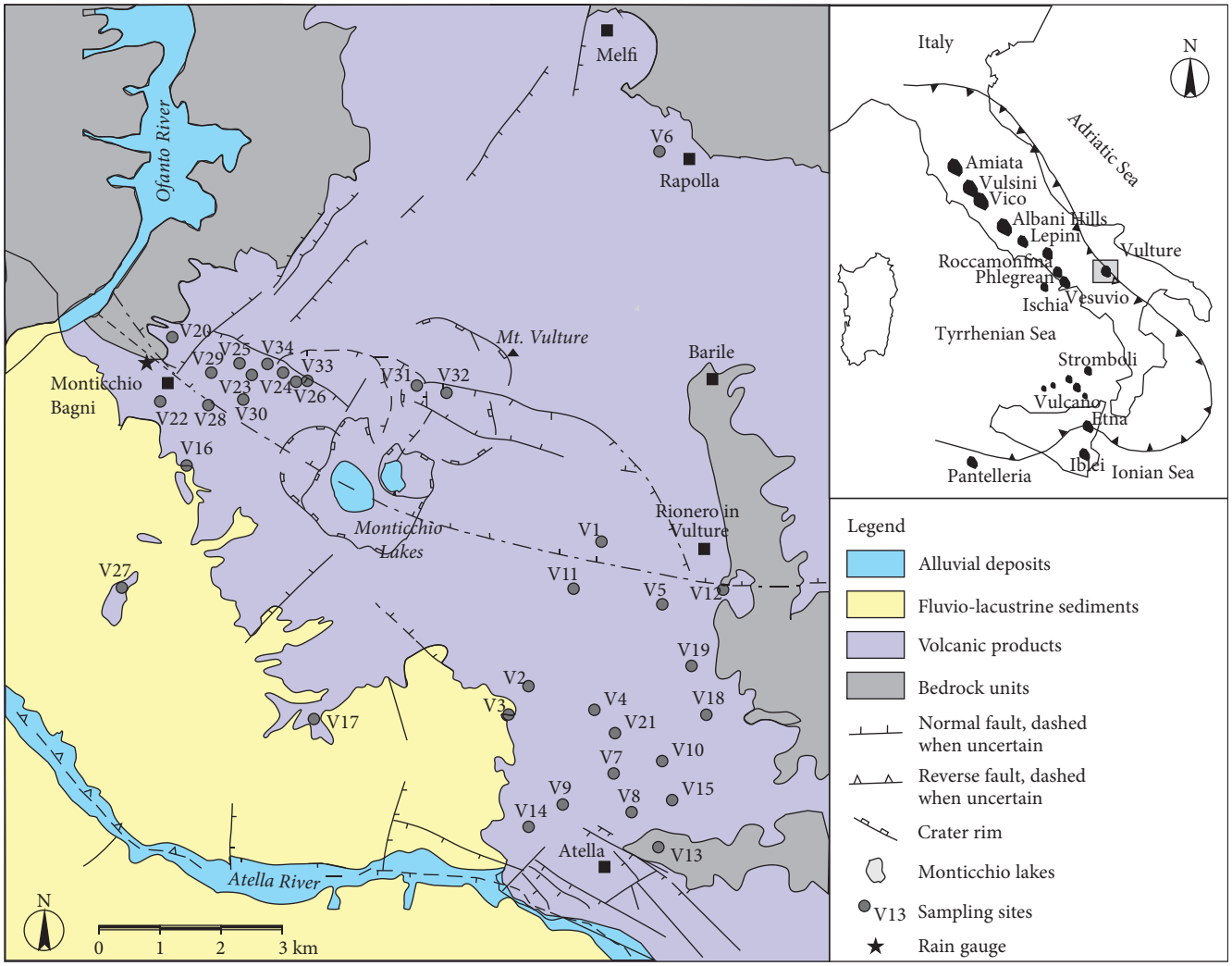

Figure 1: Geological sketch map of the Mt. Vulture area (modified from Giannandrea et al. [32]). The localization of sampling sites (grey circles), rain gauge (star), and code of the water samples are shown.

determined by replicate analyses of the NIST-SRM 951 standard. The B isotopic composition was measured with an average analytical precision (2σ) of $\pm 1\delta$‰. The boron isotopic compositions are expressed as per mil differences relative to mean $^{11}B/^{10}B$ ratios of 4.00125 determined for the NIST-SRM 951 boric acid standard.

4. Results and Discussion

4.1. Groundwater Chemistry. According to previous papers [1, 33, 35], in the Mt. Vulture area two different types of groundwater are distinguished on the basis of physical-chemical parameters and concentrations of dissolved chemical components. Most of the investigated waters have a bicarbonate alkaline-earth and alkaline composition (Figure 2). These waters show temperatures ranging from 8.8°C to 19.9°C and electrical conductivity (EC) from 140 to 1940 μS/cm. Bicarbonate is generally the main anion in solution with concentrations ranging between 66 and 1763 mg/l with an average value of about 508 mg/l [33, 35]. During basalt weathering, CO_2 is converted into bicarbonate, showing a positive correlation with the concentration of major and minor elements. The composition of bicarbonate alkaline-earth and alkaline waters (hereafter BAW) is principally due to low-temperature leaching of the host volcanic rocks [35]. The other investigated waters are bicarbonate–sulphate–alkaline (hereafter HSW) in composition and show high salinity [31, 33, 35] and 1183 to 16,400 μs/cm EC values that are higher than in the previous group. The temperature values range from 15.1 to 17.4°C. Such high-salinity springs are enriched in sodium and sulphate with respect to average groundwater composition and have the highest concentration of dissolved CO_2 that are likely due to the ongoing active, magmatic-mantle outgassing [36–38]. The HSW group is related to prolonged water circulation in alkali and feldspathoid-rich pyroclastic layers interbedded with clay deposits [33]. Previous studies [1] revealed an inhomogeneous distribution of NO_3 concentrations in the Mt. Vulture area. In the western portion, N input has been associated with an organic soil component only. In the south-eastern part, a

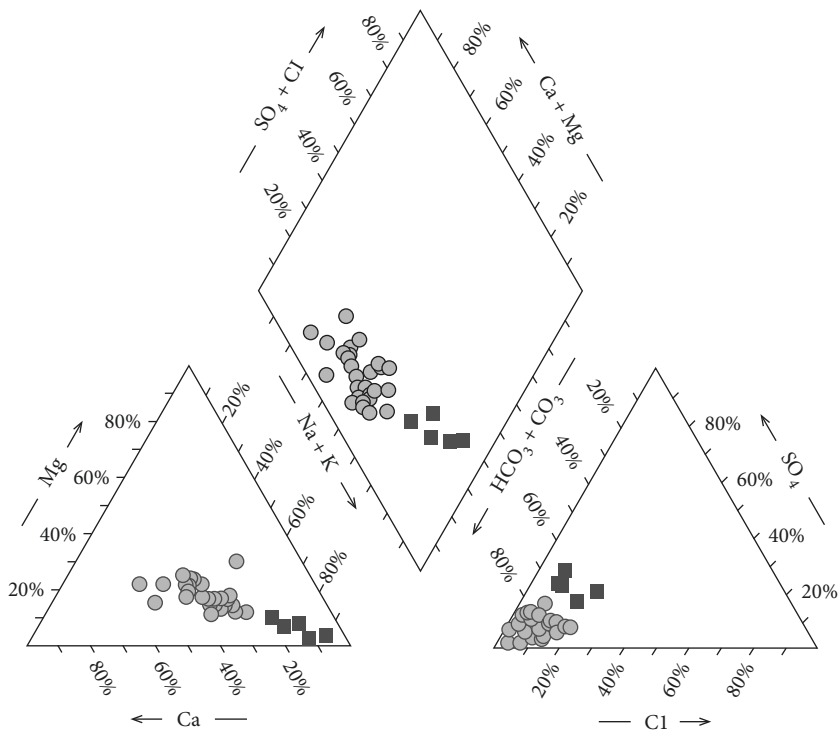

Figure 2: Piper diagram. Circles are for bicarbonate alkaline-earth and alkaline water (BAW) while squares represent the bicarbonate-sulphate-alkaline waters (high-salinity water, HSW). Data are from Parisi et al. [31, 33].

possible anthropogenic contamination (mainly derived from use of inorganic fertilizer) has been documented. Relative to groundwater origin, stable isotopic data of δ^{18}O and δD highlight that these groundwaters are meteoric in origin and they are not significantly affected by seasonal variations [39]. According to the local vertical isotopic gradient (0.17‰ for δ^{18}O/100 m) defined by Paternoster et al. [39], the meteoric recharge altitude of Mt. Vulture groundwaters is between 800 and 1200 meters above sea level.

4.2. B Concentrations and Isotopes. Boron contents and δ^{11}B isotopic values of the studied waters show a wide variability (Table 1). Boron concentrations range from 14 to 5130 μg/l, with an average value of 556 μg/l (Figure 3(a)). BAW samples of the western area range from 14 to 652 μg/l, with the only V30 sample having B contents higher than those in the WHO guideline (500 μg/l). BAW samples from the south-eastern area have B concentrations between 45 and 769 μg/l. V01 and V20 samples record B concentrations higher than those in the WHO guideline. The highest B concentrations (from 746 to 5130 μg/l) were observed in the HSW samples. Among these, V6, V14, and V17 samples have B contents higher than the maximum admissible concentration (1000 μg/l) by drinking water Directive 98/83/EC [5] and the Italian legislation [6]. Generally, the Mt. Vulture groundwaters have higher B concentrations compared with those in other volcanic systems in Italy [40, 41]. The δ^{11}B values range from −16.1‰ to +23‰ (Figure 3(b)). BAW samples from the western area have δ^{11}B values from −6.6‰ to −1.6‰. Among these, only two samples (V31 and V32) show both a significant enrichment in heavier boron isotopes (+17.8‰ and +23‰, respectively) and the lowest B concentrations (18 μg/l and 14 μg/l, respectively), similar to the local meteoric water (RW, Table 1) analyzed in this study (δ^{11}B = +26‰ and B = 12 μg/l). In the south-eastern area, based on B contents and δ^{11}B values, two BAW subsets can be identified: (a) groundwaters having B contents lower than 70 μg/l and positive δ^{11}B values (from +5.8‰ to +7.9‰), (b) groundwaters with B concentrations higher than 70 μg/l and negative δ^{11}B values (from −16.1‰ to −1.9‰) (Figures 3(a) and 3(b)). Finally, HSW have the highest B contents (from 746 to 5130 μg/l) and low δ^{11}B values (from −9.6‰ to −4.3‰).

4.3. Origin of Boron. In nature, different B reservoirs exist (mantle-derived volcanic rocks: −10‰ < δ^{11}B < 0‰, marine carbonates: +10‰ < δ^{11}B<+30‰, altered oceanic crustal rocks: 0‰ < δ^{11}B<+25‰, old continental rocks and siliciclastic sediments: −15‰ < δ^{11}B<+5‰, seawater: δ^{11}B~ + 40‰) with wide ranges of B isotope composition that sometimes overlap each other [41]. According to D'Orazio et al. [42], the Mt. Vulture volcanic rocks display negative δ^{11}B values (ranging between −9.6‰ and −5.6‰) that are strongly consistent with values of the HSW group (−9.6‰ and −4.3‰) suggesting that the water-volcanic rock interaction is the main process controlling the chemical composition of the HSW samples. The aforementioned silica-undersaturated volcanic products are thought to represent the main source of B also in the BAW group

Table 1: B concentration and isotopic composition of the Mt. Vulture groundwaters.

Sample no.	Long. (north)	Lat. (east)	Elevat.	Type	CH	T* (°C)	EC* (μS/cm)	pH*	δ^{11}B (‰)	B (μg/L)	B/Cl [1]
V1	4531210	555380	545	W	BAW	13	350	6.6	−5.1	504	4.8E − 02
V2	4528490	554302	544	W	BAW	15.2	237	6.8	−2.7	261	6.6E − 02
V3	4528250	554060	600	W	BAW	17.2	233	7.5	+7.9	59	1.4E − 02
V4	4528240	555360	545	W	BAW	15	304	6.1	+5.8	67	1.6E − 02
V5	4535826	556800	686	W	BAW	13.3	202	5.8	+7.6	54	1.0E − 02
V6	4536694	557091	365	S	HSW	17	2910	6.5	−4.3	2210	3.4E − 02
V7	4526900	556320	490	W	BAW	15.3	607	6.1	−13.1	275	9.0E − 03
V8	4526817	556303	490	W	BAW	14.1	478	6.9	−12.7	233	1.2E − 02
V9	4526707	556342	490	W	BAW	13.8	430	6.9	−2.2	175	3.1E − 02
V10	4526605	556340	483	W	BAW	16	291	7.0	+6.7	60	1.0E − 02
V11	4531235	555467	555	W	BAW	13.1	234	6.2	+6.3	57	1.2E − 02
V12	4534820	557160	519	W	BAW	15.7	265	6.5	+7.6	45	7.8E − 03
V13	4525820	555300	474	S	BAW	15.7	763	5.9	−4.5	451	3.9E − 02
V14	4525900	555260	461	S	HSW	15.1	16,4	6.9	−5.8	3470	1.1E − 02
V15	4526955	556359	487	W	BAW	14.7	896	5.9	−9	463	6.3E − 02
V16	4531940	548200	575	S	HSW	15.2	1183	5.9	−6.9	746	6.7E − 02
V17	4526867	551828	449	S	HSW	17	4350	6.5	−9.4	5130	7.0E − 02
V18	4527726	556960	550	W	BAW	15	370	5.9	−1.9	118	1.2E − 02
V19	4527739	556970	552	W	BAW	16.1	362	6.3	−12.2	213	1.4E − 02
V20	4537726	548012	554	W	BAW	18.5	1717	6.3	−16.1	769	1.3E − 02
V21	4526870	556607	493	W	BAW	16.1	435	6.1	−7.1	144	2.3E − 02
V22	4532983	547976	547	S	HSW	17.4	2149	6.2	−9.6	923	5.8E − 02
V23	4533314	549828	566	W	BAW	16.8	750	5.9	−1.6	264	2.7E − 02
V24	4533306	550031	565	W	BAW	18.1	1480	6.0	−5.2	470	3.9E − 02
V25	4533379	549532	657	W	BAW	14	351	6.1	−3.9	91	1.3E − 02
V26	4532938	551154	690	W	BAW	19.5	1147	6.0	−6.1	146	1.2E − 02
V27	4530603	547666	682	W	BAW	18.9	698	5.9	−5.4	246	2.4E − 02
V28	4532832	549658	650	W	BAW	19.9	1346	6.1	−6.6	498	3.4E − 02
V29	4533100	549100	644	W	BAW	19.5	918	5.9	−4.9	355	2.7E − 02
V30	4533672	549815	555	W	BAW	19.6	1940	6.2	−6.6	652	3.9E − 02
V31	4532900	551950	885	S	BAW	9.6	206	7.6	+17.8	18	2.6E − 03
V32	4533066	552194	960	S	BAW	8.8	140	7.0	+23	14	2.5E − 03
V33	4532966	551315	780	W	BAW	15.8	369	5.9	−4.6	84	9.5E − 03
V34	4532930	550040	735	W	BAW	16.5	448	5.7	−4.9	102	1.3E − 02
R35	rainwater								+26	12	

Notes: Elevat.: elevation in meters above sea level; S: spring; W: well; CH: chemical hydrofacies; BAW: bicarbonate alkaline-earth and alkaline water; HSW: bicarbonate–sulphate–alkaline water; EC: electric conductivity measured at 25°C; n.m.: not measured. The location of the sampling point is provided in UTM Zone 33 coordinates using the European Datum of 1950. *Data from Parisi et al. [31, 33], [1]Cl data from Parisi et al. [31, 33].

although the B isotope composition of some BAW samples is different. However, based on hydrogeological issue, the Mt. Vulture volcanic products clearly host all the analyzed groundwaters suggesting a negligible contribution from the other rocks (such as flysch sediments and basement rocks) occurring in the studied area. In order to assess the B origin in the BAW group, a mixing model between the local meteoric water and volcanic-hosted end-member (HSW) has been taken into account. The mixing model can be quantitatively estimated by means of the following equations:

$$B_{\text{mix}} = B_c \times f + B_d \times (1 - f), \quad (1)$$

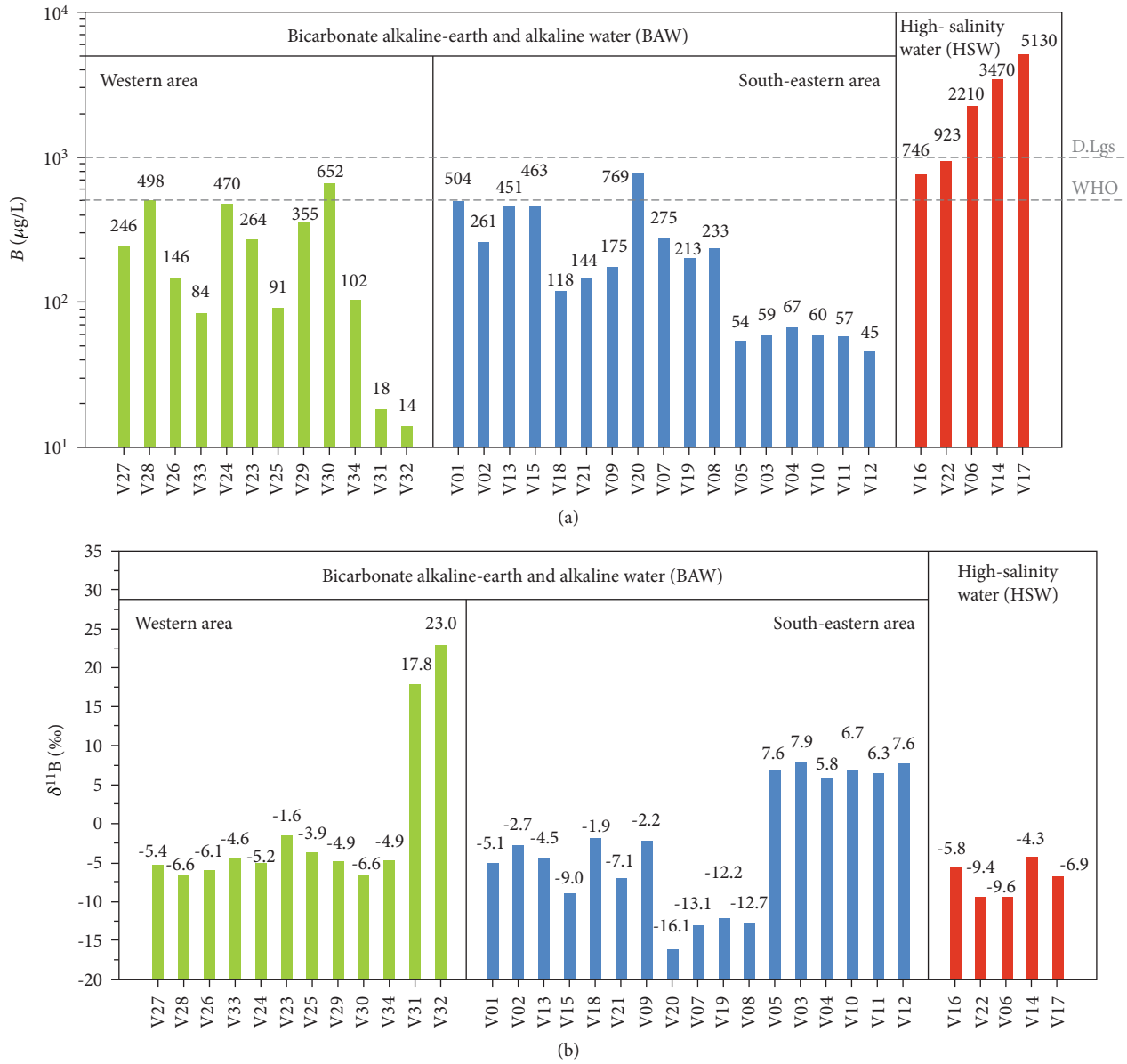

Figure 3: Boron concentrations (a) and δ^{11}B values (b) of the Mt. Vulture groundwaters divided into bicarbonate alkaline-earth and alkaline (BAW) and bicarbonate-sulphate-alkaline (high-salinity water (HSW)) water types.

$$\delta^{11}\mathrm{B}_{\mathrm{mix}} = \left(\delta^{11}\mathrm{B}_c \times \frac{B_c}{B_{\mathrm{mix}}} \times f + \delta^{11}B_d \times \frac{B_d}{B_{\mathrm{mix}}} \times (1-f)\right), \tag{2}$$

where B_{mix}, B_c, and B_d, as well as $\delta^{11}\mathrm{B}_{\mathrm{mix}}$, $\delta^{11}B_c$, and $\delta^{11}B_d$ are the B concentrations and isotopic values of mixing water, local meteoric water, and HSW group, respectively. f is the mixing ratio. For calculations, the composition of the local meteoric water sample (RW, δ^{11}B = +26‰, $B = 12\,\mu$g/l) and the highest and lowest δ^{11}B values of the HSW group were used. In Figure 4, the ML1 and ML2 mixing curves are shown along with investigated water samples. BAW samples of the western area are concentrated in a narrow range within the two mixing curves, suggesting B is mainly sourced from host volcanic rocks. V31 and V32 samples, enriched in heavier B isotopes, fall close to the local meteoric water end-member. Regarding the BAW samples from the south-eastern area, because of their compositional variability, groundwaters fall in different fields suggesting more B sources. Some water samples, similar to the western area BAW samples, lie between the two mixing curves denoting a natural B source due to water-volcanic rock interaction. The V7, V8, V19, and V20 samples, depleted in heavy B isotopes (from −16.1‰ to −12.2‰) and with B concentrations between 213 and 769 μg/l, are far from both ML1 and ML2 mixing curves falling near the MLA mixing curve between local meteoric water and water-soluble anthropogenic boron end-member consisting of synthetic Ca-borate fertilizers

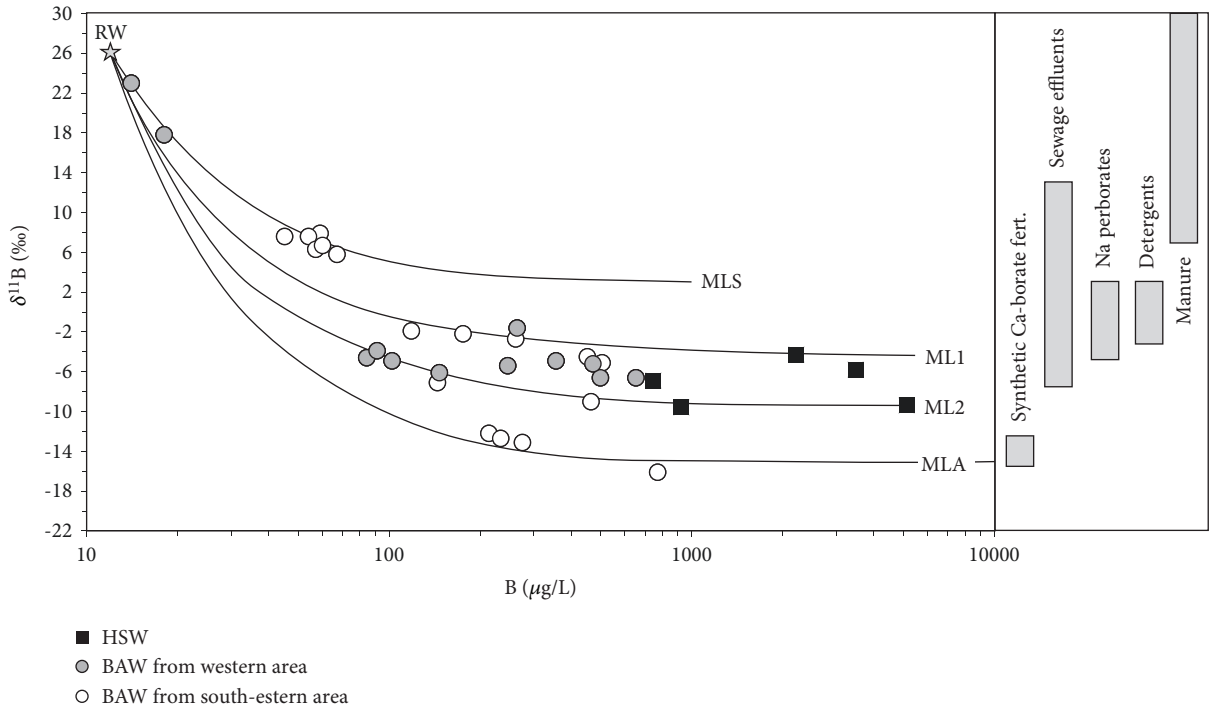

Figure 4: δ^{11}B (‰) versus B content (μg/l) binary plot. ML1 and ML2 curves indicate the mixing between local meteoric end-member (rainwater = RW, δ^{11}B = +26‰; $B = 12\,\mu$g/l) and range of isotopic values of the HSW group (δ^{11}B = −4.3‰ and −9.6‰; $B = 5130\,\mu$g/l). The MLA curve represents the hypothetical mixing behavior between local meteoric water and water-soluble anthropogenic boron compounds (synthetic Ca-borate fertilizers, average δ^{11}B value of -13.5‰ and $B = 30$ mg/l, [21]). The MSA mixing curve is drawn with following data (RW, and sewage effluents with average δ^{11}B value of +2.6‰ and $B = 1000\,\mu$g/l; from Barth [43], Xue et al. [44], and Vengosh et al. [9]). Ranges of δ^{11}B of sewage effluents (−7.7‰ to +12.9‰; [9, 43, 44]), sodium perborates (−4.8‰ to +3.1‰; [2]), detergents (−2.9‰ to +3.1‰; [2]), synthetic Ca-borate fertilizers (−15‰ to −12.1‰; [21]), and manure (+6.9‰ to +42.1‰, [17, 44]) are shown for comparison.

(Figure 4). The Ca-borate and Na-borate fertilizers are the most used synthetic compounds in the agricultural activities and along with sodium perborate, municipal wastewaters, sewage effluents, and landfill leachates represent the main anthropogenic contaminants in the groundwater and shallow water [2, 9]. According to Mongelli et al. [1], in the study area agricultural activities are widely practiced suggesting for these water samples an anthropogenic B origin mainly associated with use of synthetic Ca-borate fertilizers.

As to BAW samples with low B values (less than 70 μg/l), a marked enrichment in ^{11}B is evident (Figure 4). These water samples do not fit the ML1, ML2, and MLA mixing curves, but their path is approximated by a new mixing curve (MLS). The MLS curve is between local meteoric water and groundwater contaminated by sewage effluents (−7.7‰ < δ^{11}B<+12.9‰, Xue et al. [44], Vengosh et al. [9]). The B/Cl ratio also supported this finding. Several studies have revealed that B/Cl ratios tend to be rather homogeneous for fluids derived from a common reservoir [20, 21, 45]. In groundwater contaminated by domestic wastewater, sewage effluents, and other anthropogenic sources (mainly from Na- or Ca–borates), the B/Cl ratios coupled to a distinctive B isotopic signature allow us to distinguish different contaminant sources [20, 21]. For the studied groundwaters, the B/Cl molar ratios were calculated based on Cl data from Parisi et al. [31, 33] and range between $7.0E-2$ and $2.5E-3$ (Table 1). As shown in Figure 5 (δ^{11}B vs B/Cl molar), most of the investigated water samples fall in the field of groundwater in nonmarine aquifers [21]. Two different groups of water samples deviate from the general trend of the measured B/Cl values. In detail, the water samples with low B isotopic values show B/Cl values falling in the range of groundwater contaminated by synthetic Ca-borate fertilizers; the water samples with high B isotopic values are in the field of sewage-contaminated groundwater, although other anthropogenic contaminant sources (i.e., municipal wastewater) cannot be excluded because of overlapping between ranges of their B isotopic values (+5.3‰ to +20.5‰, [2, 46]).

5. Conclusions

B concentration and isotope composition of Mt. Vulture groundwaters were determined to assess B's origin and to distinguish between natural and anthropogenic contaminant sources. In the study area, two water types have been identified. The first type, named high-salinity water (HSW), is characterized by the highest B contents (from 746 to 5130 μg/l), and low δ^{11}B values (from −9.6‰ to −4.3‰), similar to those measured by D'Orazio [42] in the local magmas (from −9.6‰ to−5.6‰), suggesting that prolonged water-volcanic rock interaction is the main B source. The

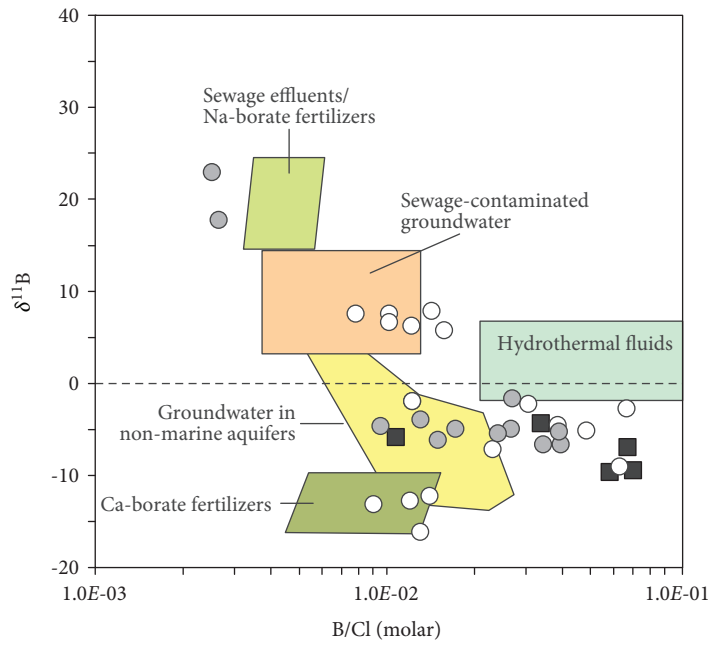

Figure 5: Pattern of typical ranges of δ^{11}B and B/Cl values of potential contamination sources, after Vengosh et al. [21]. Symbols are as in Figure 4.

second water type, named bicarbonate alkaline-earth and alkaline waters (BAW), records a wide variability in the B contents and isotopic values. The δ^{11}B values of the BAW group suggest that boron is mainly derived from leaching of volcanic rocks, although a contribution from local anthropogenic contaminants cannot be excluded for two BAW subsets. The water samples with high B concentrations and the lowest δ^{11}B values can be probably affected by water-soluble anthropogenic boron compounds consisting of synthetic Ca-borate fertilizers; other samples with high B isotopic values show B/Cl values, different from those of the HSW group, falling in the field of sewage-contaminated groundwater. This manuscript highlights that the B isotopes coupled to the B/Cl ratio in the Mt. Vulture volcanic area allow generally to define B's origin and evaluate natural and anthropogenic contaminant sources.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

Preliminary data of this manuscript were presented at the Premier International Conference on Energy, Minerals, Water, The Earth (June 16-21, 2018, Vancouver, Canada).

Conflicts of Interest

The author declares that there is no conflict of interest regarding the publication of this paper.

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