land

MDPI

*Article*

# Mediterranean Wildfires' Effect on Soil Quality and Properties: A Case from Northern Euboea, Greece

**Ifigeneia Megremi [1], Eleni Stathopoulou [2], Efstathios Vorris [1], Marios Kostakis [2], Sotirios Karavoltsos [2], Nikolaos Thomaidis [2] and Charalampos Vasilatos [1,*]**

[1] Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, 15 784 Athens, Greece; megremi@geol.uoa.gr (I.M.); svorris@geol.uoa.gr (E.V.)
[2] Department of Chemistry, National and Kapodistrian University of Athens, 15 784 Athens, Greece; estath@chem.uoa.gr (E.S.); makostak@chem.uoa.gr (M.K.); skarav@chem.uoa.gr (S.K.); ntho@chem.uoa.gr (N.T.)
* Correspondence: vasilatos@geol.uoa.gr

**Abstract:** Physical and chemical soil properties are affected by wildfires. Post-wildfire runoff may contain nutrient loads and particulate matter that negatively impact soil, surface water, and groundwater. According to data from the Copernicus Emergency Management Service, devastating wildfires on Northern Euboea Island, Greece, in August 2021 destroyed more than 50,910 ha. Coniferous and broad-leaved forests mostly covered the affected area, according to CORINE. Topsoil and subsoil samples were collected from burned areas and analyzed for physicochemical parameters: pH, electrical conductivity, and organic carbon. After digestion with aqua regia, the Pb, Zn, Cd, Cu, Mn, Fe, Cr, Ni, Co, and As 'pseudo total' contents were determined. Leaching experiments were conducted to evaluate the levels of potentially toxic elements leaching from soils and the impact of environmental conditions. The leachates were analyzed for Pb, Zn, Cd, Cu, Mn, Fe, Cr, Ni, Co, As, Ca, Mg, Na, and K. Overall, most of the concentrations of the studied elements were higher in fire-affected soils than in unburned ones. Similar findings for element concentrations have been confirmed between topsoils and subsoils, with the latter exhibiting lower values. The increased 'pseudo total' values of Cr, Ni, Fe, Co, and Mn in all the soil samples, along with the medium to high positive correlations between them, indicate that geogenic factors play a major role in controlling element enrichment. High concentrations of Mn, Ni, and As in soil leachates exceeded the EU maximum permissible limits, indicating a potential ecological risk to natural water quality and, subsequently, to human health. The correlation coefficients between elements in fire-affected and unburned soils suggested that their geogenic origins were mainly associated with the ultramafic rocks and related ores of the study area. The elements' concentrations in the leachates were significantly lower than their 'pseudo total' contents in soil, with no correlation between them. The reducing order of elements leachability did not coincide with the decreasing order of elements 'pseudo total' median values in soils. The decreasing order of element abundance in soil leachates coincides with their relative extractability and differs from the decreasing order of their 'pseudo total' median values in soils. Neutral to alkaline, soil pH conditions and organic carbon content, which substantially influence the retention and mobility of elements, presented different patterns among the studied elements, with only Mn, Cr, and Co showing correlations. The increased content of organic matter in fire-affected soils suggests that the combustion of vegetation was incomplete.

**Keywords:** wildfire effects; soil chemistry; element leachability; soil leachates; organic matter

check for updates

**Citation:** Megremi, I.; Stathopoulou, E.; Vorris, E.; Kostakis, M.; Karavoltsos, S.; Thomaidis, N.; Vasilatos, C. Mediterranean Wildfires' Effect on Soil Quality and Properties: A Case from Northern Euboea, Greece. *Land* **2024**, *13*, 325. https://doi.org/10.3390/land13030325

Academic Editors: Rossano Ciampalini, Feliciana Licciardello, Damien Raclot and Armand Crabit

Received: 3 November 2023
Revised: 28 February 2024
Accepted: 1 March 2024
Published: 3 March 2024

**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/licenses/by/4.0/).

## 1. Introduction

Wildfire and forest fire are terms used interchangeably to refer to major catastrophes that occur in forests, grasslands, or prairies. They can be caused by natural factors, such as lightning strikes or human activities such as smoking cigarettes, campfires, or arson.

Wildfires are destructive fires that occur under uncontrolled conditions, while a forest fire is a specific type of wildfire that causes damage to forests globally. Wildfires often develop when weather and environmental conditions make it impossible to manage fires [1,2]. So, wildfires and climate change are closely interconnected, with climate change playing a significant role in the increased frequency, intensity, and severity of wildfires observed worldwide, especially in the Mediterranean [1,2]. Several factors including temperature, soil moisture, the presence of trees, shrubs, and other potential fuel sources strongly impact wildfire risk. Climate change enhances reduced rainfall, longer summer dry seasons, warmer and windier conditions, and eventually extended fire periods [3,4].

Many physical, chemical, mineralogical, and biological soil properties can be affected by wildfires [5]. The quantity and quality of the fuel load determine fire behavior. Different vegetation species in burned forest land have been shown to significantly affect soil characteristics [6].

Low-severity fires can benefit soil properties due to lower temperatures and the loss of nutrients due to volatilization and reduce smoke [7]. The production of carbon-rich ash increases soil organic matter, pH, electrical conductivity, and extractable cations such as Ca, Mg, Na, and some forms of nitrogen such as ammonia, which are crucial for vegetation recovery [7]. Low- and moderate-intensity fires do not consume vegetation entirely. Dehydrated plant parts that are partially burned fall to the ground and are added to the litter biomass, increasing soil organic matter content [8].

Contrary to low-severity fires, high-severity fires consume a considerable amount of fuel and negatively impact the soil. Two important effects include a significant reduction in soil cover [7] and transformations in organic matter composition [9]. Major changes in soil organic matter composition occur at temperatures between 250 and 450 °C [7]. Substantial combustion of organic matter starts around 200–250 °C and ends at 460 °C [5]. Nutrients such as calcium, magnesium, aluminum, and manganese, which require higher temperatures to be volatilized, can be lost by evacuation with ash and smoke when wildfire temperatures reach 1100 °C. Other elements with low volatilization temperatures, such as potassium (>774 °C), sodium (>880 °C) and phosphorous (>700 °C) may be lost by direct volatilization. High-severity fires increase soil pH due to the denaturation of organic acids, increased sodium and potassium oxides, carbonates, and hydroxides, and elevated electrical conductivity due to the mineralization of organic matter. An increase in pH raises the solubility of some cations such as calcium, magnesium, sodium, and potassium while reducing the solubility of others such as copper and zinc [7]. The soil-neutralizing capacity of ash correlates well with the sum of its K, Ca, and Mg contents [5]. The increase in pH is one of the most beneficial effects of prescribed burning, as it affects the availability of the most essential nutrients, especially in low-pH soils [10].

Regardless of fire severity, the combustion of burning organic matter increases soil nutrients such as Fe, Al, and Zn, as well as potentially toxic trace elements such as Ni, Cd, and Pb. As soil organic carbon (SOC) decreases, nutrients increase [11]. Their concentration depends on the severity of the fire and the type of vegetation burned [6].

Wildfires have been shown to release and deposit metals on the soil's surface [3], either directly through vegetation combustion and the mineralization of soil organic matter or indirectly through ash's interactions with the underlying soil [8].

As previously stated, the burned material's composition is one of the variables determining the nature of ash. According to the type of wood wasted in combustion, element concentrations in biomass can vary [3]. Ash produced by wildfires is typically a heterogeneous material comprising oxides, hydroxides of base cations ($Ca^{2+}$, $Mg^{2+}$ and $K^{+}$), which have high adsorption affinity for other metals and metalloids, and, to a lesser extent, major and trace metals that can contaminate soil [7,8,12]. Furthermore, these contaminants can leach into the soil profile or be transported downslope and downstream by runoff, affecting surface water and groundwater bodies and generating a potential ecological risk to benthic biota [8,13].

In 2019, a high-severity wildfire in Croatia was followed by noticeably elevated Cu and Zn concentrations in soils [6]. According to a recent soil study conducted after a wildfire in Greece, Al, As, Co, Cr, Fe, Mn, Ni, and V in burned topsoil were higher than the residential soil-screening thresholds or soil-quality requirements for residential land use, threatening potential harm to human health and the environment [14]. Regarding fire-induced temporal variations of element concentrations in soils, a study conducted in Portugal found that Cu and Pb levels barely changed throughout the study period, whereas Cd, Co, Mn, Ni, and V contents varied depending on the sampling time following the wildfire [8]. A study in Lithuania showed that higher values of some major elements, such as Ca and Mg, were only recorded in the burned area shortly after the fire, regardless of the sampling date. However, the potassium content was always much higher in the burned area [7].

Scientists studying the effects of fire on soil properties are interested in the extent to which heat generated by fire alters the chemical and physical characteristics of soils and affects post-fire properties, such as soil fertility, soil erodibility, or runoff generation [15]. For high-severity wildfires, burning biomass over soil can transfer heat to the soil surface, reaching depths of up to 30 cm [16]. Temperatures can reach about 850 °C at the soil–litter interface; however, in mineral soils, temperatures at a depth of 5 cm do not exceed 150 °C, since dry soil is a good insulator [15,16]. Clay content is a physical characteristic affected by soil heating [17,18]. In general, the mineralogical assemblage is not significantly affected by fire, since the initial step of disruption in most minerals, such as dihydroxylation, occurs at >500 °C [5]. Clay minerals begin to change when soil temperatures reach approximately 400 °C, as clay hydration and the clay lattice structure begin to collapse. In severely burned soils, the complete decomposition of kaolinite can occur in the uppermost layers (1–8 cm depths) and at temperatures of 700–800 °C. At temperatures >300 °C, clays lose $OH^-$ and $H_2O$, whereas temperatures >850 °C result in the formation of anhydrous minerals [19].

According to the technical report Wildfires in Europe, Middle East, and North Africa by the European Commission's Joint Research Centre (JRC) [1], the year 2021 was regarded as significant, with growing international concern about wildfires, their impact on the European Union, and its neighboring countries. More than 5500 $km^2$ of land was burned, 1000 $km^2$ of which was in the Natura 2000 network of protected areas in Europe. The damage caused to many of these invaluable ecosystems will take many years to restore.

Among the five Southern EU countries (Greece, Italy, Spain, Portugal, and France) with longer time series' of available forest fire data (1980–2021), Greece had the worst season compared to previous years. The average fire size in Greece was the largest documented and has increased nearly tenfold since 2020 [1]. A total of 131,254 ha was mapped from 222 fires, including the second-largest fire of over 51,000 ha recorded by EFFIS (European Forest Fire Information System), which burned a significant portion of the island of Euboea. Almost half of the area burned by wildfires that year occurred in August, which was considered the most destructive month. Extremely high temperatures, >39 °C, prevailed in Greece from mid-June until the end of August 2021. Combined with the longest heat wave in 35 years and a prolonged period of drought, these conditions increased the risk of fire danger, resulting in the North Euboea wildfires recorded on 3 and 11 August 2021. Although wildfires encompass uncontrolled prescribed fires too, this is not the case in north Euboea, since 'prescribed fires' have not been employed in the study area as a practice of land management.

In this work, we assessed the impact of Mediterranean wildfires on soil quality and soil properties by (a) evaluating and comparing topsoil and subsoil compositional changes in wildfire-affected areas; (b) estimating the potential effects of fire-impacted soils on human health and the environment through leaching tests simulating natural conditions; (c) discriminating the impact of different origins, besides fire, on soil geochemistry. According to our knowledge, this is the first integrated work examining the overall effects of fire on soil geochemistry (major and trace element composition and leachability capacity), mineralogy, and various soil properties, such as soil pH and organic carbon content.

## 2. Materials and Methods

### *2.1. Study Area*

The study area was strongly affected by wildfires in the northern part of Euboea Island, the second-largest Greek island, Central Greece, in 2021. The fire extended from the Agriovotano municipal district (in the north) to Kamatriades (in the west), Agia Anna (in the east), and Rovies (in the south) (Figure 1). That area is adjacent to Megalo kai Mikro Livari–Delta Xeria in the northwest, a European Union protected area of Natura 2000, and a world-class magnesite mine (Mantoudi municipal district) in the east (Figure 1).

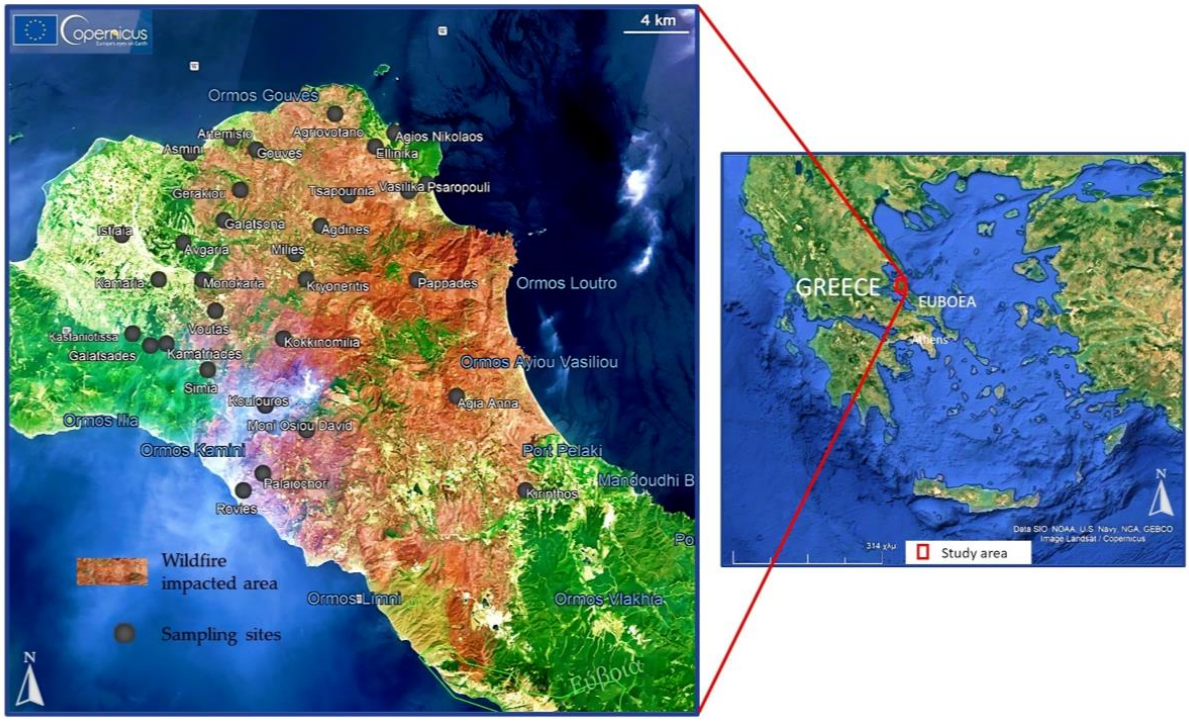



**Figure 1.** Map presenting the study area, wildfire-impacted area, and the spatial distribution of sampling sites (modified from https://www.copernicus.eu/el/node/11160 (accessed on 1 August 2023)).

The primary landcover categories heavily impacted by the wildfires included predominantly coniferous woodlands, a blend of mixed and broad-leaved forests, and to a lesser degree, areas designated for agroforestry practices. Unfortunately, the studied area lacks consistent implementation of targeted forest management practices that could effectively prevent or enhance wildfire management.

Abrupt slopes, downcutting erosion, and a dense drainage system characterize the fire-affected area. Most of the drainage basins were small with small hydrographic networks; however, there are a few large drainage basins covering a significant part of the fire-affected area, including at Gouves, Rovies, Neochori, and Krya Vrysi [20,21]. All studied areas are characterized by a Mediterranean climate on its northern shore, i.e., a decrease in annual rainfall, dry summers, and mild winters [21].

The main geological outcroppings in the study area are peridotites and mafic volcanic rocks, covered by extensive Neogene deposits [20]. Alluvial deposits occur along the drainage networks' major channels and at the mouths of the rivers [22].

### *2.2. Soil Sampling and Analysis*

The soil-sampling campaign was conducted one month after the wildfires. Sampling sites were selected in accordance with the severity and degree of the fire spread in most affected areas (Figure 1). According to the burn severity map of the area [20], all samples came from impacted areas of moderate to high severity. A total of 34 topsoil (0–10 cm

depth) and subsoil (15–30 cm depth) samples were collected from the burned areas. The samples mainly comprised loam-type soils.

The collected soil samples were dried overnight at 45 °C, disaggregated with a porcelain pestle and mortar, and sieved to <2 mm. The finer fraction (<2 mm) was homogenized and pulverized in an agate mill. The soil pH was measured from the sieved fraction of the soil samples. Organic carbon, mineralogical and chemical composition, and leaching tests were performed on the pulverized fraction of the soil samples.

Soil organic carbon content was assessed using the classical Walkley and Black (1934) method. Soil pH was determined by mixing the soil with deionized water in a solid-to-liquid ratio of 1:2.5. A slurry was created by shaking 8 g of soil with 20 ml of deionized water in an orbital shaker at 200 rpm for 15 min, allowing it to settle for 30 min. The pH was measured in this mixture using a Consort 561 portable multiparameter analyzer (Consort, Turnhout, Belgium).

Aqua regia solution extracts 'pseudo total' contents refer to element amounts associated with soil phases such as clays, Fe and Mn-oxides, and organic matter, but not to insoluble minerals such as chromite. A portion of 0.5 grams of soil sample was digested with Aqua Regia (1:3 HNO3:HCl) solution, and the Pb, Zn, Cd, Cu, Mn, Fe, Cr, Ni, and Co contents were determined by FAAS [Perkin Elmer PinAAcle 500 (PerkinElmer, 217 Inc., Waltham, MA, USA)] and ICP- MS [THERMO ICAP-Qc (Thermo Fisher Scientific 218 Inc., Bremen, Germany).

In most extraction schemes, water-soluble metals are extracted as part of the exchangeable fraction, which includes weakly adsorbed elements retained on the solid surface by relatively weak electrostatic interactions. In other words, these are elements that can be released using ion exchange processes and elements that can be co-precipitated with carbonates [23]. Two different batch leaching procedures using natural mineral water (pH 7.67) and surface water (pH 8.40) were used to determine the relative extractability of potentially toxic elements from soil samples at a 4:1 *w/s* water-to-solid ratio. Solutions were maintained under agitation for 48 h in an orbital shaker at 120 rpm. Subsequently, the leachates were centrifuged for 12 min at 3000 rpm and filtered over 0.45 μm membrane filters using a vacuum filtration device. Finally, the leachates were analyzed for Cr, Mn, Fe, Cu, Ni, Zn, Cd, As, Co, Pb, Ca, Mg, Na, and K by ICP-MS [THERMO ICAP-Qc (Thermo Fisher Scientific Inc, Bremen, Germany)].

Multivariate (factorial) statistics were applied to the soil dataset to explain the observed variation in elemental contents (MINITAB ver. 15 for Windows). The input focused on 10 elements, namely Cr, Mn, Fe, Cu, Ni, Zn, Cd, As, Co, and Pb. The data were processed using R-mode factor analysis and applying the varimax-raw rotational technique.

The mineralogical composition of the soil was investigated using an X-ray diffraction spectroscopy powder D5005 diffract meter (Siemens, Munich, Germany). Cu K(alpha) radiation was performed at 40 kV, a 40 nA, 0.020° step size, and a 1.0 s step time. The obtained XRD patterns were evaluated using Bruker DIFFRAC, EVA 2.2 software (Bruker AXS GmbH, Karlsruhe, Germany).

## 3. Results and Discussion

High-intensity wildfires can profoundly affect soil quality and properties, especially when they occur in characteristic and unique ecosystems such as those found in the Mediterranean context. The effects of the 2021 wildfires on soil erosion dynamics for multiple fire-affected areas in Greece, the study area being one of the main case studies, demonstrated a shift toward erosion hazard from very low and low (pre-fire) to severe and very severe (post-fire) [24]. The burnt areas were more susceptible to erosion events than the surrounding non-burnt areas [21]. Valkanou et al. [22] demonstrated a significant post-fire change in mean annual soil loss that corresponded to an increase of 114% compared to the pre-fire natural conditions. The dominant landcover types ravaged by the wildfires were mostly coniferous woodland (31%), mixed- and broad-leaved forest (21.30%), and to a lesser extent, agroforestry land [20,22,25,26].

The Supplementary Materials (Table S1) present 'pseudo total' compositions of soil samples. Topsoils are enriched in Pb, Zn, Cd, and Cr, compared to subsoils (Figure 2). This observation concurs with earlier studies on burnt areas of similar lithology (e.g., [14]).

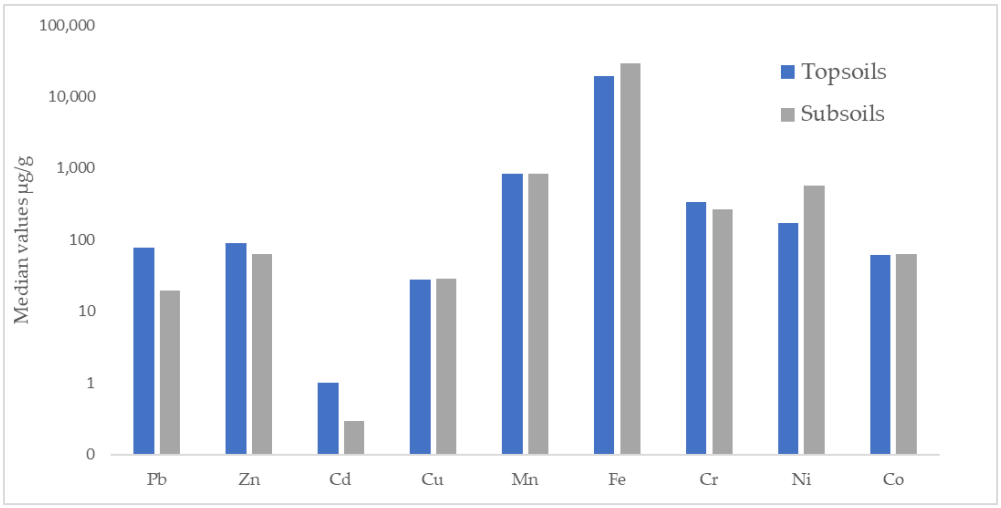



**Figure 2.** 'Pseudo total' contents of topsoils and subsoils.

All soil samples exhibited elevated median 'pseudo total' values of Pb, Zn, Cd, Mn, Cr, Ni, and Co compared to those from adjacent unburned areas [6,27,28] (Table 1). However, they were analogous to those in burned areas with similar lithology [14] or vegetation [8]. Previous studies also reported fire-induced increases in Mn, Ni, Cd, and Pb in soil concentrations [12,29]. Cd and Pb accumulation in soils is typically related to its sorption by organic matter, fixation by clay minerals, association with Mn oxides, and Fe and Al (hydro) oxides [30]. Manganese, among all elements, exhibited the highest increase in burnt soils. Copper did not vary significantly in burned and unburned areas. This observation aligns with other authors' findings [8,29].

**Table 1.** Median values (µg/g) of element contents in topsoils and subsoils collected from the study sites compared to values obtained from the literature (n = number of samples; n.d = not detected; n.m = not measured).

| | **Burned of Study Area** | | **Unburned of North Euboea [27]** | |
|---|---|---|---|---|
| | **Topsoils (n = 17)** | **Subsoils (n = 17)** | **Topsoils** | **Subsoils** |
| Pb | 77 | 20 | 18 | 16 |
| Zn | 91 | 64 | 67 | 55 |
| Cd | 1.00 | 0.29 | 0.6 | n.d |
| Cu | 27 | 28 | 35 | 46 |
| Mn | 834 | 845 | 480 | 360 |
| Fe | 19,400 | 29,455 | 27,400 | 24,100 |
| Cr | 334 | 269 | 78 | 40 |
| Ni | 174 | 564 | 44 | 34 |
| Co | 62 | 63 | 12 | 9 |
| As | n.m | 8 | 10 | 9 |

Both topsoils and subsoils were enriched with Fe, Mn, Cr, Ni, and Co. The decreasing order of elements' median 'pseudo total' values Fe > Mn > Cr > Ni > Zn > Pb > Co > Cu > Cd in topsoils did not differ significantly from those detected in subsoil Fe > Mn > Ni > Cr > Zn > Co > Cu > Pb > Cd. In both affected and unaffected soils, statistically significant ($p < 0.05$) medium to high positive correlations between Cr, Ni, Fe, Co, and Mn 'pseudo total' values in topsoils and subsoils (Figure 3) [27,28] imply their geogenic origins are from ultramafic rocks and related ores in the study area. Multivariate statistics applied to

the soil dataset confirmed this finding. The first factor included Cr, Ni, Fe, and Mn with high positive loadings, accounting for 49%, 56%, and 55% of the total variance in topsoils, subsoils, and the whole-soil dataset, respectively. Enrichment of the above metals appears to be consistent with the soil mineral phases of antigorite and chrysotile, reflecting the contribution of ultramafic rocks and related ores (Fe-Ni-laterites and chromites). In general, the soil mineralogy did not differ significantly from adjacent areas that were unaffected by fire [27,28]. The presence of clay minerals, such as kaolinite, smectite, and micas, in the subsoils and corresponding topsoils implies that the fire temperature at the mineral soil surface did not exceed 500 °C [5,16].

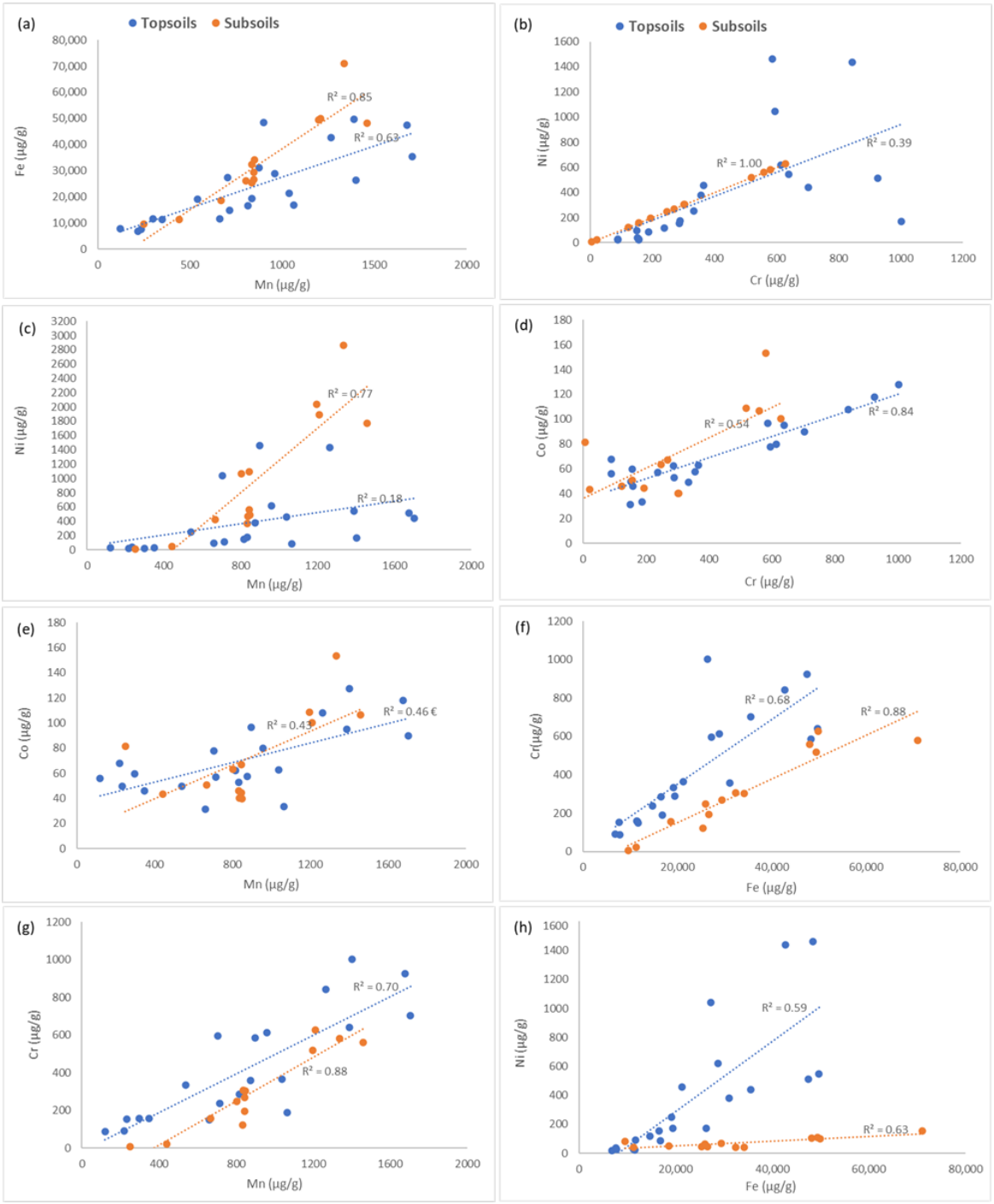



**Figure 3.** Bivariate plots of positively correlated 'pseudo total' element values in soil: (**a**) Mn vs. Fe; (**b**) Cr vs. Ni; (**c**) Mn vs. Ni; (**d**) Cr vs. Co; (**e**) Mn vs. Co; (**f**) Fe vs. Cr; (**g**) Mn vs. Cr; (**h**) Fe vs. Ni.

Table 2 presents the range and median concentration values of the investigated elements in soil leachates for each leaching agent applied. Leaching procedures using water as an extraction agent provide information on the available water-soluble metal ions that can easily transfer into aquatic systems and groundwater via water infiltration and readily bioavailable element fractions [31].

**Table 2.** Major and trace element median, min, and max concentrations in topsoil and subsoil leachates by different leaching agents compared to EU parametric values for human usage [32] and the leaching agents' composition (NMW = natural mineral water, NSW = natural surface water). The red font denotes values above EU-regulated values.

| Major and Trace Elements | | TOPSOILS LEACHATES | | | | | | Blank of NMW Leaching Agent | Blank of NSW Leaching Agent | Parametric Values |
|---|---|---|---|---|---|---|---|---|---|---|
| | | With NMW Leaching Agent | | | With NSW Leaching Agent | | | | | |
| | | Median | Min | Max | Median | Min | Max | Median Values | | |
| Pb | µg/L | 0.143 | BDL | 1.48 | 0.166 | BDL | 1.24 | 0.009 | 0.024 | 10 µg/L |
| Zn | | 13 | 4.08 | 42 | 25 | BDL | 33 | 3.24 | 1.69 | |
| Cd | | 0.059 | 0.012 | 0.143 | 0.047 | 0.009 | 0.112 | 0.014 | 0.009 | 5 µg/L |
| Cu | | 7.23 | 3.31 | 11 | 6.47 | 2.81 | 9.45 | 0.03 | 1.28 | 2mg/L |
| Mn | | 151 | 19 | 772 | 216 | 8.31 | 681 | 6.21 | 8.73 | 50 µg/L |
| Fe | | 30 | 2.32 | 142 | 25 | 2.38 | 140 | 0.025 | 0.025 | 200 µg/L |
| Cr | | 2.9 | BDL | 35 | 2.50 | BDL | 36 | 0.003 | 2.92 | 50 µg/L |
| Ni | | 78 | 9.31 | 291 | 48 | 7.42 | 293 | 0.025 | 1.80 | 20 µg/L |
| Co | | 23 | 9.26 | 195 | 26 | 9.20 | 214 | 0.296 | 0.278 | |
| As | | **23** | 4.48 | 37 | **24** | 4.99 | 40 | 0.392 | 0.418 | 10 µg/L |
| Ca | mg/L | 159 | 90 | 375 | 149 | 87 | 354 | 71 | 50 | |
| Mg | | 36 | 24 | 84 | 51 | 36 | 101 | 3.79 | 47 | |
| Na | | 13 | 8.63 | 28 | 18 | 13 | 28 | 2.83 | 11 | 200 mg/L |
| K | | 39 | 26 | 76 | 54 | 28 | 87 | 0.159 | 0.070 | |

*BDL = Below Detection Limit*

| Major and Trace Elements | | SUBSOILS LEACHATES | | | | | |
|---|---|---|---|---|---|---|---|
| | | With NMW Leaching Agent | | | With NSW Leaching Agent | | |
| | | Median | Min | Max | Median | Min | Max |
| Pb | µg/L | 0.048 | 0.001 | 0.191 | 0.005 | 0.001 | 0.373 |
| Zn | | 9.89 | 0.725 | 33 | 9.27 | 0.504 | 48 |
| Cd | | 0.020 | BDL | 0.089 | 0.022 | 0.006 | 0.169 |
| Cu | | 3.56 | 0.598 | 7.86 | 3.35 | 0.656 | 7.67 |
| Mn | | 48 | 3.63 | 2662 | 56 | 3.02 | 2423 |
| Fe | | 6.69 | BDL | 47 | 6.82 | BDL | 48 |
| Cr | | 1.18 | BDL | 12 | 4.87 | 0.003 | 10 |
| Ni | | 15 | 0.639 | 468 | 22 | 1.74 | 461 |
| Co | | 8.62 | 0.666 | 65 | 6.18 | 1.41 | 78 |
| As | | 5.87 | 2.14 | 18 | 5.99 | 2.40 | 15 |
| Ca | mg/L | 81 | 31 | 139 | 77 | 31 | 154 |
| Mg | | 19 | 8.04 | 56 | 39 | 21 | 57 |
| Na | | 9.34 | 6.60 | 13 | 15 | 13 | 18 |
| K | | 16 | 5.82 | 21 | 13 | 6.00 | 22 |

*BDL = Below Detection Limit*

Approximately 80% of topsoil and 50% of subsoil leachates exhibited Mn, Ni, and As concentrations, exceeding the EU's maximum limits for water intended for human usage [32] (parametric values in Table 2), regardless of the leaching agent.

Calcium concentrations in both natural mineral and surface waters used as leaching agents are elevated, as are magnesium concentrations in natural surface water, compared

to median values in soil leachates and those elements' average concentrations in natural waters [33]. However, due to geogenic factors, such as lithology and mineral speciation, actual levels of element concentrations in groundwater and natural surface waters can vary greatly. Elevated Mg concentrations in natural surface water leaching agents can be attributed to Mg-bearing minerals in ultramafic rocks. Topsoil leachates exhibited higher median Ca and Mg values than subsoil leachates (Figure S1 in Supplementary Materials).

The decreasing enrichment of soil leachates in trace element concentrations, presented in Table 3, differs from the reducing order of their 'pseudo total' contents and lacks correlation. The topsoil leachates exhibited a high abundance of Mn, Ni, Fe, and Co, while the subsoil leachates contained high levels of Mn, Ni, and Zn. Other researchers have also reported increased water-soluble Mn values after fires [34]. The observed decrease in subsoil leachates' Mn, as well as the statistically positive correlation ($R^2 = 0.54$, $p < 0.05$) between 'pseudo total' Mn content in subsoils and organic carbon, may indicate that precipitation events quickly bond and immobilize Mn after it is released during vegetation incineration [8].

**Table 3.** Decreasing order of soil leachate enrichment in trace element concentrations.

| Leaching Agents | Topsoils | Subsoils |
|---|---|---|
| Natural Mineral Water | Mn > Ni > Fe > As > Co > Zn > Cu > Cr > Pb > Cd | Mn > Ni > Zn > Co > Fe > As > Cu > Cr > Pb > Cd |
| Natural Surface Water | Mn > Ni > Co > Fe > Zn > As > Cu > Cr > Pb > Cd | Mn > Ni > Zn > Fe > Co > As > Cr > Cu > Cd > Pb |

The enrichment of arsenic in soil leachates is reflected by its high extractability. Besides reduction conditions [35], the presence of organic matter acts as a catalyst by forming carbon from biomass incineration in fires [36], causing As(V) reduction to the more mobile form of As(III). Additionally, the presence of organic matter accelerates the release of As associated with Fe minerals under environmental conditions [35]. The mobility of As at high pH values [37,38], such as those measured in the study area's soil samples (approximately pH 8.0), is emphasized by the statistically positive correlations between As total leachability and soil pH values.

Table 4 shows the relative extractability of the examined elements as the ratio of the extractability of all leaching agents (natural mineral and natural surface water) to their 'pseudo total' soil content.

**Table 4.** Decreasing order of the studied elements' relative extractability by leaching agents.

| Leaching Agents | Topsoils | Subsoils |
|---|---|---|
| Natural Mineral Water | Co > Mn > Ni > Cu > Zn > Cd > Cr > Pb > Fe | As > Co > Cu > Zn > Cd > Ni > Mn > Cr > Pb > Fe |
| Natural Surface Water | Co > Ni > Zn > Mn > Cu > Cd > Cr > Fe > Pb | As > Zn > Cu > Cd > Co > Ni > Mn > Cr > Pb > Fe |

The ratios of element concentrations in leachates to their 'pseudo total contents' in topsoils leached with natural mineral and surface water were very low, ranging from 0.001 to 0.15% and 0.0007 to 0.17%, respectively. In subsoil leachates, they ranged from 0.0001 to 0.30% and from 0.00007 to 0.32%, respectively. Despite the leachates' different pHs, there was no significant variation in the ratios of 'pseudo total' contents extracted by both leaching agents in topsoils and subsoils (Figure 4). Thus, natural mineral water can be used instead of 'local' natural surface water or rainwater as a leaching agent to estimate trace elements' environmental availability.

Although the soil samples displayed a specific enrichment order in trace element 'pseudo total' contents (Fe > Mn > Cr > Ni > Zn > Pb > Co > Cu > Cd in topsoils and Fe > Mn > Ni > Cr > Zn > Co > Cu > Pb > Cd in subsoils) and leachate concentrations (Table 3), other metal sequences were easily extracted from soil leachates (Table 4). Iron and chromium, enriched in all soil samples, exhibited low relative extractability from both

leaching agents, whereas Ni and Mn, also abundant in all soil samples, presented higher relative extractability in topsoils than subsoils.

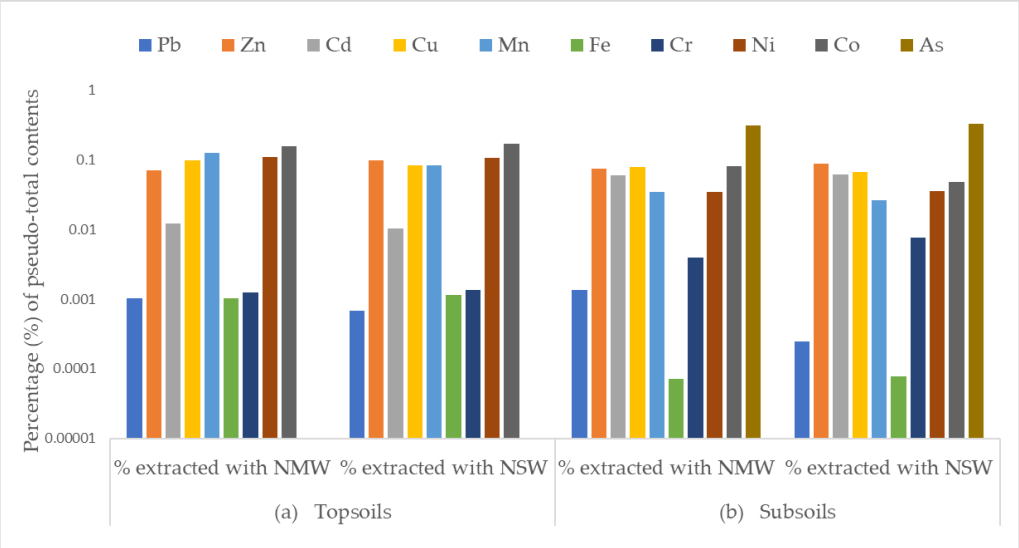



**Figure 4.** Leaching ratio (%) of elements extracted by both agents (NMW = natural mineral water and NSW = natural surface water) in topsoil (**a**) and subsoil samples (**b**).

However, statistically significant medium (in topsoil samples) to high (in subsoil samples) positive correlations have been found between Cr, Ni, Cu, and Mn 'pseudo total' contents in soil and their concentrations in leachates, implying that soil enrichment may influence their extractability (Figure 5).

Nickel and cobalt, derived from the breakdown of phyllosilicate minerals in the study area, such as antigorite and chrysotile, are also associated with manganese and iron oxides [39]. A statistically significant positive correlation between Mn and Co (Figure 3) is consistent with Co's affinity for Mn oxides. This finding may explain the high ratios of Co extracted by both leaching agents, especially in topsoil leachates where Mn concentrations were higher than in subsoils. Furthermore, Ni 'pseudo total' content positively correlates with organic carbon, implying that its distribution and mobility in soil are related more to soil organic matter than to clay minerals and Fe-oxides/hydroxides [30].

Compared to their 'pseudo total' enrichment in soil samples, the low extractability of elements such as Fe and Cr is likely due to their affinity for organic matter. Confirming this suggestion, a statistically significant ($p < 0.05$) positive correlation between the proportion of Fe and Cr 'pseudo total' contents extracted by both leaching agents and organic carbon, possibly due to insoluble organic compounds with these metals. Mn typically accumulates in tree leaves, especially needles of resinous species [30]. Manganese's high extractability and abundance in soil leachates (especially in topsoil leachates) may be related to heat-induced physicochemical breakdowns of Mn-complexes with soil organic matter as well as vegetation combustion [40] and ash deposition [41].

Organic carbon ranged from 2.75 to 10.8% in topsoils and from 0.19 to 6.75% in subsoils. In most sampling sites, topsoils exhibited higher organic carbon values than subsoils and topsoils in nearby unburned areas of similar lithologies and vegetation types [27,42] (Figure 6). Compared to adjacent unburned areas' soils, organic carbon increased by almost 80% in fire-affected areas. As observed by other authors [8], incomplete combustion of plants is responsible for the increase in organic matter content in burned soils.

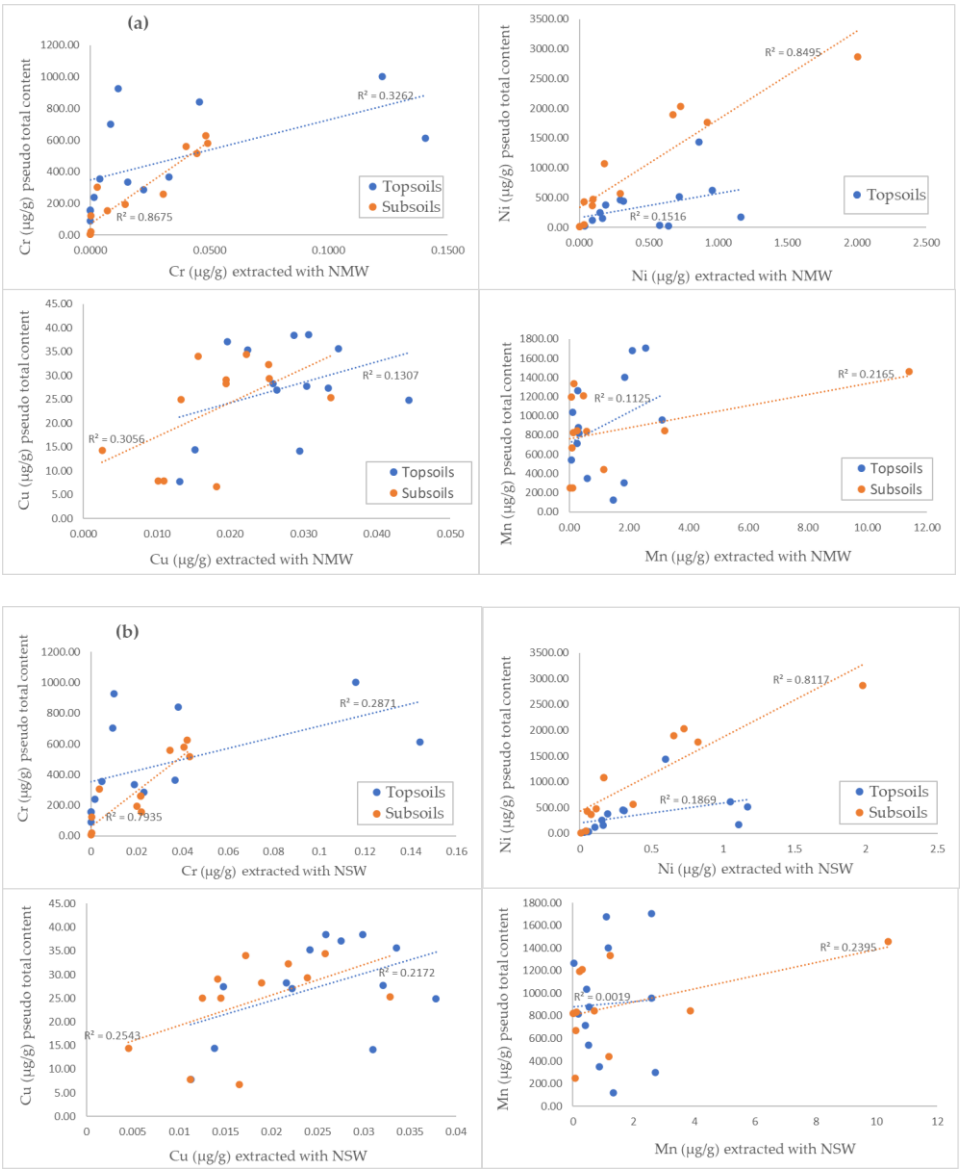



**Figure 5.** Bivariate plots of Cr, Ni, Cu, and Mn 'pseudo total' contents in soil and their leachates by (**a**) NMW = natural mineral water and (**b**) NSW = natural surface water.

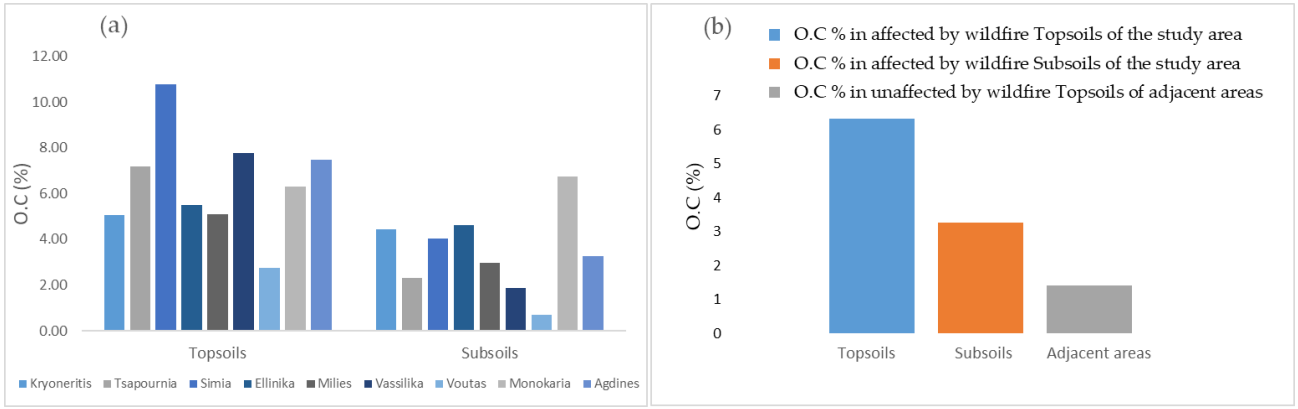



**Figure 6.** (**a**) Organic carbon content (%) of topsoils vs. subsoils in the study area; (**b**) organic carbon (%) content in wildfire-affected and unaffected topsoils and subsoils in the study and adjacent areas.

Soil pH values ranged from 6.91 to 8.46 in topsoils and 7.26 to 8.73 in subsoils, indicating neutral to alkaline conditions for all topsoils. All soil datasets demonstrated a statistically significant negative correlation between both agents' low Mn relative extractability and soil pH at more than −0.65. Compared to Mn, the higher relative extractability of As revealed a statistically significant positive trend in soil pH values. The leachability of most elements in solid samples is known to highly depend on the acidity of the solution [43]. Lowering soil pH promotes exchange. In other words, the lower the soil pH, the higher the leachability of elements from solid samples [8,43].

## 4. Conclusions

Mediterranean wildfires have significantly impacted soil quality and soil properties in the affected areas. Northern Euboea, Greece, exemplifies these impacts.

Overall, the concentrations of almost all the studied elements values were higher in fire-affected than unaffected soils. Similar variations in element concentrations were observed between topsoils and subsoils, with the latter exhibiting lower values.

However, the increased 'pseudo total' values of Cr, Ni, Fe, Co, and Mn in all soil samples, along with the medium to high positive correlations between them, indicate that geogenic factors play a major role in controlling element enrichment.

In soil leachates, Mn, Ni, and As concentrations that exceed the EU's maximum permissible limits indicate a potential ecological risk to natural water quality and, subsequently, human health.

Correlation coefficients between elements in both fire-affected and unaffected soils suggests their geogenic origin, which is mainly related to ultramafic rocks and associated ores in the study area.

Element concentrations in the soil leachates were significantly lower than their 'pseudo total' contents in the soil, with no correlation between them. The reducing order of element leachability does not coincide with the decreasing order of elements' 'pseudo total' median values in soils.

The decreasing order of element abundance in soil leachates is consistent with their relative extractability from both agents (natural mineral and surface water). However, it differs from the decreasing order of their 'pseudo total' median values in soils.

Neutral to alkaline soil pH conditions and organic carbon content, which significantly influence element retention and mobility, revealed patterns that were not evident for all the studied elements. Correlations were only found for Mn, Cr, and Co.

The increased organic matter content in fire-affected soils suggests that vegetation combustion was incomplete.

**Supplementary Materials:** The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/land13030325/s1. Table S1: Trace elements' 'pseudo total' median, minimum (min), and maximum (max) contents in topsoil and subsoil samples. Figure S1: Comparison of element concentrations in topsoil and subsoil leachates.

**Author Contributions:** Conceptualization, I.M. and E.S.; data curation, I.M., E.S., M.K. and C.V.; formal analysis, I.M. and E.S.; investigation, I.M., E.S., E.V. and M.K.; methodology, E.S., M.K., S.K., N.T. and C.V.; resources, M.K. and N.T.; supervision, C.V.; validation, S.K., N.T. and C.V.; visualization, E.V.; writing—original draft, I.M., E.S. and E.V.; writing—review and editing, N.T. and C.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not relevant.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available upon request from the corresponding author. The data are not publicly available due to confidentiality reasons.

**Acknowledgments:** We are thankful to Ioannis Konstantinidis for assisting us with sampling. We express our gratitude to the Academic Editors and anonymous reviewers for their valuable constructive criticism and insightful comments, which significantly enhanced the quality of the manuscript.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. San-Miguel-Ayanz, J.; Durrant, T.; Boca, R.; Maianti, P.; Libertá, G.; Artés-Vivancos, T.; Oom, D.; Branco, A.; de Rigo, D.; Ferrari, D.; et al. *Wildfires in Europe, Middle East and North Africa 2021*; Publications Office of the European Union: Luxembourg, 2022. [CrossRef]
2. USGCRP (U.S. Global Change Research Program). *Impacts, Risks, and Adaptation in the United States: Fourth National Climate Assessment, Volume II*; Reidmiller, D.R., Avery, C.W., Easterling, D.R., Kunkel, K.E., Lewis, K.L.M., Maycock, T.K., Stewart, B.C., Eds.; 2018. Available online: https://nca2018.globalchange.gov/downloads (accessed on 1 August 2023). [CrossRef]
3. Pacifico, L.R.; Pizzolante, A.; Guarino, A.; Iannone, A.; Esposito, M.; Albanese, S. Wildfires as a Source of Potentially Toxic Elements (PTEs) in Soil: A Case Study from Campania Region (Italy). *Int. J. Environ. Res. Public Health* **2023**, *20*, 4513. [CrossRef]
4. Abatzoglou, J.T.; Williams, A.P. Impact of anthropogenic climate change on wildfire across western US forests. *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 11770–11775. [CrossRef]
5. Certini, G. Effects of fire on properties of forest soils: A review. *Oecologia* **2005**, *143*, 1–10. [CrossRef]
6. Hrelja, I.; Šestak, I.; Delač, D.; Pereira, P.; Bogunović, I. Soil Chemical Properties and Trace Elements after Wildfire in Mediterranean Croatia: Effect of Severity, Vegetation Type and Time-Since-Fire. *Agronomy* **2022**, *12*, 1515. [CrossRef]
7. Pereira, P.; Francos, M.; Brevik, E.C.; Ubeda, X.; Bogunovic, I. Post-fire soil management. *Curr. Opin. Environ. Sci. Health* **2018**, *5*, 26–32. [CrossRef]
8. Campos, I.; Abrantes, N.; Keizer, J.J.; Vale, C.; Pereira, P. Major and trace elements in soils and ashes of eucalypt and pine forest plantations in Portugal following a wildfire. *Sci. Total Environ.* **2016**, *572*, 1363–1376. [CrossRef] [PubMed]
9. Merino, A.; Fonturbel, M.T.; Fernandez, C.; Chavez-Vergara, B.; Garcia-Oliva, F.; Vega, J.A. Inferring changes in soil organic matter in post-wildfire soil burn severity levels in a temperate climate. *Sci. Total Environ.* **2018**, *627*, 622–632. [CrossRef]
10. Arocena, J.; Opio, C. Prescribed fire-induced changes in properties of sub-boreal forest soils. *Geoderma* **2003**, *113*, 1–16. [CrossRef]
11. Badia, D.; Marti, C.; Aguirre, A.J.; Aznar, J.M.; Gonzalez-Perez, J.; De la Rosa, J.M.; Leon, J.; Ibarra, P.; Etcheverria, T. Wildfire effects on nutrients and organic carbon of a Rendzic Phaeozem in NE Spain: Changes at cm-scale topsoil. *Catena* **2014**, *113*, 267–275. [CrossRef]
12. Plumlee, G.S.; Martin, D.A.; Hoefen, T.; Kokaly, R.; Hagentan, P.; Eckberg, A.; Meeker, G.P.; Adams, M.; Anthony, M.; Lamothe, P.J. *Preliminary Analytical Results for Ash and Burned Soils from the October 2007 Southern California Wildfires*; US Geological Survey, Open-File Report 2007-1407; US Geological Survey: Reston, VA, USA, 2007.
13. Oliveira, S.; Zêzere, J.L.; Queirós, M.; Pereira, J.M. Assessing the social context of wildfire-affected areas. The case of mainland Portugal. *Appl. Geogr.* **2017**, *88*, 104–117. [CrossRef]
14. Alexakis, D.E. Contaminated land by wildfire effect on ultramafic soil and associated human health and ecological risk. *Land* **2020**, *9*, 409. [CrossRef]
15. Bento-Gonçalves, A.; Vieira, A.; Úbeda, X.; Martin, D. Fire and soils: Key concepts and recent advances. *Geoderma* **2012**, *191*, 3–13. [CrossRef]
16. DeBano, L.F. The role of fire and soil heating on water repellency in wildland environments: A review. *J. Hydrol.* **2000**, *231–232*, 195–206. [CrossRef]
17. Neary, D.G.; Ryan, K.C.; DeBano, L.F. *(Eds). Wildland Fire in Ecosystems: Effects of Fire on Soils and Water*; Gen. Tech. Rep. RMRS-GTR-42-vol.4; U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station: Ogden, UT, USA, 2005; 250p.
18. Reynard-Callanan, J.R.; Pope, G.A.; Gorring, M.L.; Feng, H. Effects of High-Intensity Wildfires on Soil Clay Mineralogy. *Phys. Geogr.* **2010**, *31*, 407–422. [CrossRef]
19. Neary, D.G.; Klopatek, C.C.; DeBano, L.F.; Ffolliott, P.F. Fire effects on belowground sustainability: A review and synthesis. *For. Ecol. Manag.* **1999**, *122*, 51–71. [CrossRef]
20. Lekkas, E.; Parcharidis, I.; Arianoutsou, M.; Lozios, S.; Mavroulis, S.; Spyrou, N.-I.; Antoniou, V.; Nastos, P.; Mavrouli, M.; Speis, P.; et al. The July–August 2021 Wildfires in Greece. *Newsl. Environ. Disaster Cris. Manag. Strateg.* **2021**, *25*, 61–91.
21. Evelpidou, N.; Tzouxanioti, M.; Gavalas, T.; Spyrou, E.; Saitis, G.; Petropoulos, A.; Karkani, A. Assessment of Fire Effects on Surface Runoff Erosion Susceptibility: The Case of the Summer 2021 Wildfires in Greece. *Land* **2022**, *11*, 21. [CrossRef]
22. Valkanou, K.; Karymbalis, E.; Bathrellos, G.; Skilodimou, H.; Tsanakas, K.; Papanastassiou, D.; Gaki-Papanastassiou, K. Soil Loss Potential Assessment for Natural and Post-Fire Conditions in Evia Island, Greece. *Geosciences* **2022**, *12*, 367. [CrossRef]
23. Filgueiras, A.V.; Lavilla, I.; Bendicho, C. Chemical sequential extraction for metal partitioning in environmental solid samples. *J. Environ. Monit.* **2002**, *4*, 823–857. [CrossRef]
24. Stefanidis, S.; Alexandridis, V.; Spalevic, V.; Mincato, R.L. Wildfire Effects on Soil Erosion Dynamics: The Case of 2021 Megafires in Greece. *Agric. For.* **2022**, *68*, 49–63. [CrossRef]

25. Corine Land Cover (CLC). 2018. Available online: https://land.copernicus.eu/pan-european/corine-land-cover/clc2018 (accessed on 10 August 2023).
26. Gemitzi, A.; Koutsias, N.A. Google Earth Engine code to estimate properties of vegetation phenology in fire affected areas–A case study in North Evia wildfire event on August 2021, Remote Sensing Applications. *Soc. Environ.* **2022**, *26*, 100720. [CrossRef]
27. Megremi, I. Distribution and bioavailability of Cr in central Euboea, Greece. *Cent. Eur. J. Geosci.* **2010**, *2*, 103–123. [CrossRef]
28. Kanellopoulos, C.; Argyraki, A. Soil baseline geochemistry and plant response in areas of complex geology. Application to NW Euboea, Greece. *Chemie der rde-Geochem.* **2013**, *73*, 519–532. [CrossRef]
29. Costa, M.R.; Calvão, A.R.; Aranha, J. Linking wildfire effects on soil and water chemistry of the Marão River watershed, Portugal, and biomass changes detected from Landsat imagery. *Appl. Geochem.* **2014**, *44*, 93–102. [CrossRef]
30. Kabata-Pendias, A. *Trace Elements in Soils and Plants*, 4th ed.; CRS Press: Boca Raton, FL, USA, 2011.
31. Seguin, V.; Gagnon, C.; Courchesne, F. Changes in water extractable metals, pH and organic carbon concentrations at the soil-root interface of forested soils. *Plant Soil* **2004**, *260*, 1–17. [CrossRef]
32. European Commission. *Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption*; European Commission: Brussels, Belgium, 1998; pp. 32–54.
33. Pashkova, G.V.; Revenko, A.G. A Review of Application of Total Reflection X-ray Fluorescence Spectrometry to Water Analysis. *Appl. Spectrosc. Rev.* **2015**, *50*, 443–473. [CrossRef]
34. Smith, H.G.; Sheridan, G.J.; Lane, P.N.J.; Nyman, P.; Haydon, S. Wildfire effects on water quality in forest catchments: A review with implications for water supply. *J. Hydrol.* **2011**, *396*, 170–192. [CrossRef]
35. Johnston, S.G.; Karimian, N.; Burton, E.D. Fire promotes arsenic mobilization and rapid arsenic(III) formation in soil via thermal alteration of arsenic-bearing iron oxides. *Front. Earth Sci.* **2019**, *7*, 139. [CrossRef]
36. Yan, X.-L.; Chen, T.-B.; Liao, X.-Y.; Huang, Z.-C.; Pan, J.-R.; Hu, T.-D.; Nie, C.-J.; Xie, H. Arsenic transformation and volatilization during incineration of the hyperaccumulator *Pteris vittata* L. *Environ. Sci. Technol.* **2008**, *42*, 1479–1484. [CrossRef]
37. Moreno-Jiménez, E.; Esteban, E.; Peñalosa, J.M. The fate of arsenic in soil-plant systems. In *Reviews of Environmental Contamination and Toxicology*; Whitacre, D.M., Ed.; Springer: Berlin/Heidelberg, Germany, 2012. [CrossRef]
38. Michopoulos, P.; Kostakis, M.; Solomou, A.; Pasias, I.; Grigoratos, T.; Thomaidis, N.S.; Samara, C. Total and bioavailable heavy metals in the soils of two adjacent forests. *Glob. NEST J.* **2022**, *24*, 65–73. [CrossRef]
39. Manceau, A.; Schlegel, M.L.; Musso, M.; Sole, V.A.; Gauthier, C.; Petit, P.A.; Trolard, F. Crystal chemistry of trace elements in natural and synthetic goethite. *Geochim. Cosmochim. Acta* **2000**, *64*, 3643–3661. [CrossRef]
40. Parra, J.G.; Rivero, V.C.; Lopez, T.I. Forms of Mn in soils affected by a forest fire. *Sci. Total Environ.* **1996**, *181*, 231–236. [CrossRef]
41. Chambers, D.P.; Attiwill, P.M. The ash-bed effect in Eucalyptus regnans forest: Chemical, physical, and microbiological changes in soil after heating or partial sterilization. *Aust. J. Bot.* **1994**, *42*, 739–749. [CrossRef]
42. European Environment Agency. Natura 2000 Network Viewer. European Environment Agency: Copenhagen. Available online: https://natura2000.eea.europa.eu/ (accessed on 10 August 2023).
43. Evans, L.J.; Spiers, G.A.; Zhao, G. Chemical aspects of heavy metals solubility with references to sewage sludge-amended soils. *Int. J. Environ. Anal. Chem.* **1995**, *59*, 291–302. [CrossRef]


**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.