Chronic drought alters extractable concentrations of mineral elements in Mediterranean forest soils.

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Abstract

Soil mineral elements play a crucial role in ecosystem productivity and pollution dynamics. Climate models project an increase in drought severity in the Mediterranean Basin in the coming decades, which could lead to changes in the composition and concentrations of mineral elements in soils. These changes can have significant impacts on the fundamental processes of plant-soil cycles. While previous studies have predominantly focused on carbon, nitrogen, and phosphorus, there is a notable lack of research on the biogeochemical responses of other mineral elements to increasing drought. In this study, we investigated the effects of chronic drought (15 years of experimental rainfall exclusion) and seasonal drought (summer period) on the extractable soil concentrations of 17 mineral elements in a Mediterranean holm oak forest. We also explored the potential biotic and abiotic mechanisms underlying the changes in extractable elemental concentrations under chronic drought conditions. Our findings reveal that soil elemental concentrations varied significantly due to seasonal changes and chronic drought, with soil microclimate, biological activity, and organic matter being the main drivers of this variability. Levels of soil water content primarily explained the observed variations in soil elemental concentrations. Most of the mineral elements (13 out of 17) exhibited higher concentrations during winter-spring (wet seasons) compared to summer-autumn (dry seasons). The chronic drought treatment resulted in potassium limitation, increasing vegetation vulnerability to drought stress. Conversely, the accumulation of sulfur in soils due to drought may intensify the risk of sulfur losses from the plant-soil system. Under drought conditions, certain trace elements (particularly manganese, vanadium, and cadmium) exhibited increased extractability, posing potential risks to plant health and the exportation of these elements into continental waters. Overall, our results suggest that alterations in mineral element concentrations under future drier conditions could promote ecosystem degradation and pollution dispersion in the Mediterranean Basin. Understanding and predicting these changes are essential for effective ecosystem management and mitigating the potential negative impacts on plant health and water quality.

Keywords: Chronic drought; Seasonality; Mediterranean holm oak forest; Soil mineral elements; Extractable concentrations; Soil water content

1. Introduction

Spatial-temporal variability of mineral elements in soils is caused by a complex range of factors including parent material, pedogenic processes, topography, climate and both biotic and anthropogenic impacts (Alloway, 2013; Beygi and Jalali, 2019; Islam et al., 2015; Salekin et al., 2021; Valladares et al., 2009). Soil mineral elements play critical roles in ecosystem productivity and pollution as a result of biogeochemical processes (Chorover et al., 2007; Huang et al., 2005; Sardans and Peñuelas, 2007a, b; Sardans et al., 2008c, 2020; Zhou et al., 2021).

Drought events in the Mediterranean Basin are likely to be more frequent and intense during the next decades (IPCC, 2014; Vicente-Serrano et al., 2014). Moreover, the changing patterns of precipitation in the Mediterranean region are also expected to intensify droughts in these ecosystems where water stress is already the principal constraint (Cramer et al., 2018; Vicente-Serrano et al., 2014; Zhou et al., 2019). These alterations are expected to affect the composition and concentrations of mineral elements in Mediterranean soils, as shown by several studies of the biogeochemical responses of soil carbon, nitrogen and phosphorus to greater drought over various time scales (Asensio et al., 2021; Marañón-Jiménez et al., 2022; Sardans and Peñuelas, 2005; Sardans et al., 2008a, 2020). However, much less attention has been paid to the effects of drought on other mineral elements that also play a role in crucial biogeochemical processes such as mineral nutrient cycling (Deng et al., 2021; Johnson and Turner, 2019; Pastor and Bockheim, 1984) and the dispersion of trace element pollutants (Hooda, 2010; Purves, 2012; Szynkowska et al., 2018).

Drought is likely to change the mobility and biological availability of mineral elements along both direct and indirect pathways (Sardans and Peñuelas, 2007a, b; Sardans et al., 2008c, d; Schlesinger et al., 2016), which can affect the cycling and loss of elements and deeply influence ecosystem structure and function (Deng et al., 2021; Sardans et al., 2008c). Water limitation and the consequent reductions in soil diffusion capacity lead to greater accumulations of organic matter (OM), which, together with less soil enzymatic activity and lower microbial mineralization rates (Manzoni et al, 2012; Peñuelas et al., 2018; Sardans and Peñuelas, 2005), slow down the release of mineral nutrients and therefore decrease soil nutrient availability, the nutrient uptake capacity of plants and microbes, and plant growth (Asensio et al., 2021; Marañón-Jiménez et al., 2022; Sardans et al., 2008c, d). These alterations can heighten the likelihood of losing mineral elements through runoff (Sardans et al., 2008c, d; Schlesinger et al., 2016). On the other hand, less soil water also decreases leaching into the soil solution and mineral weathering rates (Schlesinger et al., 2016; Slessarev et al., 2016). Greater soil OM under chronic drought conditions conditions may increase metal-OM complexes, which will improve soils' capacities to prevent the loss of mineral elements from ecosystems (Sardans et al., 2008c; Solly et al., 2020). However, on the long-term this effect can be offset by the decrease in total biomass and consequently in soil organic matter. In addition, the drying-rewetting events induced by droughts could also influence the status of mineral elements and, for example, a rise in the intensity of the drying and rewetting cycles could enhance the transformation of certain elements from available to unavailable forms (Ma and Uren, 1997; Sardans and Peñuelas, 2007b).

Extractable concentrations (EC) are crucial variables for evaluating the mobility and biological availability of mineral elements (Beygi and Jalali, 2019; Li et al., 2014; Rees, et al., 2014; Valladares et al., 2009). Changes in EC caused by drought may depend on the balance of input and output concentrations that represent the combined effects of the biological and abiotic processes described above. The effects of drought on the EC of individual elements differ in terms of the element and a range of factors such as the type of ecosystem and the cause and degree of the drought (Deng et al., 2021; Sardans et al., 2008c, d). Previous studies in the Mediterranean Basin reported increases in the EC of iron, magnesium, sulphur, arsenic and titanium, but decreases in the EC of potassium, nickel and lead in holm oak forest soils after a 6-year experimentally induced continuous drought (Sardans and Peñuelas, 2007a, b; Sardans et al., 2008c); conversely, there was no significant effect on the EC of mineral elements in shrubland soils (Sardans et al., 2008b, d, e). However, our knowledge about how soil mineral elements respond to long-term drought conditions is still highly incomplete. A comprehensive analysis of the effects of drought on soil mineral elements can provide insights into the complex mechanisms controlling the variability in their EC and how drought reshapes soil element composition in the field. Any such analysis will thus enhance our ability to accurately model and predict biogeochemical responses to future climatic conditions. Therefore, we studied the effects of seasonal (summer drought) and long-term chronic drought on the EC of mineral elements in soils in 2014, after 15 years of continuous water exclusion treatment (started in 1999) and investigated the relationship between EC and possible biotic (soil respiration, soil enzymatic activity, microbial biomass) and abiotic environmental factors (soil moisture and temperature) in a Mediterranean holm oak forest. We hypothesized that 1) both seasonal and chronic drought affect the quantity and composition of soil mineral elements even though the effects are more significant due to season than chronic drought and 2) the mechanisms driving the responses of soil elements to changing environmental conditions differ from one element to another because their concentrations involve different biological and abiotic controls and have different physico-chemical traits such as distinct solubility, responses to pH changes or chelating interactions with soil organic matter.

2. Materials and methods

2.1. Study site and experimental design

The study was conducted in a natural holm oak forest in the Prades Mountains in Catalonia, NE Iberian Peninsula (41◦21′N, 1◦2′E). The study sites have been described elsewhere in detail by Mu et al. (2018, 2019) and Ogaya et al. (2020). Briefly, the climate is typically Mediterranean characterized by hot dry summers and moderately wet and cold winters; springs and autumns are usually also wet. The average annual temperature and rainfall are 12.2ºC and 616.1 mm, respectively. The soil is a Dystric Cambisol at a depth of 35–90 cm and the vegetation is dominated by *Quercus ilex* with an abundance of shrubs such as *Phillyrea latifolia* and *Arbutus unedo*.

Eight plots (15×10 m) were established at the same altitude (950 m) along a slope (25°), four of which were subject to the drought treatment and four left as control plots under natural conditions. The drought treatment was carried out from 1999 to 2014 (15 years) and consisted of partial rain exclusion caused by the installation of PVC strips above the ground that intercepted 30% of plot precipitation; moreover, water runoff was intercepted by a 0.8-m deep ditch excavated along the entire top edge of the plot. Further details of the plot location and drought treatment are given by Mu et al. (2018) and Ogaya et al. (2020).

2.2. Soil CO_2 efflux and temperature and core sampling

Soil sampling in 2014 was performed mid-season, on 25–27 January (winter), 16–18 May (spring), 31 July–2 August (summer) and 24–26 October (autumn). Five soil cores (5-cm diameter, 10-cm depth) were taken per plot per season (total n = 160).

The soil CO_2 efflux (SR) was measured between 09.00–15.00 and prior to soil core sampling (see below) using five soil collars permanently inserted into the soil (2 cm) of each plot in a closed system with a SRC-1 soil chamber connected to an EGM-4 portable system (PP-systems, Hitchin, UK), as described by Zuccarini et al. (2020) and Mu et al. (2022). Simultaneously, soil temperature (ST) was measured at one point near the collars at a depth of 10 cm using a TO 15 digital soil thermometer (Jules Richard Instruments, Argenteuil, France). The soil cores were collected at around 15:00 and the soil samples were transported to the laboratory, sieved to 2 mm and stored in hermetically closed plastic bags.. The <2 mm fraction was selected and divided into subsamples for the analysis of gravimetrical soil water content, concentrations and activities of soil extracellular enzymes, soil extractable element concentrations, and microbial biomass element concentrations. The subsamples were stored in hermetic plastic bags at 4ºC prior to analysis. Gravimetrical soil water content (SW) was determined by measuring weight loss after drying at 105°C for 24 h.

2.3. Extracellular enzyme activity

Fresh soil subsamples (2 mm sieved) were used for colorimetric analyses of soil extracellular enzyme activity, as described by Zuccarini et al. (2020) and Mu et al. (2022). Briefly, acid and alkaline phosphomonoesterase (acp and akp), β-glucosidase (bgl), protease (prot) and urease (ure) enzyme activity were determined and expressed as the μmol of substrate released per gram of dry soil and incubation time (h). These values were used as enzymatic indicators of the biogeochemical cycling of C (bgl), N (prot + ure) and P (acp + akp), which were labelled as enzC, enzN, and enzP respectively.

2.4. Soil extractable elements

Soil extractable organic carbon (EOC) and extractable total nitrogen (ETN) were measured in 0.5 M K_2SO4 extracts (4:1 v:w; fresh soil) using a total carbon/total nitrogen (TC/TN) analyser (Multi N/C 3100; Analytik Jena AG, Jena, Germany). Extractable total phosphorus (ETP) and extractable arsenic (As), calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), potassium (K), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), sulphur (S), strontium (Sr), vanadium (V) and zinc (Zn) in 0.5 M $NaHCO_3$ extracts (10:1 v:w; fresh soil) were measured using inductively coupled plasma/optical emission spectrometry (ICP-OES Optima 4300DV, PerkinElmer, Wellesley, USA) after digestion with 1% HNO3, as described by Zuccarini et al. (2020). The elemental concentrations in the extracts were expressed as µg of extractable element per unit of soil dry mass. The mineral elements targeted in this study were As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Ni, Pb, S, Sr, V and Zn, the EOC, ETN and ETP having been reported before (Asensio et al., 2021) and were only used as explanatory variables for the concentrations of the target elements.

The extraction with bicarbonate at pH 8.5 is considered the most suitable for the analysis of inorganic P forms in calcareous to slightly acidic soils (Olsen et al., 1954; FAO, 2021), although the low acidity of the sodium bicarbonate reduces the solubility of other elements like Al, Co, Cu, Fe, Ni and Mn but increases that of Mo and S (Truog 1948). Other standard extraction methods such as Mehlich-3, the use of chelating agents such as diethylenetriaminepentaacetic acid or monocalcium phosphate extractions can be more suitable for specific elements (Antonangelo et al., 2022), but it would take several extractions for the same sample and the use of hazardous chemicals as compared to the simple bicarbonate extraction. Thus, since our aim was to perform a screening of the elemental concentrations to determine biologically available elements in these soils and their links to environmental parameters, we have selected the simplest method. It should be noted that soil water content at sampling can affect the extractability of soil elements, with lower concentrations measured under low soil water content (Ross et al., 1989). Given that we did not adjust the soil water content of samples to equal values, the elemental concentrations during the driest seasons could be underestimated.

2.5. Microbial elemental concentrations

Microbial biomass C, N and P were measured using chloroform fumigation-extraction (Jenkinson and Powlson, 1976) as described by Marañón-Jiménez et al. (2022). Briefly, each fresh soil sample was divided into two, with one subsample being fumigated for 24 h with ethanol-free chloroform and the other not fumigated. Extractable C, N and P in both subsamples were measured as described above, and the microbial biomass C (MicC), N (MicN) and P (MicP) concentrations were calculated as the difference between the fumigated and unfumigated samples. All elemental concentrations in the microbial biomasses were expressed as μg of element per unit of soil dry mass.

2.6. Data analysis

The effects of season and the chronic drought on SW, ST, SR and the target mineral elements were analysed using two-way ANOVAs, with season and treatment as fixed effects and plot as a random factor. For the target mineral elements, statistical differences were further tested between treatments for each season with a Student's *t*-

test and within seasons using one-way ANOVAs. The correlations between target mineral elements and SW for the year and each season were tested using Pearson's correlations. The effects of season on the relationships between target mineral elements and SW were tested using analyses of covariance (ANCOVAs), with season as a fixed factor and SW as the covariate. The effects of season and treatment on the EC of the 17 target mineral elements considered as a whole were investigated in a PERMANOVA using the *vegan* package in R (v. 4.1.1). Effects and differences were considered significant at $P < 0.05$.

Pairwise Pearson correlations between the soil chemical-biological variables were performed and represented in heatmaps using the *reshape2* package in R (v. 4.1.1) that highlighted significant and strong correlations. A principal component analysis was performed with the *FactoMineR* and *factoextra* packages to visualize the multivariate correlations between the previously standardized soil chemical-biological variables. Vector variables were marked as target mineral elements (red) or other soil variables (blue), while cases were marked by treatment and season. Finally, a redundancy analysis was performed to visualize the multivariate correlations of macroelements with the explicable soil chemical-biological variables ($P < 0.1$) using the *vegan* and *ggrepel* packages. The *ggplot2* package was used for visualization in R.

3. Results

3.1. Effects of chronic drought and seasonal drought on soil water content, temperature, and CO_2 efflux

Soil water content was higher in winter coinciding with the lowest temperatures, while the minimum soil water content was recorded in summer (Fig. 1). There were seasonal variations in soil water content ($P < 0.001$), temperature ($P < 0.001$) and CO_2 efflux ($P < 0.001$); variations in water content were also observed between the treatment plots ($P < 0.05$, Fig. 1A). The average soil water content over the sampling period was lower in the chronic drought treatment plots (12.31 ± 1.87%) than in the control plots (18.58 ± 3.24%, $P < 0.001$), with significant differences occurring in winter ($P < 0.01$), summer ($P < 0.05$) and autumn ($P < 0.05$, Fig. 1A). The chronic drought treatment also provoked a reduction in soil CO_2 efflux in all seasons ($P < 0.05$, Fig. 1), although no effects of drought on soil temperature were observed (Fig. 1).

3.2. Effects of chronic drought and seasonal drought on soil extractable element concentrations

Ca, K, Mg and S were the most abundant elements in water extracts during the sampling periods, all with a mean EC above 100 μg g^{-1} (Table 1 and Fig. 2A), followed by Fe, Sr, Mn and Cu, whose means were above 1 μg g^{-1} (Table 1 and Fig. 2B). The mean EC of Zn, Mo, Ni, V, Pb, Cr, As, Cd and Hg were below 1 μg g^{-1} (Table 1). Season explained 46% ($P = 0.001$) of variation in EC of soil mineral elements when the 17 elements were analysed as a whole in a PERMANOVA, while the effects of chronic drought treatment and Season × Treatment interaction were not significant (Table 2). The seasonal changes observed on 13 of the studied elements were greater than the changes induced by the chronic drought treatment (Fig. 2 and Table S1). The chronic drought treatment significantly increased the EC of S, Mn, V and Cd but decreased those of K and Cu;

other than for Cu, these changes in elemental EC were consistent over the sampling periods (Fig. 2 and Table S1).

The EC of K, Mg, Sr, and Cu were strongly positively correlated with soil water content ($r > 0.60$ and $P < 0.001$), with correlations strongest – i.e. with steeper slopes than in other seasons – in spring for K ($r = 0.93$ and $P < 0.001$) and Sr ($r = 0.83$ and $P < 0.05$) (Fig. 3 and Table S2). The EC of S was negatively correlated with soil water content ($r = 0.49$ and $P < 0.01$; Table S2). The responses of Zn and Mo to soil water content varied seasonally (SW × Season interaction: $P < 0.05$), with strong correlations only found in one season (Table S2). The EC of Zn was positively correlated with water content in spring ($r = 0.84$ and $P < 0.01$), while for Mo the correlation was negative in autumn ($r = 0.78$ and $P < 0.05$).

The chronic drought treatments did not affect soil element EC significantly in any of the seasons analysed separately ($P > 0.05$, Table S3), although the seasonality of Cu, Zn and Hg may have been slightly affected by the treatment (Table S1, Season × Treatment interaction: $P < 0.05$). Thus, we used data combining control and drought treatments to investigate the seasonal dynamics of soil element EC (Table 3), which represent the average seasonal variation in response to current and future climate conditions. There were similar seasonal patterns in soil element EC, the highest EC of most elements being recorded in winter (Ca, K, Mg, Sr, Cu, Zn, Pb, Cr and Hg) or spring (Fe, Ni, V, As), with minimums recorded in autumn (K, Fe, Sr, Mn, Cu, Pb, Ni, V, As, Cd and Hg). The exception was S, whose EC was highest in summer and autumn and lowest in spring (Table 3).

3.3. Associations in the soil chemical-biological variables

Pairwise correlation analysis identified 13 strong positive correlations in the soil extractable elements ($r > 0.60$ and $P < 0.05$, Fig. 4 and S1). The EC of Ca, K, Mg and Sr were correlated with each other, while Mn was correlated with Fe, V and Cd. Ni was correlated with Fe and Hg, K with Cu, and Mg with Pb (Fig. 4).

The EC of some elements were also strongly correlated with other soil variables ($r > 0.60$ and $P < 0.05$, Fig. 4 and S1). K, Mg, Sr and Cu were positively correlated with soil water content. Mn was positively correlated with EOC and ETN, as was Cd. There were also positive correlations between K and EnzP, MicN and MicP, and Cu and MicP. The only negative correlation was between Cr and soil temperature (Fig. 4).

The first (PC1) and second (PC2) principal components of the PCA performed with the soil chemical-biological variables explained 29.72 and 18.35% of the total variance, respectively (Fig. 5). The elements K, Sr, Cu and Mg, and SW, ST and micN mainly contributed to PC1, while the elements Mn, Cd, V and Fe, and EOC and ETN mainly contributed to PC2 (Fig. 5C and Table S4A). The EC of Ca, K, Sr and Cu were positively related to SW and microbial activities, while the EC of S showed the opposite and was positively associated with ST (Fig. 5C). The EC of Mn and Cd were most closely correlated with EOC and ETN. Samples differed between the chronic drought and control treatments along PC1 ($P = 0.0358$) and PC2 ($P = 0.0163$). Samples also differed seasonally along PC1 ($P < 0.0001$; Table S4B). The ellipses grouping the data were not well separated for either the four seasons or between the chronic drought and control treatments (Figs. 5A and B).

The redundancy analysis of eight macroelements showed that variation in mean soil element EC was best explained by water content (r^2 = 0.45, P < 0.01; Table S5). Selected soil chemical-biological variables explained 48.76 and 6.54% of variation in macroelement EC along axes 1 and 2, respectively, above all for Ca, K, S and Fe (Fig. 6). The seasonal variation in soil element EC (winter-spring and summer-autumn) was separated along the first axis by soil temperature, moisture and respiration: the EC in winter-spring were positively associated with higher levels of soil respiration and moisture, while those in summer-autumn were positively associated with higher soil temperatures (Fig. 6). Overall, the EC of Ca was the dominant soil extractable element in winter, whereas the EC of K and Fe were more abundant in winter and spring and the EC of S was more abundant in summer and autumn (Fig. 6). The EC of Ca was positively correlated with soil water content and microbial N and P concentrations, while the EC of K was more associated with CO_2 efflux and the activity of N- and P-degrading enzymes. The EC of S was positively correlated with soil temperature but negatively correlated with soil water content and CO_2 efflux (Fig. 6).

4. Discussion

4.1. Effects of chronic and seasonal drought on extractable element concentrations in Mediterranean soils

The response of individual mineral elements to water stress, as indicated by their elemental concentrations (EC), varied depending on the element and season. While chronic drought did not cause significant seasonal differences, it predominantly affected element EC in spring. Notably, it resulted in decreased extractable Ca, K, Sr, Zn, and Pb at lower levels of soil moisture, whereas extractable Ni and Mo tended to increase during drier winter and autumn, respectively ($r > 0.70$ and $P < 0.05$, Table S2). Additionally, chronic drought increased the EC of S, Mn, V, and Cd but decreased the EC of K and Cu throughout the year ($P < 0.05$, Table S1), aligning with previous studies on the effects of medium-term drought at the study site (Sardans and Peñuelas, 2007a; Sardans et al., 2008c).

Our findings indicate that soil moisture strongly influenced the movement and allocation of K in plant-soil compartments, which is closely related to biotic retention processes (Deng et al., 2021; Sardans and Peñuelas, 2007a). Under drier conditions, K leaching declines (Deng et al., 2021; Schlesinger et al., 2016; Slessarev et al., 2016) partly due to increased binding by enzymes in dehydrated K forms (Deng et al., 2021; Maathuis et al., 2009). We also observed lower microbial activity, indicated by reduced soil CO_2 efflux ($P < 0.05$, Fig. 1C) and soil enzyme activity (Asensio et al., 2021; Marañón-Jiménez et al., 2022), in drought plots, which may limit the release capacity of soil soluble K by decreasing mineralization rates under low water availability (Sardans and Peñuelas, 2007a). Consequently, the decrease in the EC of K could be attributed to reduced leaching and microbial mineralization rates. However, other factors, such as lower weathering rates under drought conditions, could also contribute to the decline in soluble K concentrations at the study site (Sardans and Peñuelas, 2007a). Reduced soluble concentrations, combined with poorer diffusion capacity under low soil moisture, further limit the availability of K and subsequently its uptake by plants (Sardans et al., 2020). Considering that K plays a critical role in controlling leaf water losses, K limitation can increase plant vulnerability to drought stress, resulting in reduced tree growth and potential forest mortality (Gessler et al., 2017; Sardans and Peñuelas, 2015).

Regarding extractable S, our results suggest that its increase is due to lower microbial consumption activity. However, the decrease in plant uptake may be a more significant factor, as previous studies have reported increased extractable S and reduced S concentrations in aboveground biomass in response to drought at the study site (Sardans and Peñuelas, 2007a). Leaf S concentrations have been found to be negatively correlated with sclerophylly, which tends to increase in response to drier conditions in Mediterranean ecosystems (Bacelar et al., 2004; Sardans et al., 2006, 2008c). This could lead to a decline in plant S uptake and subsequent S accumulation in the soil. Additionally, the upward transportation of salts from deep groundwater under drier conditions may contribute to the increase in S (Luo et al., 2016) if there are greater net mass gains of sulphate in drought plots than in control plots. The cation exchange capacity of these soils is low (Table S6) due to the slightly acidic soil pH, which decreases the number of negative charges on the colloids, and the high percentage of the sand fraction, which has no electrical charge and therefore no capacity to exchange cations. Thus, the extractable forms of S and other elements accumulated in the soil during the driest periods are not ionically bonded to the soil surfaces or molecules in the soil solution, being more prone to be lost by leaching after heavy rain events. This makes the ecosystem susceptible to net S and other element losses under a scenario in the Mediterranean Basin of ever more frequent drought crises and a rise in the amount of torrential rainfall (IPCC, 2014; Vicente-Serrano et al., 2014).

The increases in EC of Mn, Cd, and V (Table S1) were primarily attributed to higher levels of metal-organic matter (OM) complexes, as evidenced by their strong correlations with extractable organic carbon (EOC) and extractable total nitrogen (ETN) (Figs. 4 and 5C). Previous studies conducted at the study site have demonstrated increased soil EOC and ETN under progressively drier conditions (Asensio et al., 2021; Marañón-Jiménez et al., 2022). The formation and destruction of complexes, influenced by drying-rewetting events, are likely to have a minor role in this process, as the intensified drying and rewetting cycles induced by drought would have insignificant or unclear effects on their availability (Sardans and Peñuelas, 2007b; Sardans et al., 2008b).

In the case of Cu, its response to drought exhibited different patterns but is expected to be similar to that of K, considering the close correlation between K and Cu (Fig. S1). Consequently, lower leaching and microbial mineralization levels may have contributed to the decrease in extractable Cu. Apart from Mn, V, and Cd, the EC of other elements such as Zn, Cr, and Ni also showed tendencies of increase (Table 1), indicating a generally higher accumulation of trace elements in soluble forms. This could exacerbate the negative effects of drought on plant productivity and accelerate the export of trace elements from soils to continental waters after torrential rainfall, as observed in similar studies (Sardans and Peñuelas, 2007b; Sardans et al., 2008b).

4.2. Biological and abiotic controls of extractable elemental concentrations in

Mediterranean soils

Increases in soil temperature may enhance the solubility of all the elements in soil solutions but may also decrease soil water content to a greater extent, as shown by the strong negative relationship between temperature and moisture (r = 0.82 and P < 0.05, Fig. S1). In addition, soil CO_2 efflux was positively correlated with soil water content but not with soil temperature (Fig. 5C). As a result, the variations in EC were best explained by levels of soil water content (Fig. 5C and Table S5) in this Mediterranean forest.

The EC of Ca, K, Mg, Sr, Cu, Pb and Cr were positively correlated with soil water content (Figs. 4 and 5C), which suggests that these elements are more prone to leaching into the soil solution than others and so have a higher risk of being lost to the ecosystem. By contrast, the EC of S was negatively correlated with moisture and CO_2 efflux (Figs. 4 and 5C), indicating that increases in microbial and/or root activities could promote S uptake to a greater degree than physical passive leaching and/or weathering at high soil moisture levels. It is likely that our results reflect the complex biophysical interactions taking place in soils: soil enzyme activity releases soluble S from OM, which enhances the sulphate reduction to sulphide via microbial respiration under higher levels of soil water content (Hao et al., 1996; Muyzer and Stams, 2008), thereby indirectly leading to decreases in the concentrations of soluble S in the soil solution. The EC of Mn, Cd, V and Mo were positively correlated to levels of OM (EOC and ETN, Fig. 4 and 5C), probably due to the formation of dissolved metal-OM complexes (Filipović et al., 2018; Li et al., 2013). The strong soil retaining power of Mn and Cd (Figs. 4 and 5C) coincides with previous findings suggesting that the biological availability of Mn (Li et al., 2021; Tian et al., 2016; Wang et al., 2017) and Cd (Li et al., 2013; Wang and Zhou, 2017; Yang et al., 2020) increases with rising concentrations of soluble C and N in the soil. Their relationship with ETN may also indicate that soil acidification caused by excessive soil N enhances the leaching of heavy metals (Atafar et al., 2010; Ata-ul-karim et al., 2020; Mitchell et al., 2000; Raza et al., 2020), especially by increasing the concentrations of soluble Mn and Cd.

Soil Cu and K were related with the storage of N and P in the microbial biomass pool, as indicated by the positive relationship of their EC with microbial variables (Figs. 4, 5C and 6). Higher extractable K levels boost enzyme activities, thereby increasing the potential mineralization of N and P and their acquisition by both microbes and plants (Figs. 4 and 6), although increased microbial storage of N and P may reduce their availability to plants under higher extractable Cu levels (Fig. 4).

The EC of Mn, Cd, Ni, V, Hg and Fe were all positively correlated among themselves, which probably indicates the strong adsorption of these heavy metals to the oxides of Mn and/or Fe-Mn in soils (Tack et al., 2006; Violante et al., 2010), as shown by the close correlations between Mn and the other elements (Figs. 5C and S1). Ca, Mg, Cu, Sr, Pb and K constitute another closely correlated group of elements (Figs. 5C and S1), probably due to their high levels of cation-exchange reactions (Liu et al., 2019; Martins et al., 2014; Miller et al., 1993; Ross et al., 2008; Sharma et al., 2015; Sanderson et al., 2015). In addition, the strongly synergistic behaviour in EC between Ca, Mg and Sr (Fig. S1) could be attributed to their geochemical similarity since they are all naturally occurring alkaline earth metal elements (Bunde et al., 1997; Frei et al., 2020; Scott et al., 2020).

4.3. Seasonal variability in extractable elemental concentrations in Mediterranean soils

Although the seasonality of EC varied with the elements, the most common pattern was characterized by higher EC in winter-spring (wet seasons) than in summer-autumn (dry seasons) (Table 3), which indicates that temporal variations in EC were mainly driven by soil water content.

Throughout the study period the EC generally tracked seasonal variations in soil microclimate, biological activity and OM. Extractable Ca, Mg, Sr and Cr showed similar seasonal patterns of change, whereby the EC were higher in winter than in other seasons, probably due to the greater soil moisture in winter (Fig. 1A and Table 3). Like these previous four elements, the EC of K, Cu and Pb were also strongly correlated with soil water content (Fig. 4), although these latter elements had relatively higher EC in spring (Table 3) given that high levels of microbial and/or root activities may increase their availability during the growing season (spring) (Fig. 1C). By contrast, the EC of S was higher in summer and autumn when biological activity is lower, suggesting that less uptake by microbes and/or plants causes an accumulation of soluble S in the dry seasons (Fig. 1C and Table 3). Fe, Mn and As had lower EC in autumn than in the other seasons (Table 3), probably linked to the multiple effects of lower levels of water content and biological activity in the dry seasons (Fig. 1), and lower levels of OM in autumn than in summer (Asensio et al., 2021). The EC of V was seasonally irregular, with maxima in spring and minima in autumn (Table 3). The close association between V and Mn, however, may indicate that these two elements are involved in biogeochemical processes in similar ways, although their lower magnitude may ensure that the EC of V is highly variable. The EC of the other elements (Zn, Ni, Mo, Cd and Hg) did not oscillate seasonally (Table 3), which suggests that they are less affected by seasonality in climate and phenology and more dependent on parent material and soil mineralogy.

5. Conclusions

The study revealed that variations in EC were primarily associated with soil water content. The EC of elements exhibited seasonal responses linked to changes in soil microclimate, biological activity, and organic matter levels. Generally, the EC of most elements was higher during winter-spring (wet seasons) compared to summer-autumn (dry seasons). Chronic drought had notable effects on soil element composition, resulting in decreased concentrations of extractable potassium (K) but increased concentrations of sulfur (S) and, to a lesser extent, other trace elements studied. These alterations have implications for the cycling and loss of soil mineral elements, potentially contributing to ecosystem degradation and pollution dispersion under future drier conditions in the Mediterranean Basin. By assessing EC, the fundamental mechanisms governing soil mineral element dynamics can be identified, enabling projections of soil elemental composition, as well as the bioavailability of nutrients and trace elements, under scenarios of global environmental change.

Credit authorship contribution statement

Zhaobin Mu: Data curation, Formal analysis, Software, Investigation, Validation, Writing – original draft, Writing – review & editing. **Dolores Asensio**: Conceptualization, Methodology, Data curation, Investigation, Validation, Writing – original draft, Writing – review & editing. **Jordi Sardans**: Conceptualization, Methodology, Validation, Writing – review & editing. **Romà Ogaya**: Methodology, Investigation, Writing – review & editing. **Joan Llusià**: Methodology, Writing – review & editing. **Iolanda Filella**: Writing – review & editing. **Lei Liu**: Writing – review & editing. **Xinming Wang**: Writing – review & editing. **Josep Peñuelas**: Conceptualization, Methodology, Validation, Project administration, Supervision, Funding acquisition, Writing – original draft, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online.

References

Alloway, B.J., 2013. Heavy metals in soil: trace metals and metalloids in soil and their bioavailability. In: Reading. Springer, UK.

Armson, K., 1977. Forest Soils: Properties and processes. University of Toronto Press, Toronto, Canada.

Asensio, D., Zuccarini, P., Ogaya, R., Marañón-Jiménez, S., Sardans, J., Peñuelas, J., 2021. Simulated climate change and seasonal drought increase carbon and phosphorus demand in Mediterranean forest soils. Soil Biol. Biochem.163, 108424.

Atafar, Z., Mesdaghinia, A., Nouri, J., Homaee, M., Yunesian, M., Ahmadimoghaddam, M., Mahvi, A.H., 2010. Effect of fertilizer application on soil heavy metal concentration. Environ. Monit. Assess. 160, 83–89.

Ata-ul-karim, S.T., Cang, L., Wang, Y., Zhou, D., 2020. Interactions between nitrogen application and soil properties and their impacts on the transfer of cadmium from soil to wheat (*Triticum aestivum* L.) grain. Geoderma 357, 113923.

Bacelar, E.A., Correira, C.M., Moutinho-Pereira, J.M., Goncalves, B.C., Lopes, J.I., Torres-Pereira, J.M.G., 2004. Sclerophylly and leaf anatomical traits of five field-grown olive cultivars growing under drought conditions. Tree Physiol. 24, 233–239.

Beygi, M., Jalali, M., 2019. Assessment of trace elements (Cd, Cu, Ni, Zn) fractionation and bioavailability in vineyard soils from the Hamedan, Iran. Geoderma 337, 1009–1020.

Boehm, M.M., Anderson, D.W., 1997. A landscape-scale study of soil quality in three prairie farming systems. Soil Sci. Soc. Am. J. 61, 1147–1159.

Bunde R.L., Rosentreter J.J., Liszewski M.J., Hemming C.H., Welhan J., 1997. Effects of calcium and magnesium on strontium distribution coefficients. Environ. Geol. 32, 219–229.

Chorover, J., Kretzschmar, R., Garcia-Pichel, F., Sparks, D.L., 2007. Soil biogeochemical processes within the critical zone. Elements 3, 321–326.

Cramer, W., Guiot, J., Fader, M., Garrabou, J., Gattuso, J.-P., Iglesias, A., Lange, M.A., Lionello, P., Llasat, M.C., Paz, S., Peñuelas, J., Snoussi, M., Toreti, A., Tsimplis, M.N., Xoplaki, E., 2018. Climate change and interconnected risks to sustainable development in the Mediterranean. Nat. Clim. Chang. 8, 972–980.

Deng, M., Li, P., Wang, Z., Guo, L., Wu, Y., Huang, J., Wang, X., Liu, L., 2021. Drought and salinization stress induced by stand development alters mineral element cycling in a larch plantation. J. Geophys. Res. Biogeo. 126, e2020JG005906.

Filipović, L., Romić, M., Romić, D., Filipović, V., Ondrašek, G., 2018. Organic matter and salinity modify cadmium soil (phyto)availability. Ecotox. Environ. Safe. 147, 824–831.

Frei, R., Frei, K.M., Kristiansen, S.M., Jessen, S., Schullehner, J., Hansen, B., 2020. The link between surface water and groundwater-based drinking water-strontium isotope spatial distribution patterns and their relationships to Danish sediments. Appl. Geochem. 121, 104698.

Gessler, A., Schaub, M., Mcdowell, N.G., 2017. The role of nutrients in drought-induced tree mortality and recovery. New Phytol. 214, 513–520.

Hao, O.J., Chen, J.M., Huang, L., Buglass, R.L., 1996. Sulfate-reducing bacteria. Crit. Rev. Environ. Sci. Technol. 26, 155–187.

Hooda, P.S., 2010. Trace Elements in Soils. Wiley-Blackwell, New Jersey, US.

Huang, P.-M., Wang, M.-K., Chiu, C.-Y., 2005. Soil mineral-organic matter-microbe interactions: Impacts on biogeochemical processes and biodiversity in soils. Pedobiologia 49, 609–635.

IPCC, 2014. Part A: global and sectoral aspects. Contribution of Working Group II to the fifth assessment report of the Intergovernmental Panel on Climate Change. In: En IPCC, Barros, V., Dokken, D., Mach, K., Mastrandrea, M., Bilir, T., Chatterjee, M., Ebi, K., Estrada, Y., Genova, R. (Eds.), Climate Change 2014: Impacts, Adaptation, and Vulnerability (Field C). Cambridge University Press, Cambridge, pp. 485–533.

Islam, S., Ahmed, K., Al-Mamun, H., 2015. Distribution of trace elements in different soils and risk assessment: a case study for the urbanized area in Bangladesh. J. Geochem. Explor. 158, 212–222.

Jenkinson, D.S., Powlson, D.S., 1976. Effects of biocidal treatments on metabolism in soil. 5. Method for measuring soil biomass. Soil Biol. Biochem. 8, 209–213.

Jiménez-Ballesta, R., Bravo, S., Amorós, J. A., Pérez-de-los-Reyes, C., García-Pradas, J., Sanchez, M., García-Navarro, F. J., 2022. Soil and leaf mineral element contents in Mediterranean vineyards: Bioaccumulation and potential soil pollution. Water, Air, Soil Pollut. 233, 20.

Johnson, D.W., Turner, J., 2019. Nutrient cycling in forests: a historical look and newer developments. For. Ecol. Manag. 444, 344–373.

Li, H., Santos, F., Butler, K., Herndon, E., 2021. A critical review on the multiple roles of manganese in stabilizing and destabilizing soil organic matter. Environ. Sci. Technol. 55, 12136−12152.

Li, L., Wu, H., van Gestel, C.A., Peijnenburg, W.J., Allen, H.E., 2014. Soil acidification increases metal extractability and bioavailability in old orchard soils of Northeast Jiaodong Peninsula in China. Environ. Pollut. 188, 144–152.

Li, T., Tao, Q., Liang, C., Shohag, M.J.I., Yang, X., Sparks, D.L., 2013. Complexation with dissolved organic matter and mobility control of heavy metals in the rhizosphere of hyperaccumulator *Sedum alfredii*. Environ. Pollut. 182, 248–255.

Liu, Q., Deng, Y., Tang, J., Chen, D., Li, X., Lin, Q., Yin, G., Zhang, M., Hu, H., 2019.

Potassium lignosulfonate as a washing agent for remediating lead and copper co-contaminated soils. Sci. Total Environ. 658, 836–842.

Luo, W., Dijkstra, F.A., Bai, E., Feng, J., Lü, X.T., Wang, C., Wu, H., Li, M.H., Han, X., Jiang, Y., 2016. A threshold reveals decoupled relationship of sulfur with carbon and nitrogen in soils across arid and semi-arid grasslands in northern China. Biogeochemistry 127, 141–153.

Ma, Y.B., Uren, N.C., 1997. The fate and transformations of Zinc added to soils. Aust. J. Soil Res. 35, 727–738.

Maathuis, F.J.M., 2009. Physiological functions of mineral macronutrients. Curr. Opin. Plant. Biol. 12, 250–258.

Manzoni, S., Schimel, J.P., Porporato, A., 2012. Responses of soil microbial communities to water stress: results from a meta-analysis. Ecology 93, 930–938.

Marañón-Jiménez, S., Asensio, D., Sardans, J., Zuccarini, P., Ogaya, R., Mattana, S., Peñuelas, J., 2022. Seasonal drought in Mediterranean soils mainly changes microbial C and N contents whereas chronic drought mainly impairs the capacity of microbes to retain P. Soil Biol. Biochem.165, 108515.

Martins, A.P., de Andrade Costa, S.E.V.G., Anghinoni, I., Kunrath, T.R., Balerini, F., Cecagno, D., Carvalho, P.C.D.F., 2014. Soil acidification and basic cation use efficiency in an integrated no-till crop–livestock system under different grazing intensities. Agric. Ecosyst. Environ. 195, 18–28.

Miller, E.K., Blum, J.D., Friedland, A.J., 1993. Determination of soil exchangeable-cation loss and weathering rates using Sr isotopes. Nature 362, 438–441.

Mitchell, L.G., Grant, C.A., Racz, G.J., 2000. Effect of nitrogen application on concentration of cadmium and nutrient ions in soil solution and in durum wheat. Can. J. Soil Sci. 80, 107–115.

Mu, Z., Asensio, D., Llusià, J., Filella, I., Ogaya, R., Yi, Z., Peñuelas, J., 2022. Annual and seasonal variations in soil volatile organic compound concentrations in a Mediterranean shrubland and holm oak forest. Geoderma 405, 115401.

Mu, Z., Llusià, J., Liu, D., Ogaya, R., Asensio, D., Zhang, C., Peñuelas, J., 2019. Profile of foliar isoprenoid emissions from Mediterranean dominant shrub and tree species under experimental nitrogen deposition. Atmos. Environ. 216, 116951.

Mu, Z., Llusià, J., Liu, D., Ogaya, R., Asensio, D., Zhang, C., Peñuelas, J., 2018. Seasonal and diurnal variations of plant isoprenoid emissions from two dominant species in Mediterranean shrubland and forest submitted to experimental drought. Atmos. Environ. 191, 105–115.

Muyzer, G., Stams, A.J.M., 2008. The ecology and biotechnology of sulphate-reducing bacteria. Nat. Rev. Microbiol. 6, 441–454.

Ogaya, R., Liu, D., Barbeta, A., Peñuelas, J., 2020. Stem mortality and forest dieback in a 20-years experimental drought in a Mediterranean holm oak forest. Front. For. Glob. Chang. 2, 89.

Pastor, J., Bockheim, J.G., 1984. Distribution and cycling of nutrients in an aspen-mixed-hardwood-Spodosol ecosystem in northern Wisconsin. Ecology 65, 339–353.

Peñuelas, J., Sardans, J., Filella, I., Estiarte, M., Llusià, J., Ogaya, R., Carnicer, J., Bartrons, M., Rivas-Ubach, A., Grau, O., Peguero, G., Margalef, O., Pla-Rabés, S., Stefanescu, C., Asensio, D., Preece, C., Liu, L., Verger, A., Rico, L., Barbeta, A., Achotegui-Castells, A., Gargallo-Garriga, A., Sperlich, D., Farré-Armengol, G., Fernández-Martínez, M., Liu, D., Zhang, C., Urbina, I., Camino, M., Vives, M., Nadal-Sala, D., Sabaté, S., Gracia, C., Terradas, J., 2018. Assessment of the impacts of climate change on Mediterranean terrestrial ecosystems based on data from field experiments and long-term monitored field gradients in Catalonia. Environ. Exp. Bot. 152, 49–59.

Purves, D., 2012. Trace Elements Contamination of the Environment. Elsevier Pub. Co, Amsterdam, p. 216.

Raza, S., Miao, N., Wang, P., Ju, X., Chen, Z., Zhou, J., Kuzyakov, Y., 2020. Dramatic loss of inorganic carbon by nitrogen-induced soil acidification in Chinese croplands. Glob. Change Biol. 26, 3738–3751.

Rees, F., Simonnot, M.O., Morel, J.L., 2014. Short-term effects of biochar on soil heavy metal mobility are controlled by intra-particle diffusion and soil pH increase. Eur. J. Soil Sci. 65, 149–161.

Ross, D.S., Matschonat, G., Skyllberg, U., 2008. Cation exchange in forest soils: The need for a new perspective. Eur. J. Soil Sci. 59, 1141–1159.

Salekin, S., Bloomberg, M., Morgenroth, J., Meason, D.F., Mason, E.G., 2021.Within-site drivers for soil nutrient variability in plantation forests: A case study from dry sub-humid New Zealand. Catena 200, 105149.

Sanderson, P., Naidu, R., Bolan, N., Lim, J.E., Ok, Y.S., 2015. Chemical stabilisation of lead in shooting range soils with phosphate and magnesium oxide: Synchrotron investigation. J. Hazard. Mater. 299, 395–403.

Sardans, J., Peñuelas, J., 2005. Drought decreases soil enzyme activity in a Mediterranean *Quercus ilex* L. forest. Soil Biol. Biochem. 37, 455–461.

Sardans, J., Peñuelas, J., 2007a. Drought changes phosphorus and potassium accumulation patterns in an evergreen Mediterranean forest. Funct. Ecol. 21, 191–201.

Sardans, J., Peñuelas, J., 2007b. Drought changes the dynamics of trace element accumulation in a Mediterranean *Quercus ilex* forest. Environ. Pollut. 147, 567–583.

Sardans, J., Penuelas, J., Estiarte, M., 2008a. Changes in soil enzymes related to C and N cycle and in soil C and N content under prolonged warming and drought in a Mediterranean shrubland. Appl. Soil Ecol. 39, 223–235.

Sardans, J., Peñuelas, J., Estiarte, M., 2008b. Warming and drought change trace element bioaccumulation patterns in a Mediterranean shrubland. Chemosphere 70, 874–885.

Sardans, J., Peñuelas, J., Ogaya, R., 2008c. Drought' s impact on Ca, Fe, Mg, Mo and S concentration and accumulation patterns in the plants and soil of a Mediterranean evergreen *Quercus ilex* forest. Biogeochemistry 87, 49–69.

Sardans, J., Peñuelas, J., Prieto, P., Estiarte, M., 2008d. Changes in Ca, Fe, Mg, Mo, Na, and S content in a Mediterranean shrubland under warming and drought. J. Geophys. Res. 113, G03039.

Sardans, J., Peñuelas, J., Prieto, P., Estiarte, M., 2008e. Drought and warming induced changes in P and K concentration and accumulation in plant biomass and soil in a Mediterranean shrubland. Plant Soil 306, 261–271.

Sardans, J., Peñuelas, J., Rodà F., 2006. Plasticity of leaf morphologic traits, leaf nutrient content, and water capture in the Mediterranean evergreen oak *Quercus ilex* subsp. *ballota* in response to fertilization and changes in competitive conditions, Ecoscience, 13, 250–270.

Sardans, J., Urbina, I., Grau, O., Asensio, D., Ogaya, R., Peñuelas, J., 2020. Long-term drought decreases ecosystem C and nutrient storage in a Mediterranean holm oak forest. Environ. Exp. Bot. 177, 104135.

Schlesinger, W.H., Dietze, M.C., Jackson, R.B., Phillips, R.P., Rhoades, C.C., Rustad, L.E., Vose, J.M., 2016. Forest biogeochemistry in response to drought. Global Change Biol. 22, 2318–2328.

Scott, V., Juran, L., Ling, E.J., Benham, B., Spiller, A., 2020. Assessing strontium and vulnerability to strontium in private drinking water systems in Virginia. Water 12, 1053.

Sharma, A., Weindorf, D.C., Wang, D.D., Chakraborty, S., 2015. Characterizing soils via portable X-ray fluorescence spectrometer: 4. Cation exchange capacity (CEC). Geoderma 239, 130–134.

Slessarev, E.W., Lin, Y., Bingham, N.L., Johnson, J.E., Dai, Y., Schimel, J.P., Chadwick, O.A., 2016. Water balance creates a threshold in soil pH at the global scale. Nature 540, 567–569.

Solly, E.F., Weber, V., Zimmermann, S., Walthert, L., Hagedorn, F., Schmidt, M.W.I., 2020. A critical evaluation of the relationship between the effective cation exchange capacity and soil organic carbon content in Swiss forest soils. Front. For. Glob. Change 3, 98.

Szynkowska, M. I., Pawlaczyk, A., Maćkiewicz, E., 2018. Bioaccumulation and biomagnification of trace elements in the environment. In: Chojnacka K, Saeid A (eds) Recent Advances in Trace Elements. 251–276.

Tack, F.M.G., Van Ranst, E., Lievens, C., Vandenberghe, R.E., 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: The role of hydrous oxides of Fe and Mn. Geoderma 137, 83–89.

Tian, Q.Y., Liu, N.N., Bai, W.M., Li, L.H., Chen, J.Q., Reich, P.B., Yu, Q., Guo, D.L., Smith, M.D., Knapp, A.K., Cheng, W.X., Lu, P., Gao, Y., Yang, A., Wang, T.Z., Li, X., Wang, Z.W., Ma, Y.B., Han, X.G., Zhang, W.H., 2016. A novel soil manganese mechanism drives plant species loss with increased nitrogen deposition in a temperate steppe. Ecology 97, 65–74.

Valladares, G.S., Camargo, O.A.D., Carvalho, J.R.P.D., Silva, A.M.C., 2009. Assessment of heavy metals in soils of a vineyard region with the use of principal component analysis. Sci. Agric. 66, 361–367.

Vicente-Serrano, S.M., Lopez-Moreno, J.I., Beguería, S., Lorenzo-Lacruz, J., Sanchez-Lorenzo, A., García-Ruiz, J.M., Azorin-Molina, C., Morán-Tejeda, E., Revuelto, J., Trigo, R., Coelho, F., Espejo, F., 2014. Evidence of increasing drought severity caused by temperature rise in southern Europe. Environ. Res. Lett. 9, 044001.

Violante, A., Cozzolino, V., Perelomov, L., Caporale, A., Pigna, M., 2010. Mobility and bioavailability of heavy metals and metalloids in soil environments. J. Soil Sci. Plant Nutr. 10, 268–292.

Wang, R., Dungait, J.A.J., Buss, H.L., Yang, S., Zhang, Y., Xu, Z., Jiang, Y., 2017. Base cations and micronutrients in soil aggregates as affected by enhanced nitrogen and water inputs in a semi-arid steppe grassland. Sci. Total Environ. 575, 564–572.

Wang, G., Zhou, L., 2017. Application of green manure and pig manure to Cd-contaminated paddy soil increases the risk of Cd uptake by rice and Cd downward migration into groundwater: Field micro-plot trials. Water, Air, Soil Pollut. 228, 29.

Yang, W., Zhou, H., Gu, J., Liao, B., Zhang, J., Wu, P., 2020. Application of rapeseed residue increases soil organic matter, microbial biomass, and enzyme activity and mitigates cadmium pollution risk in paddy fields. Environ. Pollut. 264, 114681.

Zahoor, R., Dong, H., Abid, M., Zhao, W., Wang, Y., Zhou, Z., 2017. Potassium fertilizer improves drought stress alleviation potential in cotton by enhancing photosynthesis and carbohydrate metabolism. Environ. Exp. Bot. 137, 73–83.

Zhou, S., Zhang, Y., Williams, A.P., Gentine, P., 2019. Projected increases in intensity, frequency, and terrestrial carbon costs of compound drought and aridity events. Sci. Adv. 5, eaau5740.

Zhou, W., Yang, H., Xie, L., Li, H., Huang, L., Zhao, Y., 2021. Hyperspectral inversion of soil heavy metals in Three-River Source Region based on random forest model. Catena 202, 105222.

Zuccarini, P., Asensio, D., Ogaya, R., Sardans, J., Peñuelas, J., 2020. Effects of seasonal and decadal warming on soil enzymatic activity in a P-deficient Mediterranean shrubland. Glob. Chang. Biol. 26, 3698–3714.

Table 1

Mean (±SEM) extractable concentrations of soil mineral elements (μg g^{-1} dry soil), from control and chronic drought plots over the study period (n = 4 seasons × 4 plots). The elements were classified based on the concentrations of control plots in this study, as 'Macroelement' (≥1 μg g^{-1}) or 'Microelement' (<1 μg g^{-1}). The elements were indicated as nutrients and/or pollutants and classified into different categories.

Element	Treatment		Concentration class	Nutrient class	Pollutant class
	Control	Drought			
Ca	479.87 ± 58.24	473.31 ± 47.40	Macroelement	Macronutrient	(-)
K	349.66 ± 28.10	297.56 ± 12.90	Macroelement	Macronutrient	(-)
Mg	132.30 ± 9.13	136.73 ± 6.17	Macroelement	Macronutrient	(-)
S	107.51 ± 17.48	151.66 ± 17.98	Macroelement	Macronutrient	(-)
Fe	36.77 ± 3.07	41.24 ± 5.26	Macroelement	Micronutrient	Minor heavy metal pollutant
Sr	4.03 ± 0.46	3.60 ± 0.34	Macroelement	(-)	Radioactive metal pollutant
Mn	2.26 ± 0.34	3.53 ± 0.45	Macroelement	Micronutrient	Minor heavy metal pollutant
Cu	1.72 ± 0.51	0.72 ± 0.12	Macroelement	Micronutrient	Minor heavy metal pollutant
Zn	0.334 ± 0.069	0.468 ± 0.069	Microelement	Micronutrient	Minor heavy metal pollutant
Pb	0.314 ± 0.050	0.313 ± 0.040	Microelement	(-)	Major heavy metal pollutant
Cr	0.179 ± 0.025	0.203 ± 0.027	Microelement	(-)	Major heavy metal pollutant
Ni	0.157 ± 0.014	0.179 ± 0.021	Microelement	Micronutrient	Minor heavy metal pollutant
V	0.134 ± 0.031	0.180 ± 0.039	Microelement	Non-essential nutrient	Minor heavy metal pollutant
As	0.080 ± 0.010	0.068 ± 0.007	Microelement	(-)	Major heavy metal pollutant
Mo	0.019 ±0.001	0.021 ± 0.001	Microelement	Micronutrient	Minor heavy metal pollutant
Cd	0.006 ± 0.001	0.008 ± 0.001	Microelement	(-)	Major heavy metal pollutant
Hg	0.006 ± 0.001	0.006 ± 0.001	Microelement	(-)	Major heavy metal pollutant

Table 2

Results of a PERMANOVA (season × treatment) for the extractable concentrations of the 17 soil mineral elements treated as covariables (permutations = 999; ****P*<0.01).

	Df	SumsOfSqs	MeanSqs	Model *F*	R^2	Pr(>*F*)	
Season	3	0.311	0.104	7.612	0.460	0.001	***
Treatment	1	0.021	0.021	1.533	0.031	0.213	
Season:Treatment	3	0.017	0.006	0.421	0.025	0.895	
Residuals	24	0.327	0.014		0.484		
Total	31	0.676			1.000		

Table 3

Mean (±SEM) seasonal concentrations of soil mineral elements (μg g^{-1} dry soil) (*n* = 2 treatments × 4 plots). Different letters indicate significant differences among seasons according to one-way ANOVAs.

Element	Season			
	Winter	Spring	Summer	Autumn
Ca	709.29 ± 108.75^{a}	383.27 ± 36.75^{b}	418.50 ± 10.85^{b}	395.30 ± 21.69^{b}
K	399.13 ± 37.11^{a}	346.85 ± 34.24^{ab}	289.57 ± 9.58^{b}	258.90 ± 13.75^{b}
Mg	164.66 ± 11.73^{a}	122.16 ± 12.04^{b}	124.12 ± 5.63^{b}	127.14 ± 5.83^{b}
S	92.48 ± 11.57^{a}	58.81 ± 10.77^{a}	186.96 ± 24.63^{b}	180.09 ± 19.23^{b}
Fe	43.03 ± 6.74^{ab}	52.44 ± 6.76^{a}	35.41 ± 2.02^{ab}	25.14 ± 2.99^{b}
Sr	5.71 ± 0.75^{a}	3.17 ± 0.32^{b}	3.36 ± 0.15^{b}	3.02 ± 0.14^{b}
Mn	2.57 ± 0.54^{ab}	3.58 ± 0.75^{a}	3.97 ± 0.34^{a}	1.47 ± 0.30^{b}
Cu	2.37 ± 0.81^{a}	1.72 ± 0.49^{ab}	0.46 ± 0.03^{b}	0.34 ± 0.02^{b}
Zn	0.535 ± 0.082	0.495 ± 0.093	0.257 ± 0.094	0.317 ± 0.110
Pb	0.445 ± 0.073^{a}	0.383 ± 0.059^{ab}	0.239 ± 0.036^{b}	0.187 ± 0.028^{b}
Cr	0.303 ± 0.044^{a}	0.173 ± 0.015^{b}	0.138 ± 0.007^{b}	0.150 ± 0.034^{b}
Ni	0.167 ± 0.028	0.193 ± 0.033	0.166 ± 0.010	0.146 ± 0.024
V	0.079 ± 0.009^{a}	0.302 ± 0.020^{b}	0.199 ± 0.020^{c}	0.019 ± 0.008^{d}
As	0.107 ± 0.029^{ab}	0.094 ± 0.012^{a}	0.080 ± 0.013^{ab}	0.044 ± 0.007^{b}
Mo	0.017 ± 0.001	0.019 ± 0.001	0.022 ± 0.001	0.022 ± 0.002
Cd	0.007 ± 0.001	0.007 ± 0.001	0.009 ± 0.001	0.005 ± 0.001
Hg	0.007 ± 0.001	0.005 ± 0.001	0.006 ± 0.001	0.005 ± 0.001

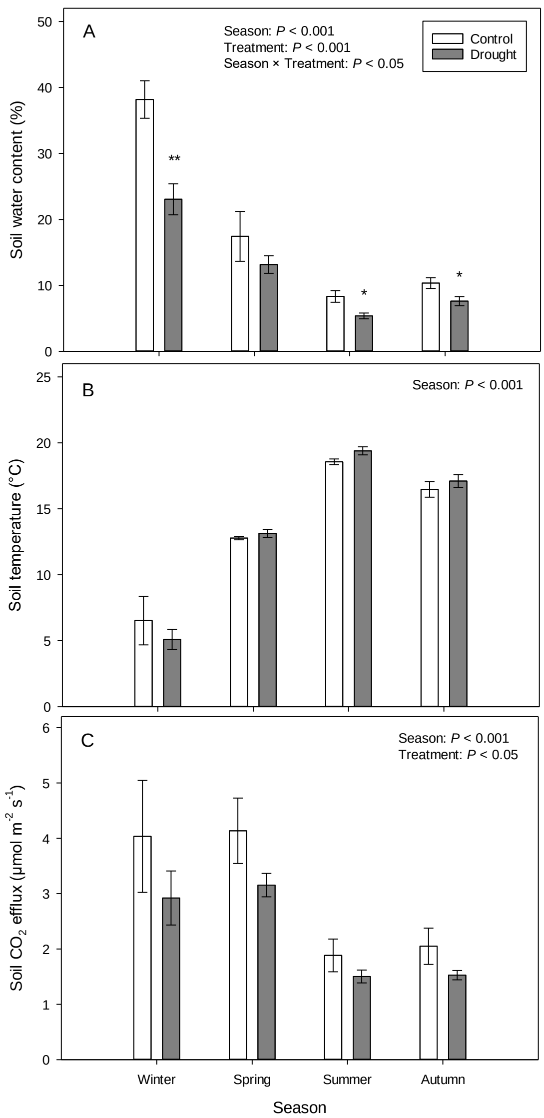
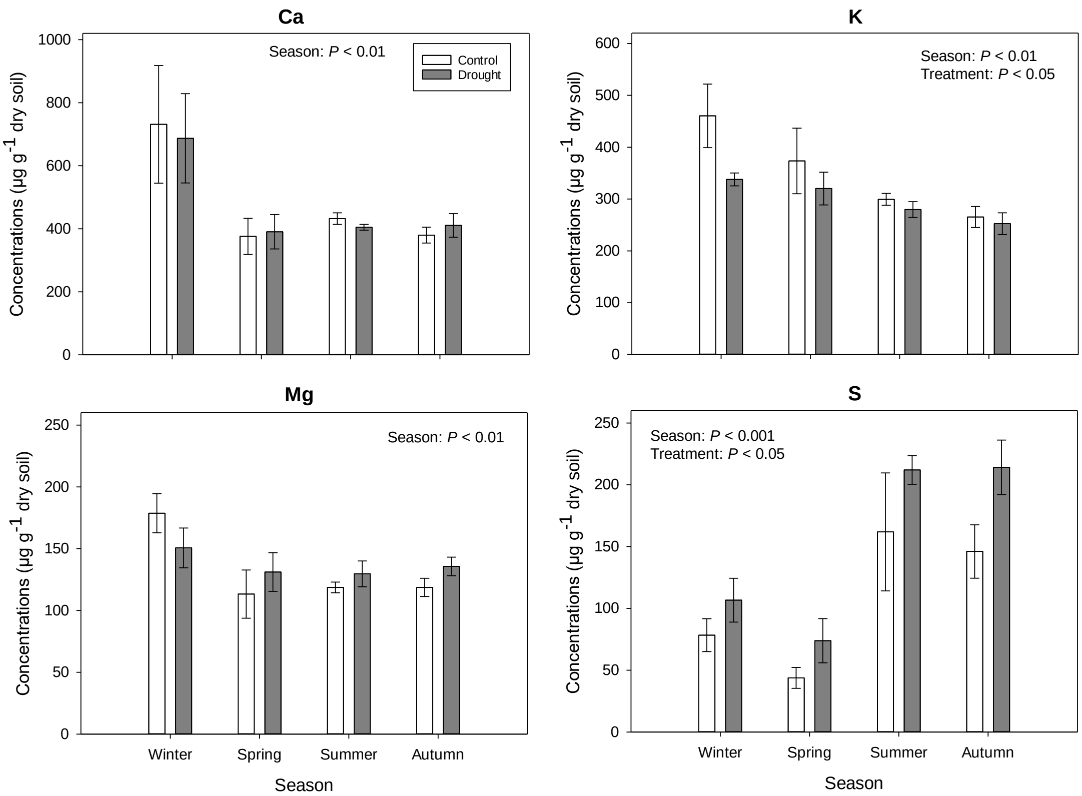


Fig. 1. Seasonal soil (A) water content, (B) temperature, and (C) CO_2 efflux in control and drought plots. Data are means ± standard error (*n* = 4 plots). Treatment differences between seasons are indicated with asterisks (Student's *t*-tests, **P* < 0.05 and ***P* < 0.01). The effects of season and treatment (two-way ANOVAs) are depicted in the panels when significant.

A)


Ca
Season: P < 0.01
Control
Drought
K
Season: P < 0.01
Treatment: P < 0.05
Mg
Season: P < 0.01
S
Season: P < 0.001
Treatment: P < 0.05
Concentrations (µg g-1 dry soil)
Winter
Spring
Summer
Autumn
Season

B)

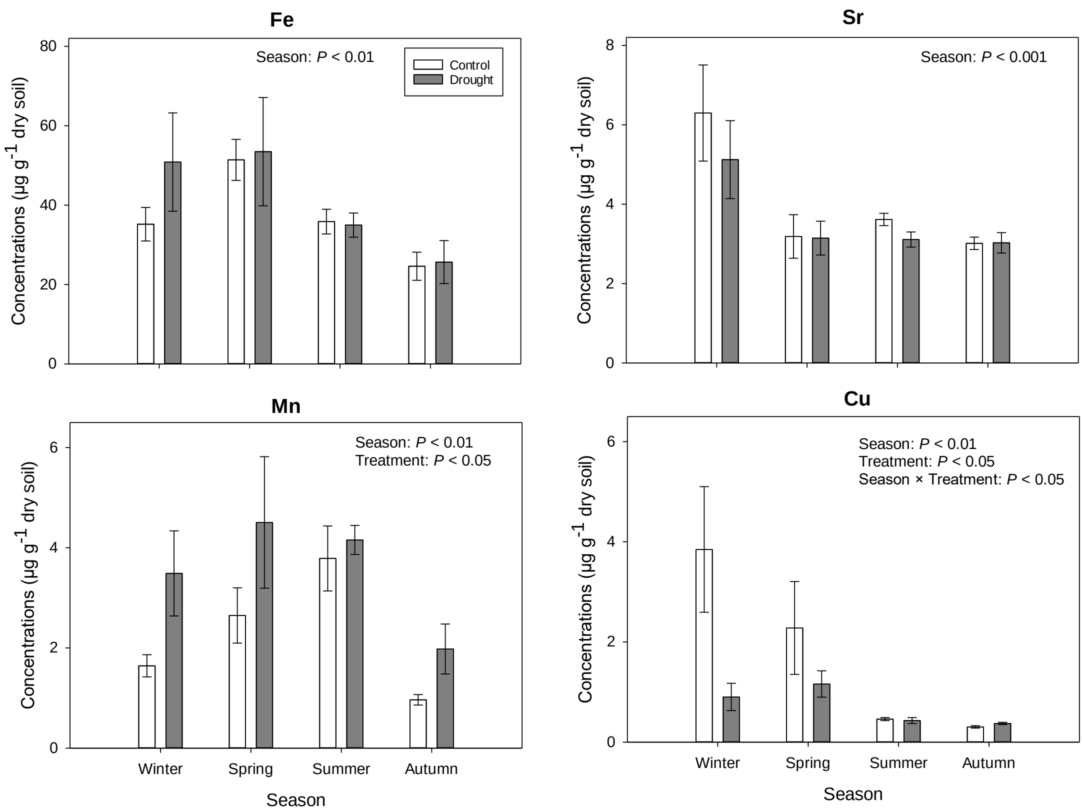

Fe
Season: P < 0.01
Control
Drought
Sr
Season: P < 0.001
Mn
Season: P < 0.01
Treatment: P < 0.05
Cu
Season: P < 0.01
Treatment: P < 0.05
Season × Treatment: P < 0.05
Concentrations (µg g-1 dry soil)
Winter
Spring
Summer
Autumn
Season

Fig. 2. Seasonal extractable concentrations of soil (A) Ca, K, Mg, and S, and (B) Fe, Sr, Mn, and Cu in control and drought plots. Data are means ± standard error (n = 4 plots). The effects of season and treatment (two-way ANOVAs) are depicted in the panels when significant. The P values (Student's t-tests) between treatments for each season are shown in Table S3.

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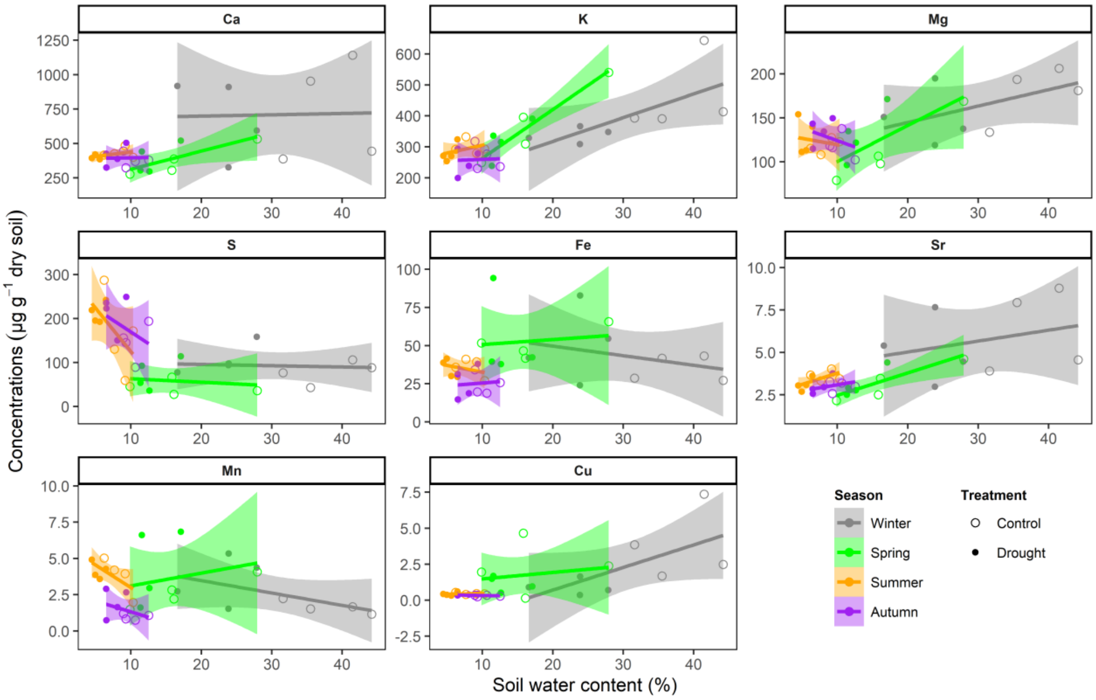

Fig. 3. Correlations between extractable Ca, K, Mg, S, Fe, Sr, Mn and Cu concentrations and soil water content. Shaded areas are the 95% confidence intervals of the regression lines. Chronic drought samples are represented by filled dots, control samples are represented by empty dots. Different seasons are represented by different colors. *r* coefficients and *P* values for each season are shown in Table S2.

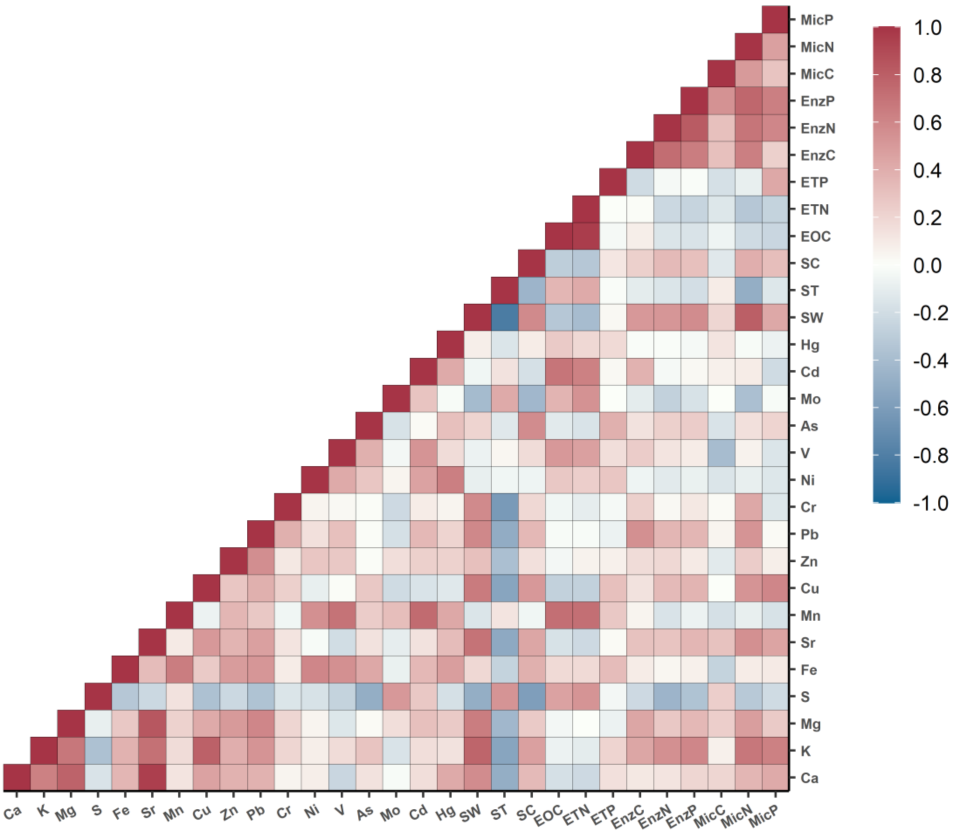

Fig. 4. Heat map of pairwise correlation coefficient (*r*) between the soil chemical-biological variables. The colors represent the coefficient of correlation between each pair of variables, where red represents a positive correlation and blue represents a negative correlation. The *r* values are shown in Figure S1.

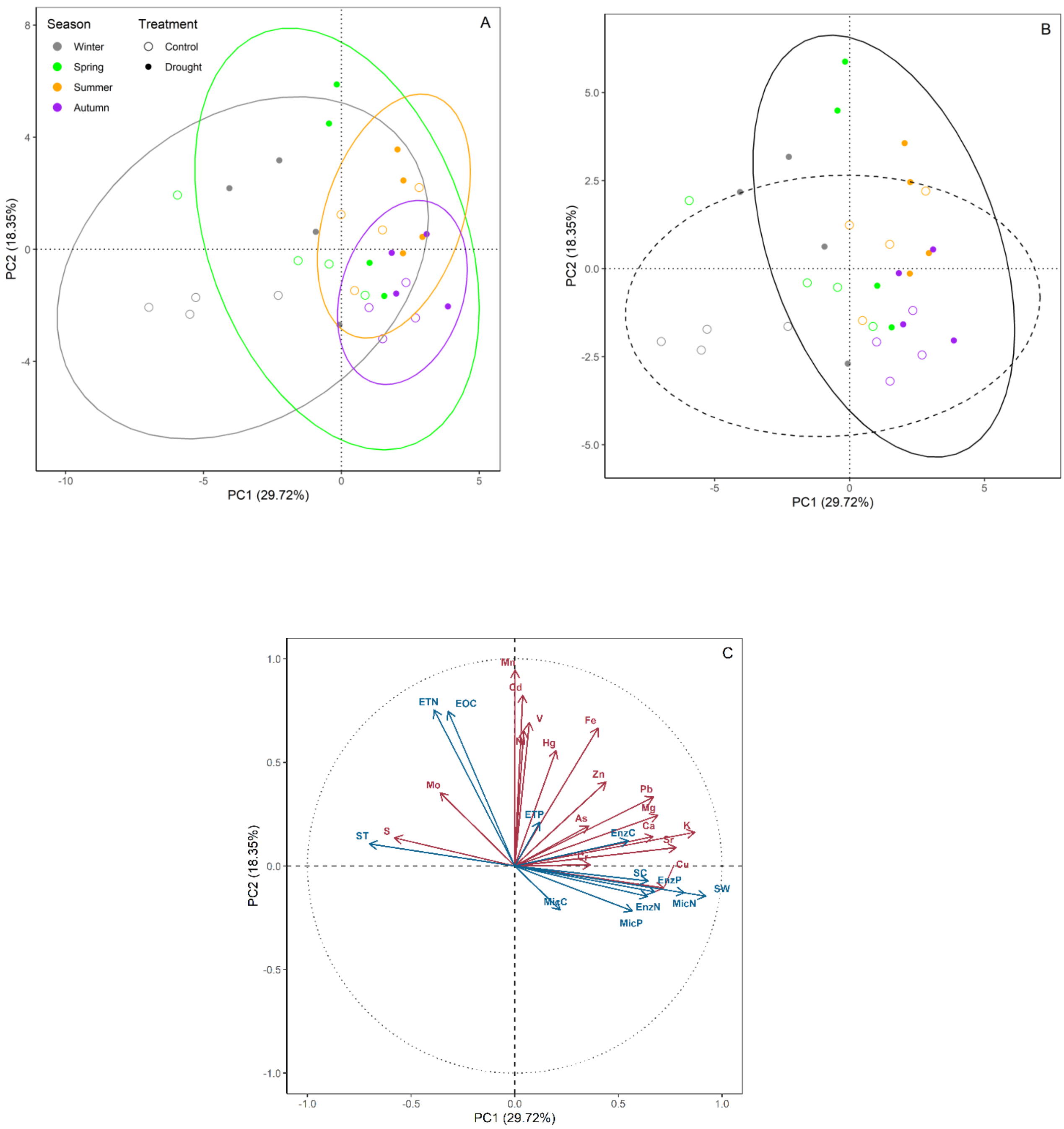

Fig. 5. Two-dimensional representation of the areas defined by the first two principal components (PC1 and PC2) of the principal component analysis of season, treatment, and soil chemical-biological variables. A) Values assigned to each soil sample for PC1 and PC2 grouped by season. B) Values grouped by treatment. C) Relative contribution of each variable to PC1 and PC2. Chronic drought samples are represented by filled

dots, control samples are represented by empty dots. Different seasons are represented by different colors. Vectors are divided into target mineral elements (red) and other soil variables (blue). The percentages contributions to the total variability are in parentheses.

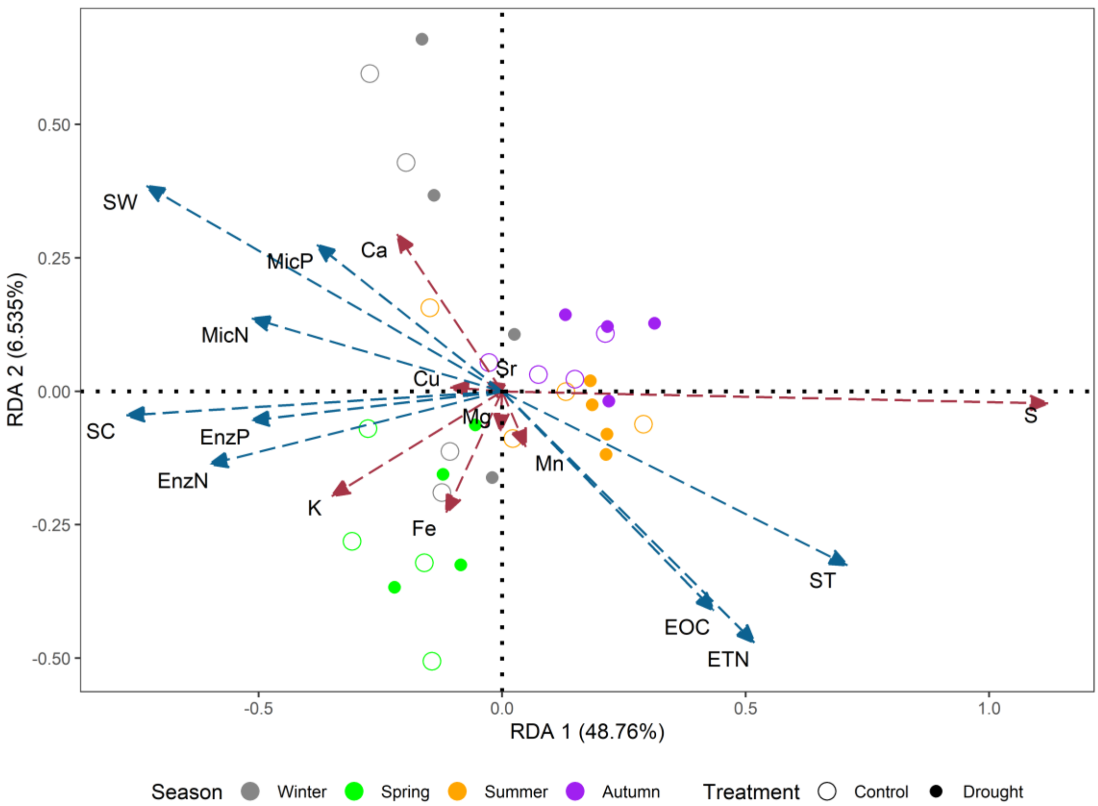

Fig. 6. Redundancy analysis (RDA) based on correlations between macroelement concentrations (red) and explicable soil chemical-biological variables ($P < 0.1$) (blue) in this study. Chronic drought samples are represented by filled dots, control samples are represented by empty dots. Different seasons are represented by different colors. Correction of R squares and significance test for the constrained axes (permutations = 999) of soil variables are shown in Table S5.