


## Article

# Contaminated Land by Wildfire Effect on Ultramafic Soil and Associated Human Health and Ecological Risk

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**Abstract:** The purpose of this study is the evaluation of fire effect on contaminated land and the assessment of the associated risk of human health and terrestrial ecological receptors. Ash and soil samples were gathered from burned and unburned areas (central Evia, Greece) which are adjacent with a Natura 2000 area. The geochemical dataset includes 20 sampling sites and 35 elements. The wildfire severity was investigated by applying a macroscopic approach and field observations. Statistical and spatial analysis were applied for delineating the distribution of elements in ash and soil. Elemental balance approach was performed for estimating net gain (+) or loss (−) to the ash. Element contents in sampling sites were compared to screening values proposed by the literature. Hundreds of hectares of burned land including wildland areas in central Evia are contaminated with (contents in mg Kg<sup>−1</sup>), Co (up to 43.5), Cr (up to 244), Mn (up to 1158), Ni (up to 463) associated with geogenic sources such as serpentinite peridotites and Ni-laterite deposits. Aluminum, As, Cd, Co, Cr, Fe, Mn, Ni, Pb, V and Zn contents recorded in the sampling sites are posing a potential risk to human health and ecological receptors.

**Keywords:** ultramafic soils; chromium; manganese; nickel; Natura 2000 area; Evia island

## 1. Introduction

Climatically driven wildfire events are expected to increase in response to predicted global warming [1]. Forest fire is a key agent of environmental change through its sensitivity to drought and climatic factors [2]. Fires are widespread in Pinus forests at Mediterranean region and can rearrange the vertical and horizontal distribution of elements in soils as well as mobilization of particulates into the environment. Fire events not only release vast amounts of methane, carbon dioxide and carbon monoxide directly to the atmosphere but also particulates [2]. Furthermore, wildfires are among the natural sources of aerosols containing trace elements [3]. Cadmium has been estimated up to 0.32 mg Kg<sup>−1</sup> in forest fire emissions [3]. Mobilization, geochemical dispersion of toxic elements in soils and sediments, land contamination and associated human health risk is a crucial research field in recent years [4–8].

The redistribution of elements by wildfires is an increasing concern due to the expected increase of frequency of fires worldwide [9]. The fate of elements mineralized or volatilised during the burning of biomass has been the subject of investigation of many researchers [9–16]. Wildfire events are able to remobilize elements into the water-sediment-soil-biota system. This may be more significant in areas where high background contents of elements present in the soil. The factor influencing the genesis of ultramafic soils is the weathering of ultramafic rocks (peridotites, dunites, serpentinites) [17]. Ultramafic soils are found in many places of the world: Costa Rica, Greece, Italy, France, Portugal, Spain, Cameroon, Morocco, India, Japan, Sri Lanka, Brazil, and New Zealand [17]. Elements are mobile immediately after the wildfire event because their surface exposure is increased and their contents

are increased into ash. The mobilization of trace elements after wildfire may be related to increased risk to human health and ecological receptors [10,18]. Wildfire burns nearly  $650 \times 10^6$  ha/year of forest area around the globe [19]. In the Mediterranean region, wildfire events generally occur in the presence of dry conditions which may significantly contribute to the fire severity. In last decades, millions of hectares of forest area were burned in Greece (2007, 2018, 2019), in Australia (2013, 2015, 2016, 2017, 2019), in Brazil (2019) and in the USA (2007, 2013, 2015, 2016, 2018, 2019, 2020). In modern societies, the most known issue related to wildfires is that it is a disastrous phenomenon that can considerably impact human lives and properties as well as ecosystems. However, very little is known related to the role of fire as an additional diffuse source of elements to the water-soil-plant system. Major forest fires in contaminated land may create significant pulse inputs of contaminants to terrestrial and coastal ecosystems by remobilizing elements which were previously deposited on land or absorbed in vegetation [10,20]. While trace elements are essential for the proper functioning of biological systems some of them have toxic effects on living organisms even at low concentrations [15,18,21,22]. Trace element mobility after fire increases the pathways to human ingestion and inhalation [18].

The primary purposes of this study are: (a) to determine the present quality status of the soils with respect to trace elements; (b) to investigate the impact of the 2019 wildfire in Kontodespoti-Makrimalli area; and (c) to evaluate the health and ecological risk of the potential toxic element contents in ash and soil.

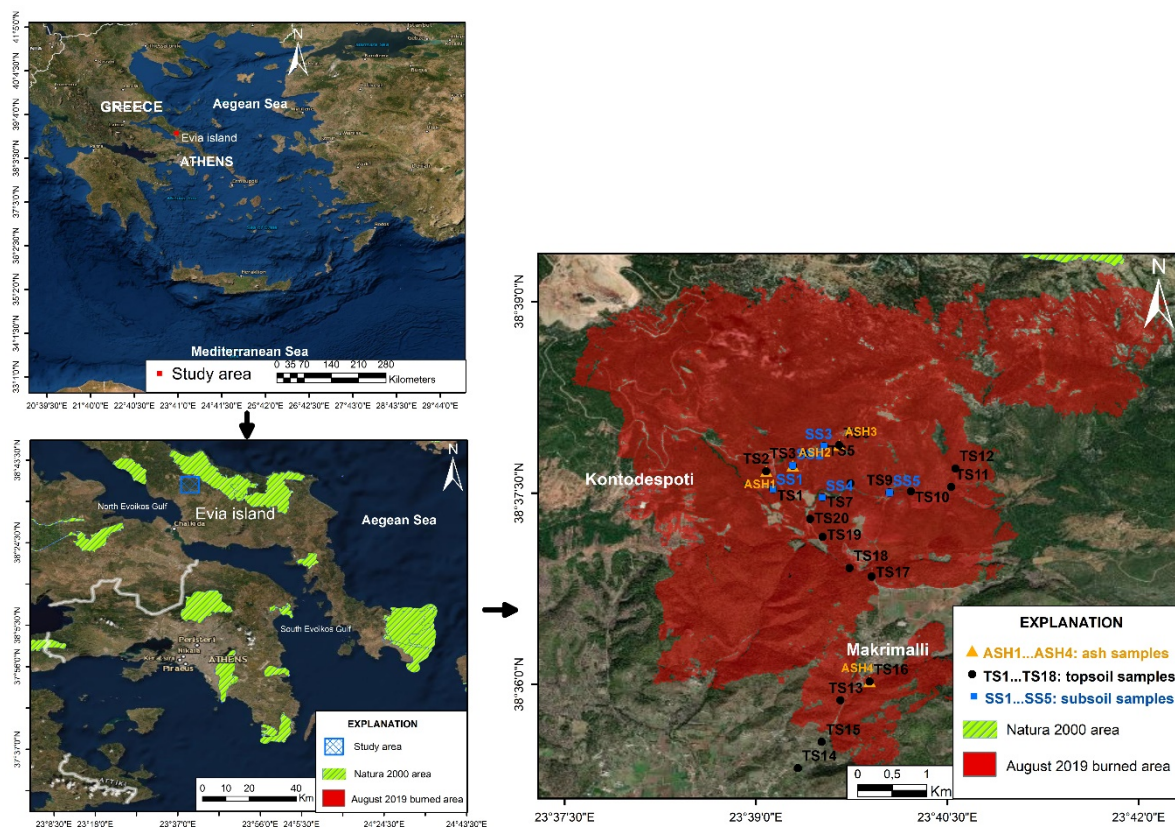
## 2. Materials and Methods

The area studied is located in Evia Island, an island 70 km northeast from Athens and lies between latitudes  $38^{\circ}35'$  and  $38^{\circ}39'$  N and longitudes  $23^{\circ}37'$  and  $23^{\circ}42'$  E (Figure 1). The study area, includes the Kontodespoti and Makrimalli villages and is characterized by mountainous relief. It is adjacent in the north to Natura 2000 area (Site name: Ori Kentrikis Evvoias, Paraktia Zoni kai Nisides—GR 2420011) (Figure 1). *Castanea sativa* trees and meadows cover the area in the peaks, fir forests and Pinus trees in middle altitudes, as well as phrygana, broadleaved evergreen scrub and cultivations in lower altitudes [23]. Important species of fauna of the broader area include [23]: Birds- *Aquila fasciata*, *Circus gallicus*, *Pernis ptilorhynchus*, *Buteo rufinus*, *Falco biarmicus* and *Falco peregrinus* nest in significant numbers. Furthermore, *Bubo bubo* is also found in significant numbers, as well as *Emberiza caesia*.

The wildfire occurred on 13 August 2019 in Evia island (Figure 1), burned four cars and caused evacuations of Kontodespoti and Makrimalli villages while burning hundreds of hectares of forestry. Within the area studied, the wildfire mainly affected [24]: (a) residential (0.1 ha) settlements; (b) arable land (7.5 ha); (c) permanent crops (49.2 ha); and (d) heterogeneous cultivated areas (72.3 ha), forests (918.7 ha), shrub and herbaceous vegetation association (1302.8 ha).

The geological formations outcropping in the broader area from top to bottom are [25]: (a) Flysch of Paleocene age which is composed of clastic sediments and limestone intercalations that form its lower part; (b) Upper Cretaceous limestones; (c) Upper Triassic–Lower Cretaceous chert formation consists of schists, sandstones, red cherts and ophiolitic outcrops which are consisted mainly of serpentinites and peridotites; and (d) Upper Triassic–Middle Jurassic limestones.

The Ni-laterite deposits underlying the transgressive Upper Cretaceous limestones occur in the form of lens-like layers on the weathered surface of peridotites and serpentinites mainly in the north part of the area studied. Ni-laterite deposits include mainly goethite, hematite, Ni-silicate hydroxide and magnetite [25,27]. Neogene and Quaternary alluvial deposits are rich in weathered ophiolite material. In the sampling sites of the area studied, the following formations were recorded from top to bottom: (a) Neogene and Quaternary deposits; (b) Upper Cretaceous limestones; (c) Nickeliferous deposits; and (d) peridotites and serpentinites.



**Figure 1.** Location map showing area studied, Natura 2000 areas, wildfire impacted area and spatial distribution of ash, topsoil and subsoil samples (modified from [23,24,26]).

The sampling campaign was conducted on 7 and 8 of September 2019. There is no observed rainfall event between the wildfire event and the sampling campaign according to NOA-National Observatory of Athens. Ash, topsoil (0–5 cm depth) and subsoil (5–30 cm depth) samples were gathered from 20 sampling stations of the Kontodespoti and Makrimalli areas (Figure 1). A total of 18 topsoil, 5 subsoil and 4 ash samples were taken from burned areas; while 2 topsoil samples were collected from unburned areas. Sites were selected to sample the range of geological formations, vegetation, burn severity and land use. Since ash was recorded in the area studied as patches of brown, grey and white color, it was collected randomly from the Kontodespoti-Makrimalli area. Ash samples were gathered from locations where an ash layer thicker than 1 cm was deposited to limit any soil or other contamination. Metal free tools were used for the sampling procedure. Sampling procedures applied in this study were reported in more detail by Alexakis [10] and Alexakis et al. [11].

For estimating the combustion temperature in the wildfire affected area, a method was applied at the field which is based on the macroscopic comparison of ash colour in each sampling station with the Munsell® soil colour chart [28]. Many researchers [10,12,29–31] applied this method for estimating the combustion temperature and fire severity at sampling sites.

All ash and soil samples were dried indoor at temperature lower than 25 °C for one week, sieved firstly to <2 mm and secondly to <0.2 mm using nylon sieve cloths. Then samples were digested with aqua-regia acid solution (HCl: HNO<sub>3</sub>; 3:1 v/v) in a graphite heating block, further treated by applying a protocol which is described by Alexakis [10] and analysed by using inductively coupled plasma-atomic emission spectrometry (ICP-AES) for the elements: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Sc, Sr, Th, Ti, Tl, U, V, W, and Zn at the ALS OMAC Laboratories Limited (ISO 17025: 2005 Accredited). The Montana Soil Reference Materials (SRM) SRM 2710 and SRM 2711 obtained from the National Institute of Standards and Technology and an in-house soil reference material were used to monitor the chemical analysis procedure. The element

contents of soil reference samples were routinely measured to determine analytical errors (accuracy <10%). The 10% of the measurements of the soil samples were performed in duplicate (precision 2–3%)

An elemental mass balance model was applied to estimate net gain (+) or loss (−) to the ash. The applied approach is proposed for the quantification of net elemental changes to the ash of the area studied where elements can be inherited (from vegetation ash or dust), lost (during burning combustion), or conserved (not lost or inherited in relation to other elements). This approach has been applied by many researchers worldwide [2,32,33]. The elements Al and Fe are selected as the stable indices for the estimation of elemental gains and loss during burning because Al and Fe are not susceptible to combustion [2]. Harden et al. [2] reported that Al shows the following characteristics: (a) it is less abundant in organic than mineral compounds; and (b) it is a non-combustible element.

Iron present the following characteristics [2]: (a) participates in pyrogenic reactions; (b) it is not likely combusted during burning; (c) its contents are not associated with Al; and (d) it is a major element in both organic and inorganic compounds.

The total element concentrations in the soil are just appropriate for worst-case scenarios [34]. For this reason, the total element contents in ash, topsoil and subsoil are compared against the most current regulations and standards given from Environmental Protection Agency (EPA) [35], Canadian Council of Ministers of the Environment (CCME) [36] and Department of Environment and Conservation (DEC) [37].

### 3. Results and Discussion

#### 3.1. Element Contents of Ash and Soil

The median values of the investigated 35 elements are tabulated in Table S1 (Supplementary Material). The elements Ag, Bi, Ga, Hg, La, Mo, Th, Tl, U and W in all topsoil, subsoil and ash samples present concentration below the corresponding detection limit (DL). The median values of major constituents of Kontodespoti-Makrimalli ash samples are classified in the following decreasing order: Ca (15.65%) > Mg (3.09%) > Fe (2.67%) > Al (1.37%) > K (0.53%) > Ti (0.095%) > S (0.09%) > Na (0.05%). Major nutrients were inherited from vegetation ash. Alexakis [10] documented the following median values of major constituents in wildland ash of Kineta area (in decreasing order): Ca (14.25%) > Mg (3.07%) > Fe (2.24%) > Al (1.52%) > K (0.49%) > S (0.10%) > Na (0.04%) > Ti (0.03%). The recorded composition of wildland ash from 2018 Kineta wildfire, which also combusted similar type of vegetation with Kontodespoti-Makrimalli area is similar to the observed composition of wildland ash from the area studied. Median values ( $\text{mg Kg}^{-1}$ ) of Ba (130), Cd (0.55), Cu (49), Sb (2), V (29) in ash samples (Table S1; Figure 2) were generally comparable to median values of these elements determined in wildland ash of Kineta area (West Attica, Greece) which is dominated by similar rock types and weathered ophiolite material [10], but the median values ( $\text{mg Kg}^{-1}$ ) of B (180; ~fourfold), Co (27.5), Cr (135), Mn (1003; ~ twofold), Ni (363; ~ twofold), P (2315; ~ twofold), Zn (285; ~ twofold) were higher than those recorded in Kineta area (West Attica, Greece). Differences in the element contents in wildland ash of Kontodespoti-Makrimalli and Kineta area could be attributed to several factors. Factors controlling element variation in wildland ash include, among others, their different affinities to soils, different combustion temperatures and burn severity [2,9]. Odigie and Flegal [38] also reported fire remobilized elements in the soil of Los Angeles National Forest (USA) ( $\text{mg Kg}^{-1}$ ): Co (3–11), Cu (15–69), Ni (6–15), Pb (7–42) and Zn (65–500).



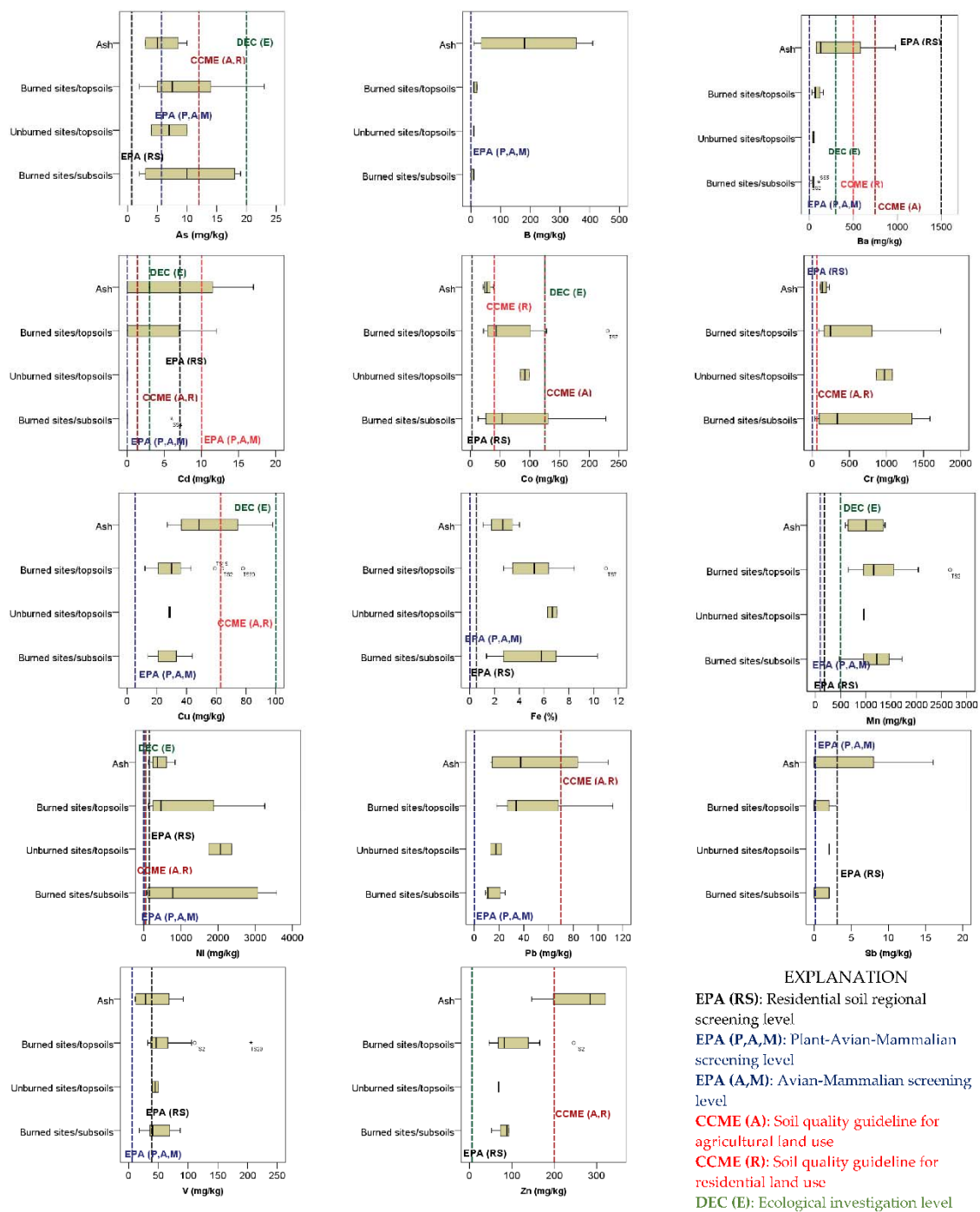


Figure 2. Boxplot comparing element concentrations to criteria given from the literature [35–37].

Moreover, As, Cd, Cr, Cu, Ni and Zn found to increase in burned soils when compared to unburned soils [13,14,16,18]. In fact, forest fire effect on element soil contents tend to be very convoluted. The contents of Co, Cr, Fe, Mg, Ni and P in unburned soil are higher than those in burned soil of the study area (Table S1). Many researchers [20,39] reported transportation, among others, of Cr, Fe, Mg, Ni, Pb, and P via smoke plumes and fine particles ( $PM_{10}$  and  $PM_{2.5}$ ) produced from forest fires, suggesting their escape from the burned sites which can explain their lower contents in burned than unburned soil. The median concentrations of trace element found in burned topsoil of the area studied are in decreasing order ( $mg\ Kg^{-1}$ ):  $Mn > P > Ni > Cr > Zn > Ba > V > Co > Sr > Pb > Cu > B > Sc > As$  (Figure 2 and Table S1). While trace

elements recorded in unburned topsoil of the study area are in the following decreasing order of median concentration: Ni > Cr > Mn > P > Co > Zn > Ba > V > Cu > Pb > Sr > B > Sc > As > Sb (Figure 2 and Table S1). Campos et al. [13] observed in forest soils of north-central Portugal that the contents of Cd, Mn, Ni and Pb were consistently lower in the unburned soils compared with burned soils. Young and Jan [20] recorded a distinct increase in dry aerial deposition of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn along the sections of the southern California coast covered by a forest-like smoke plume. Moreover, after the first rainfall event in forest soils of north-central Portugal, levels of Co and Ni increased during the first eight months [13]. The median values of elements observed in subsoils of the burned area from highest to lowest are Mn > Ni > Cr > P > Zn > Co > Ba > V > Cu > Sr > Pb > Sc > As > Sb > Be (Figure 2 and Table S1).

The primary sources of Co, Cr, Fe, Mn, Ni and Zn for the enrichment of soil and vegetation and subsequently of the ash formed at the area studied are the Ni-laterite deposits, serpentinites and peridotites of Kontodespoti-Makrimalli area. Most of the above-mentioned elements are recorded to be enriched in topsoil. The soil geochemical survey conducted by Vardaki and Kelepertsis [27] in an adjacent area (Triada, central Evia), in which ultramafic rocks and nickeliferous mineralization are also the dominant geological formations, provided useful data about the contaminant levels in soil and vegetation before the wildfire. According to Vardaki and Kelepertsis [27], the heavy metal ranges (in mg Kg<sup>-1</sup>) for soil samples are: Co 40–208, Cr 240–2720, Cu 2–82, Fe 24.000–380.000, Mn 46–1680, Ni 480–4000, Pb 16–56 and Zn 40–144; while the heavy metal ranges (in mg Kg<sup>-1</sup>) for vegetation samples are: Co 1–21.5, Cr 0–24, Cu 0–10.5, Fe 20–680, Mn 10–206, Pb 0–14 and Zn 14–70.

### 3.2. Estimation of the Combustion Temperature and Fire Severity

The Munsell® colour name and code of the ash samples of the study area are the following (Figure 3): very dark brown, grey and white. However, the grey and white ash samples present the highest Ca content (up to 24.0%) and shows that the temperature of the combustion is about 500 °C, which is the highest of the investigated stations. The white color in an ash sample indicates that [12]: (a) the dominant component of that sample is CaCO<sub>3</sub>; and (b) the temperature of combustion is around 500 °C.



**Figure 3.** Illustration of ash samples collected from Kontodespoti-Makrimalli area depicting ash colour and corresponding Munsell® colour code (modified from [28]).

According to Pereira et al. [40], grey and white ash denotes high severity fire. Goforth et al. [41], reported that white ash is the product of complete combustion. Therefore, the wildfire severity at these sampling sites is classified as high. The very dark brown colour is a result of oxidation and dehydration of Fe compounds [12]; while dark ash is the product of incomplete combustion [40]. The very dark brown ash sample present the highest Fe concentrations (4.01%) and shows that the wildfire severity at these sampling sites is moderate. Many researchers [10,12,29,31] applied the macroscopic comparison

of each ash sample with a coloured scale. According to this macroscopic comparison, the wildfire severity of Kontodespoti-Makrimalli area is classified as moderate to high.

### 3.3. Quantification of Net Elemental Changes to the Ash

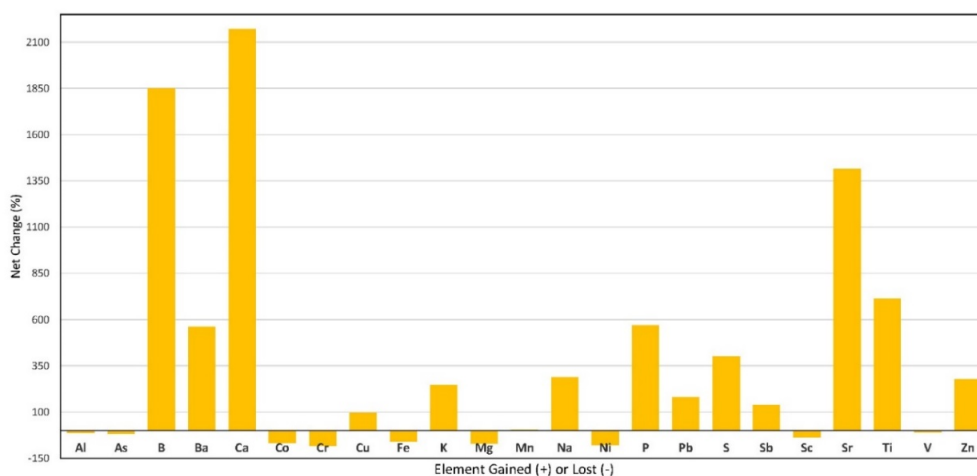
Brimhall et al. [32] proposed a combination of Fe, Al, and Si to be included in the stable constituent S for the calculation of strain and Tau. Since in this study, Si contents are not available, Si is not included in S and Tau calculations. Tau equation which is proposed by Brimhall et al. [32] and revised from White et al. [33] is the following:

$$\text{Tau } C_{(s)} = \left[ 1 - \frac{\frac{C_b}{C_u}}{\frac{S_b}{S_u}} \right] \times (-1) \quad (1)$$

In which *Tau* is the net loss (−) or gain (+) of elements; *S* is the sum of the stable constituents Al and Fe of unburned samples the subscript *b* is burned; the subscript *u* is unburned; *C* is the combusted elements.

Individual combustion calculations for Al and Fe are varying between −11.8 and −60.9%, respectively. These variations between −11.8 and −60.9%, represents: (a) elemental variations in ash; (b) errors of determination; and (c) uncertainties associated with ash inheritance.

Therefore, Tau values within 61% of zero should not be considered as significantly different from zero. Harden et al. [2] has applied this approach to estimate elemental balance in a forest floor located in interior Alaska during an experimental burn. Harden et al. [2] reported that Tau values derived from the calculations of the experiment which were within about ±25% of zero should not be considered as significantly different from zero. Applying approach proposed by Harden et al. [2], absolute values of net changes in As, Mn, Sc and V which are less than 61% should not be considered as significantly different from zero. Net gains relative to Al and Fe were indicated for many elements (B, Ba, Ca, Na, P, S, Sr, Ti, and Zn) (Figure 4). Gains which reflect inheritance onto the ash from ash blow in, and/or vegetation ash were exceptionally elevated for B, Ba, Ca, P, Sr and Ti. The inheritance of small amounts of B, Ba, Ca and Sr may be related to combusted foliage of forest tree species, fire retardants or seawater applied in the area during wildfire fighting. Stone [42] reported foliage B contents in forest tree species varying between 5 and 2400 mg Kg<sup>−1</sup>. Bogunovic et al. [43] recorded after fire an increase of soil Ca<sup>2+</sup>, and can be attributed to the effect of ash and saltwater used for suppression. Moreover, wildfire fighting tools include mainly: (a) ground applications of water added with fire retardants; and (b) aerial application of seawater which according to Hem [44] contains B (4.6 mg L<sup>−1</sup>), Ba (0.03 mg L<sup>−1</sup>), Ca (400 mg L<sup>−1</sup>) and Sr (8 mg L<sup>−1</sup>).



**Figure 4.** Changes in elemental abundance of ash, topsoil and subsoil of the area studied, based on data in Table S1 and calculations of Tau using Al and Fe as S and using composite of unburned samples.

Net losses relative to Al and Fe were recorded for As, Co, Cr, Mg, Ni, Sc and V (Figure 4). It should be noted that data in Figure 4 are Tau-derived calculations of combustion applying the mean values of Al and Fe as the stable component. Arsenic is a volatile element which tend to vaporize and recondense on fine particles [45]. The net losses of Cr and Ni in the ash of area studied can be explained by the pyrogenic remobilization and transportation of fine particles which usually absorb these elements. A similar mechanism of pyrogenic remobilization and transportation of trace elements during combustion and gasification of contaminated biomass is reported by many researchers [20,39,45].

### 3.4. Human Health and Ecological Risk Assessment

However, little work has been carried out to the effects of wildfire on trace elements mobilization from ultramafic soil and the associated human health and ecological risk. Impacts of wildfire in the Kontodespoti-Makrimalli area include emissions of Cr, Cd, Cu, Fe, Mn, Ni, Pb and Zn that vary significantly as a function to topsoil element content and combustion temperature. The median ash, topsoil and subsoil contents for Al and Fe exceed the corresponding criteria [35–37] (Table S1). Therefore, Al and Fe contents observed in ash, topsoil and subsoil of Kontodespoti-Makrimalli area pose a potential risk to human health and plant, avian species.

The median values of burned, unburned topsoil and subsoil for As exceed both the residential soil regional screening levels (RS) [35] and plant-avian-mammalian screening level (P,A,M) [35] provided by EPA; while As median content in ash exceed the EPA (RS) [35] (Table S1 and Figure 2). Exposure to As by inhalation and ingestion can cause developmental abnormalities, hearing loss, peripheral disease, hypertension, cardiovascular disease, hematologic and gastrointestinal disorders, respiratory and renal disorders [16,18,46–48] and range of cancers, including skin, kidney, lung and liver [18,49–51]. Arsenic causes chlorosis and decrease in growth of vegetables [48]. The median topsoil and ash content of Cd exceed the EPA (P,A,M) (Table S1). Median contents of Co and V in topsoil and subsoil exceeds the EPA (RS). The median ash, topsoil and subsoil contents of B and Ba are higher only than the EPA (P,A,M); except only subsoil B contents which are below the detection limit of 10 mg Kg<sup>-1</sup> (Table S1). The median contents of Cd in burned topsoil and ash exceed only the EPA (P,A,M). The role of Co in the formation of vitamin B<sub>12</sub> in the human body and animals is very crucial [52]. On the other hand, exposure of human and animals in elevated Co contents results in heart diseases, allergic reactions and lung diseases [52–55]. The median contents of Co in topsoil, subsoil and ash are higher than the EPA (RS, P,A,M); while the median concentration of Co in topsoil and subsoil are higher than the soil quality guidelines for agricultural use (A) given by CCME [36]. The median Co contents in the subsoil and unburned topsoil are higher than soil quality guidelines for residential land use (R) given by CCME [36] and ecological investigation level (E) provided by DEC [37]. Iron median values in soils and ash of the area studied are greater than the EPA (RS) and EPA (P,A,M). Chronic exposure of vertebrate species and humans in ingesting large amounts of absorbable Fe, can lead to the storage of Fe in the liver; while in severe cases hepatic damage may occur [56,57]. The median values of Cu and Pb in all examined samples were higher only than the EPA (P,A,M). The decrease in plants' chlorophyll content is one of the crucial symptoms of Pb toxicity [58]. According to Jin et al. [59] P toxicity stimulates the growth of lung tumors in mammalian species. Ohnishi and Razzaque [60] reported that P toxicity accelerates the mammalian aging process by reducing survival and inflicting tissue damage. Razzaque [61] concluded that P toxicity due to excessive retention of P in the body can cause various tissue and cellular injuries. The lethal dose of P in humans is not known yet; while common causes of P toxicity in humans include, among others tumor lysis syndrome and impaired renal function [61]. Martin et al. [62] reported that the lethal dose of P for pigs was 35 mmol Kg<sup>-1</sup> of body weight. The median content of Sb in the burned subsoil, ash and unburned topsoil exceeds the EPA (P,A,M). The median contents of Sc in burned topsoil, burned subsoil, ash and unburned topsoil of the study area is 9, 11, 4.5 and 10 mg Kg<sup>-1</sup>, respectively. Elemental Sc is considered non-toxic and there is limited data about Sc testing on animals [63]. Criteria or screening values for assessing human



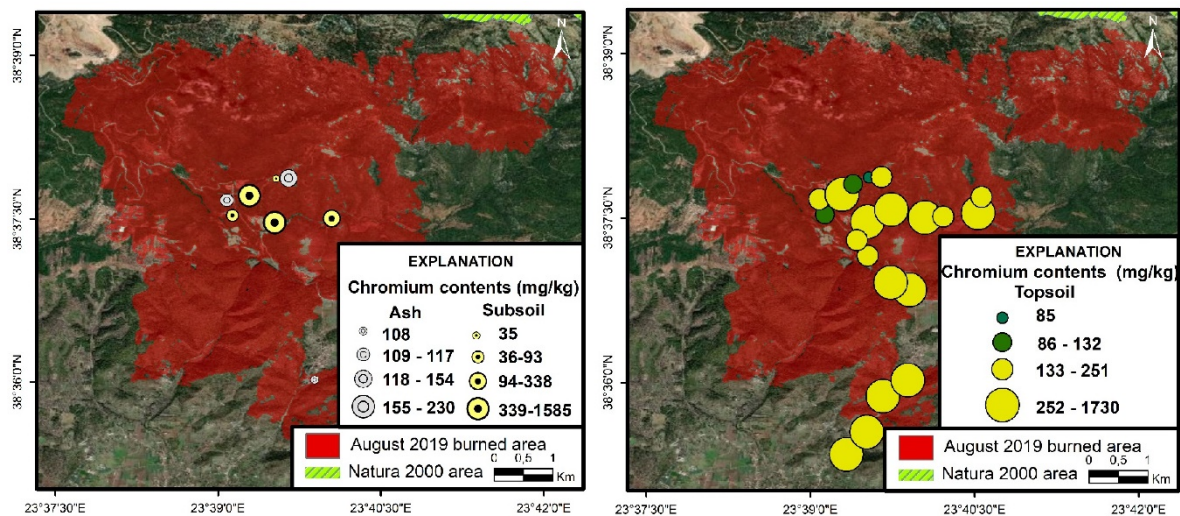
health and ecological risk of P and Sc are not proposed by the literature. Regarding Sr concentration in topsoil, subsoil and ash of the study area, it is lower than the EPA (RS) [35] (Table S1); while soil screening levels are not provided by CCME [36] and DEC [37]. Titanium median contents in topsoil and subsoil is 0.02% (Table S1); while Ti in ash samples is enriched showing median concentration 0.095% (Table S1). The main sources of anthropogenic Ti in the environment are from the combustion of fossil fuels and its behavior in the environment is dominated by its low solubility [64]. Threats to human health related to Ti are negligible because in case that Ti enters the human body by inhalation or ingestion most of the ingested Ti is eliminated unadsorbed [64]. The EPA has not proposed soil screening levels for residential land use or drinking water guidelines for Ti. The median content of V in the burned subsoil, ash and unburden topsoil exceeds the EPA (RS, P,A,M). Moreover, V concentrations of 0.5 mg Kg<sup>-1</sup> or higher in nutrient solutions are deleterious for crop plants [65].

The ingestion of contaminated dust and the dietary trace element intake (cereals and vegetables) are the main human exposure routes in the contaminated areas. In principle, exposure pathways to toxic elements in wild mammals and birds may occur by dermal contact with, inhalation or ingestion of toxic element compounds. Among these exposure pathways, the most important is the ingestion of food because the element contents in vegetation and soil are much higher than the corresponding concentrations in air [66–68]. Since soil and wildfire ash element contents exceeds at least one of the criteria and screening values established by the literature [35–37], it can be reported that the birds (*Aquila fasciata*, *Circus gallicus*, *Pernis apivorus*, *Buteo rufinus*, *Falco biarmicus*, *Falco peregrinus*, *Bubo bubo* and *Emberiza caesia*) which are the main species live in the adjacent Natura 2000 area are under potential risk.

#### 3.4.1. Chromium

Toxicological hazards such as dermatitis and skin ulceration related to Cr compounds have been first recognized in the 1880s [68,69]. Custer et al. [70] found that Cr contents in the birds' livers at the most polluted ecosystem is up to 18.3 mg Kg<sup>-1</sup> dry weight. According to Eisler [71] Cr contents in tissue of wildlife species higher than 4 mg Kg<sup>-1</sup> dry weight may indicate Cr contamination. Outridge and Scheuhammer [68] reported that the few available data indicated that dietary sources are more important Cr sources for wildlife than inhalation. Taylor and Parr [72] proved that Cr contents in the hair, bone and liver of cotton rats inhabiting vegetation of a Cr contaminated area are several times higher than in rats from a pristine ecosystem. Moreover, Reichrtova et al. [73] concluded that *Chinchilla lanigera* after exposed for 6-months to dust aerosols from a waste dump of a Ni smelter, exhibited high Cr contents in all internal organs except the lungs. Regarding absorption of Cr for animals, it is reported that inhaled gases or aerosols are significantly more efficient than the oral exposure [68]. Exposure of wild animals to hazardous levels of Cr, is most likely to occur via ingestion [69]. Contents of Cr in tissues of birds from pristine ecosystems varied between 0.1 and 15 mg Kg<sup>-1</sup> dry weight; while Cr concentration in specimens gathered in polluted ecosystems ranged from 1 to 700 mg Kg<sup>-1</sup> dry weight. Moreover, birds in polluted areas tend to accumulate greater Cr contents than mammals in similar habitats [68]. Chromium is a toxic element targeting the skin, liver and neural tissue [18,74,75].

The median content of Cr in all examined samples was greater than the EPA (P,A,M), CCME (A) and CCME (R). Chromium contents in ash and topsoil of the area studied exceeding the EPA (P,A,M), CCME (A) and CCME (R) are recorded in the entire map (Figure 5). Chromium concentrations in the subsoil of the area studied exceeding the EPA (P,A,M) are recorded in the entire map (Figure 5); while Cr contents in subsoil exceeding the CCME (A) and CCME (R) are recorded only in the central part of the area studied (Figure 5). Chromium contents in ash, topsoil and subsoil exceed at least one of the criteria given by the literature [35–37] and therefore pose a potential risk to human and ecological receptors.

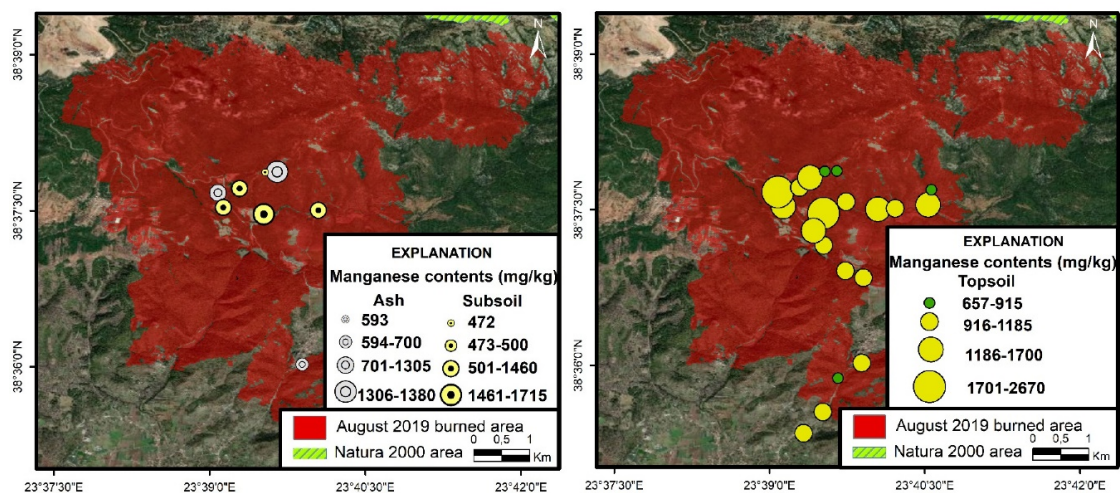


**Figure 5.** Map showing chromium contents in ash, topsoil and subsoil at the area studied (modified from [23,24,26]).

### 3.4.2. Manganese

Manganese is associated with Parkinson's disease and various effects on the central nervous and gastrointestinal system [76]. According to many researchers [77,78], Mn may pose adverse effects on vegetables, including decreased plant growth and chlorosis. Howe et al. [79] performed a research study in various geographical areas recording Mn contents in wild mammals, birds' eggs and tissues. The mean Mn concentration in birds' egg varied between 1 and 5 mg Kg<sup>-1</sup> dry weight; while mean liver content varied between 3 and 11 mg Kg<sup>-1</sup> dry weight [79]. In tissues of wild mammals and reptiles (whole body, kidney and liver) the mean Mn contents were recorded up to 17 mg Kg<sup>-1</sup> dry weight [79].

The median ash, topsoil and subsoil contents for Mn exceed the corresponding screening values given by the literature [35–37] (Figure 2). All the sampling stations present Mn concentrations in ash and topsoil exceeding EPA (RS,P,A,M) and DEC (E) (Figure 6); whereas only at one sampling station the Mn subsoil content did not exceed the DEC (E). Many researchers concluded that Mn is the highest remobilized element in the post-fire soil environment [35–37]. Because Mn concentration in soil and ash is higher than the EPA (RS,P,A,M) and ecological investigation level [37], there is a potential risk to human health and ecological receptors.

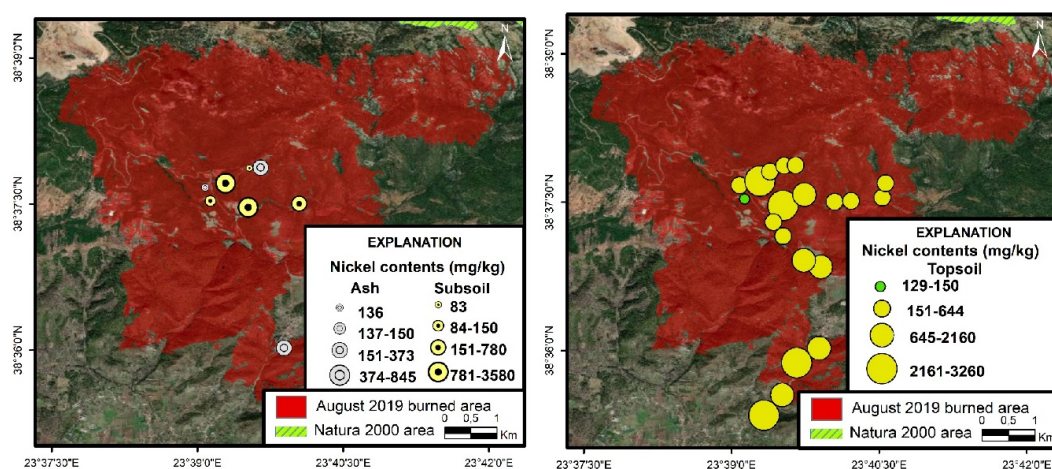


**Figure 6.** Map presenting manganese contents in ash, topsoil and subsoil at the study area (modified from [23,24,26]).

### 3.4.3. Nickel

Nickel affects modifications in DNA bases and is a known neuro-toxic, haematotoxic agent [80]. Symptoms of Ni toxicity in human include asthma and conjunctivitis [81]. Nickel is a potential carcinogen for the lung and may cause lung fibrosis, skin allergies and cancer of respiratory tract [82,83]. In pristine ecosystems, Ni contents in the organs of most bird wildlife species varied between  $\sim 0.1$  and  $5 \mu\text{g Kg}^{-1}$  dry weight; while those in polluted ecosystems ranged from  $\sim 0.5$  and  $80 \mu\text{g Kg}^{-1}$  dry weight [67]. According to Outridge and Scheuhammer [67], most avian species from both polluted and unpolluted areas contained Ni concentrations similar to those in mammal species. Moreover, Outridge and Scheuhammer [67], reported that some bird species bioaccumulated higher Ni contents in polluted ecosystems than in relatively pristine ecosystems. Symptoms of Ni toxicity in plants includes dark brown necrotic spots and reduction in growth [84]. Li et al. [85] performed a study in staple crops grown in Ni-contaminated soil at Xuyi county (China) and concluded that Ni intake from direct soil ingestion was negligible; while there is a potential health risk of staple crops when cultivated in high geogenic Ni areas.

Median ash, topsoil and subsoil concentrations for Ni are greater than the corresponding criteria proposed by the literature [35–37] (Figure 2). Nickel levels in the ash of the area studied exceeding the EPA (P,A,M), CCME (A), CCME (R) and DEC (E) are observed in the northern and southern parts of the area studied (Figure 7). Only at one sampling site the Ni subsoil content did not exceed the EPA (RS); whereas at all sampling sites Ni subsoil concentrations are higher than the EPA (P,A,M), CCME (A), CCME (R) and DEC (E) (Figure 7). Nickel contents in topsoil of the area studied exceeding the EPA (RS) are recorded in the northern, central and southern parts of the area; while at all sampling sites the Ni topsoil contents exceed the EPA (P,A,M), CCME (A), CCME (R) and DEC (E). Because Ni exceeds these criteria there is a potential risk to residents and ecological receptors of the area studied.



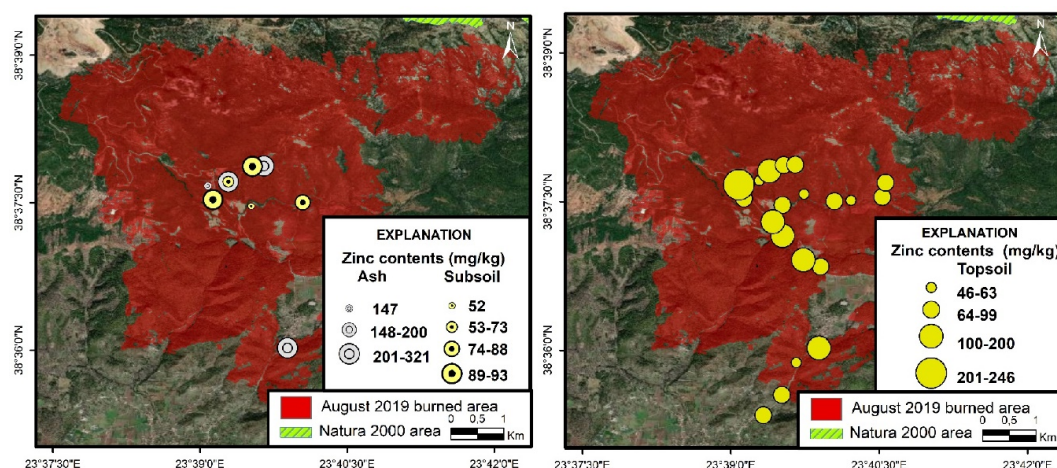
**Figure 7.** Map showing nickel contents in ash, topsoil and subsoil at the study area (modified from [23,24,26]).

### 3.4.4. Zinc

Chronic Zn exposure results in an increased risk of damage to the pancreas and increase of the Low-Density Lipoprotein (LDL) cholesterol concentration and lowering of the High-Density Lipoprotein (HDL) cholesterol and may possibly develop anemia symptoms [18,78]. Zinc causes on plants alteration in the structure of chloroplast and reduction of chlorophyll contents [86].

The median content of Zn in all examined samples exceed only the EPA (P,A,M). Zinc contents in ash, subsoil and topsoil of the study area exceeding the EPA (P,A,M) are recorded in the entire map (Figure 8); whereas Zn concentrations in ash and topsoil higher than the CCME (A) and CCME (R) are recorded mainly at the northern and southern part of the area (Figure 8).





**Figure 8.** Map presenting zinc contents in ash, topsoil and subsoil at the area studied (modified from [23,24,26]).

#### 4. Conclusions

The findings of this study showed that median ash contents for B, Ba, Ca, Cd, Cu, K, P, Pb and Sr are higher compared to the corresponding median values of the underlying ultramafic soil. The wildfire severity of the area studied is classified as moderate to high. The ash composition of vegetation grown in ultramafic soils present elevated contents for Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The net losses relative to Al and Fe for Cr and Ni can be attributed to the transportation of fine particles. Wildfire effect on vegetation grown on ultramafic soil could be a particularly large atmospheric source of Cr and Ni. Consequently, it is hypothesized that the pyrogenic remobilization of Cr and Ni from ultramafic soil and vegetation will facilitate their aerial transportation. Since element contents of topsoil and ash exceed at least one of the plant-avian-mammalian screening levels, the avian species live in the adjacent Natura 2000 area are under potential risk. Aluminum, As, Co, Cr, Fe, Mn, Ni and V in unburned topsoil, subsoil and burned topsoil are higher than the residential soil screening levels or soil quality guidelines for residential land use. Aluminum, As, Co, Cr, Mn, Ni and Zn contents in wildfire ash of the study area exceed at least one of the criteria given by the literature. Manganese is the only element presenting ash, topsoil and subsoil contents higher than all the corresponding screening and investigation levels. Contents of Al, As, Cd, Co, Cr, Fe, Mn, Ni, Pb, V and Zn in the examined samples of the study area exceed one or more of the criteria provided by the literature and subsequently are posing a potential risk to human health and terrestrial ecological receptors.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-445X/9/11/409/s1>, Table S1: Detection limits, median values of thirty-five (35) element contents in topsoil, subsoil and ash samples collected from the study sites compared to levels obtained from the literature (values are presented in mg Kg<sup>-1</sup> except other stated; DL: Detection limit; n.d.: not determined; screening level refers only to avian and mammalian; n.v.: no value; [35–37]).

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