BEHAVIOUR OF MAJOR CHEMICAL ELEMENTS IN A FIRE AFFECTED HILLSIDE FROM LYULIN MOUNTAIN, BULGARIA

I. ATANASSOVA, M. TEOHAROV and E. ZLATAREVA
Nikola Poushkarov Institute of Soil Science, BG – 1080 Sofia, Bulgaria

Abstract


We analysed the post fire effects from the late summer of 2007 on the behaviour of major chemical elements in surface soils and soil profiles (Luvisols and Gleysols) characterised as a catena sequence in a hillside of Lyulín Mountain, Bulgaria. The objectives of our study were to assess the P, N, K, Ca, Mg, Na contents in soils on the ridge and the hillside and define relationships between major chemical elements and other soil characteristics with the purpose to point at the origin and behaviour of these elements as influenced by fire. Distributions of available major chemical elements were compared to interpret processes and sources involved in element redistribution. Our key findings are the following: (1) changes concern mainly N, K, P and Mn and are related to significant increases in the upper surface (0-6 cm) layer; (2) no major changes in the exchangeable Ca and Mg contents in the surface of the burnt and unburnt control soils, as well as between the surface and the lower depths of the soil profiles were found, i.e. no additional release of bases as a result of burning was accounted for; (3) elevated concentrations of Na ions in the lower depths of the soil profiles and in the surface soils of the lower boggy parts of the hillside were related to the prevailing conditions of soil genesis. Statistical analysis including the burnt and unburnt control soils did not reveal any significant modifications in the major relationships between the measured parameters. The results show a biogenic source for the elements N, P, K, Mn, e.g. plant residues mineralization including fire induced. The elements Ca, Mg and Na did not increase in the upper layers of the burnt soils, but increased downwards the soil profile and were mainly related to the physico-chemical soil properties, such as cation exchange capacity and carbonate content and indicated a geopedogenic source.

Key words: forest fire; major chemical elements, exchangeable cations, biogenic source, geopedogenic source

Introduction

Wildfires are one of the most widespread factors responsible for ecosystem degradation around the world, by destroying the vegetation cover and increasing nutrient and soil losses by leaching and erosion (Chandler et al., 1983). Fires also introduce changes in the physico-chemical characteristics of soils (Giovanini and Lucchesi, 1997).

Fire may also influence soil aggregate stabili-
ity due to consumption of soil organic carbon and changing soil organic matter quality. Slash burning results in large transformations of non-plant-available organically bound P and N in soil into mineral forms readily available to plants (Giardina et al., 2000). These mineralised elements can become available to plants or leached from the soil (DeBa-no et al., 1998). Fire has the so called “fertilizing effect”, affects soil microbial populations and is related to an increase of soil pH due to increase of exchangeable cations in soil (Pyne, 2001). It has been widely accepted that the physical, chemical, mineralogical, and biological soil properties are affected by forest fires depending on temperature, duration, vegetation and topography of the burnt area (Certini, 2005). Forest fires introduce organic burn residues, charcoal and ash into soils. Ulery et al. (1993) found increases in topsoil pH immediately after burning due to the production of K and Na oxides and hydroxides which however did not persist through the wet season.

The fate of soil organic N following heating is volatilisation but a substantial part of it is subject to transformations (Knicker et al., 1996) including amide N and heterocyclic compounds such as pyrroles, imidazoles and indoles. Weston and Attiwill (1990) observed a fire-induced inorganic N (Ammonium (NH$_4^+$) and nitrate (NO$_3^-$)) increase three times the original concentration over the first 205 days, however, after 485 days, a return to the pre-fire level was observed. Ammonium is a direct product of the combustion, while nitrate forms from ammonium some weeks or months after fire due to nitrification (Covington and Sackett, 1992). Both NH$_4^+$–N and NO$_3^-$–N follow quite different pathways: nitrate is soon leached downwards, while ammonium is adsorbed onto the negatively charged clay minerals and organics and, thus, is held tightly by the soil (Mroz et al., 1980). However, unless it is fixed in the interlayer of clay minerals, ammonium tends to transform into nitrate. In a soil under P. pinaster, Prieto-Fernandez et al. (1993) studied the effects of a high intensity wildfire on the N status in the surface (0–5 cm) and subsurface (5–10 cm) layers. One month after burning, total inorganic N, which previously was mainly in the form of NH$_4^+$–N, was increased in both layers, while NO$_3^-$–N was increased only in the subsurface layer, perhaps as a consequence of leaching.

In a P. edulis/Juniperus spp. stand, Covington et al. (1991) found that slash pile burning caused an immediate strong increase (approximately 50-fold) in soil ammonium. Nitrate concentrations were not affected immediately but 1 year after burning they had become dramatically higher than the pre-fire level. Five years after burning the increase of both forms of inorganic nitrogen had disappeared. These findings were substantially confirmed by Covington and Sackett (1992) under P. ponderosa. The combustion of vegetation and litter cause’s modifications in the biogeochemical cycle of P. Burning converts the organic pool of soil P to orthophosphate (Cade-Menun et al., 2000) which is available to soil biota. Losses of P through volatilisation or leaching are small due to sorption reactions to soil Al, Fe, and Mn oxides in acid conditions or precipitation as discrete Ca-phosphate. Forest fires result in an enrichment of available P (Serrasolsas and Khanna, 1995). In a Eucalyptus forest, 7 months after clearfelling and slash burning, Romanya et al. (1994) found soil concentrations of available P (NaHCO$_3$- extractable) and labile P (NH$_4$F+HCl-extractable) even higher than pre-fire levels. In a Picea dominated forest, Macadam (1987) even found that 9 months after slash burning, available P in the upper 30 cm mineral soil had increased by up to 50% and this increase persisted, although somewhat diminished 21 months after the fire event.

The objectives of our study were to: (i) analyse the contents of major chemical elements in a fire affected hillside from Lyulin mountain; (ii) carry out statistical analysis with the aim to define the sources and interrelationships of these elements in the surface and sub-surface soils of the catena 6 months after the occurrence of fire and assess the differences in the measured contents of the
elements, as well as the changes that may have occurred following fire.

Materials and Methods

The study sites were cinnamonic forest soils (Luvisols) on the ridge and the hillside, a bogged soil at the footslope (Gleysols) and a control (unburned) soil on the opposite site of the hill of Lyulin mountain (Regosols) subject to a fire in the late summer of 2007 (FAO classification, Teoharov, 2004). For the investigations the surface soil (0-6 cm) and lower horizons at five sites were studied: on the ridge (Soil 601), the upper and the lower parts of the hill (Soil 602 and 603), as well as at the foot of the mountain (Soil 604).

A control soil (Soil 606) was sampled on the opposite side of the hill, not affected by fire. Sampling took place in the spring of 2008 after eliminating the litter layer. The vegetation was represented by black pine (Pinus nigra) mostly affected by the fire. At the foot of the hill due to bogging and waterlogging, the predominant vegetation is bullrush Typha angustifolia. Other vegetation species are represented by meadow fescue, Festuca Pratensis. The morphological characteristics of the area and the organic biogeochemical markers were presented in Atanassova et al. (2009) and Atanassova and Teoharov (2010).

The major cation contents (K, Ca, Mg, Na) were determined by extraction with 1 M NH$_4$NO$_3$ (Zeien and Brümmer, 1989), mineral N by the method of Bremner and Keeny (1965) and available P by the method of Egner et al. (1960). Data for the organic carbon contents and cation exchange capacity were given in Atanassova et al. (2009).

Statistical Analysis

Multivariate statistical analysis was employed using SPSS 19 in order to identify distribution patterns and interrelations among measured parameters in the surface and subsurface soils of the catena affected by fire, distinguish between parameter groups and point at the origin of these parameters. Principal component analysis (PCA) was conducted and the factors with an eigenvalue > 1 were extracted. In addition, cluster analysis was also carried out. Differences between chemical elements contents were analysed using the t-test ($P \leq 0.05$).

Results and Discussion

Variation of major nutrients in the surface layers

Variation of major cation composition is presented in Figure 1a, b for profiles 601 and 602 most affected by fire. No statistically significant changes ($p<0.05$) in the exchangeable Ca and Mg cations were accounted for on comparing the surface depths of the burned and control soils similarly to our previous study (Atanassova et al., 2009). Release of the alkaline cations (Ca, Mg) bound to the organic matter as a consequence of the release of bases from the combusted organic matter was observed by Simard et al. (2001) and Arocena and Opio (2002). Some authors have also found decreases in CEC of soils following fire (Badia and Marti, 2003; Ekinci, 2006) due to loss of organic matter and/or collapse of clay minerals at high temperature.

Our findings correspond to observation of Adams and Boyle (1980) who found that within a month after a wildfire, available Ca and Mg were significantly higher than pre-fire levels, but after further 3 months the increases were almost gone. In our study exchangeable Na did not show a statistically significant difference between the burned and unburned soils (Soil 601 and 606, Figure 1b). A possible reason for this phenomenon is leaching of this cation and the higher solubility of its oxides and hydroxides during the wet winter and spring seasons following the fire similarly to the findings of Ulery et al. (1993). However, some increases in exchangeable Na and Mn were observed in Soil 604 and the unburnt Soil 606.

These increases of Na can be due to the boggy conditions in the mountain meadow soil 604
which could contribute to accumulation of elevated concentrations (Popandova and Zlatareva, 2005). Increases of Mn in the slightly burnt and control soils (Soils 603 and 606) are obviously not caused by burning of organic matter but are due to the presence of natural exchangeable biogenic forms of Mn in these soils (Figure 1b). Our data for exchangeable Mn coincide with results of Gonzalez et al. (1996) that exchangeable Mn did not show any variation in soil after fire while only total content and easily reducible amorphous and crystalline oxides forms of Mn supplied by the ash increase significantly following fire.

Available K values were higher in the burnt soils than in the unburnt control soil, which points at the slower leaching rate of this element, increased input from the burnt plant biomass and accumulation in the upper soil layer (Figure 1b).

The behaviour of the available P after fire in the burnt soils was similar to that observed by Macadam (1987), Romanya et al. (1994) and Serrasolsas and Khanna (1995), i.e. an increase of nearly 9 times the amount in the unburnt soil was observed (Figure 1c).

Ammonium-N and NO₃-N contents also showed marked increases in the upper layer of the soils on the ridge of the hillside, most affected by fire, due to enhanced rates of mineralisation of soil organic matter leading to higher concentrations of NH₄⁺ which persisted for more than 6 months in the surface soils (Figure 1c).

Our results correspond to the data of Khanna and Raison (1986), Covington et al. (1991) and Prieto-Fernandez et al. (1993) who also observed such increases.

These elevated contents correspond to the data for the total organic carbon which reached ~ 19% in the surface horizon as a consequence of exter-

![Figure 1a: Ca and Mg](image1a)  
![Figure 1b: Mg and K](image1b)  
![Figure 1c: P, NH₄-N, NO₃-N](image1c)
nal inputs from deposition of partially burnt plant material (Atanassova et al., 2009).

**Variation of major nutrients in the sub-surface layers**

We followed the behaviour of the measured elements in the soil profiles of the catena in order to assess the accumulation of the elements, as influenced by the depth and the geochemistry of the substrate. Exchangeable calcium, magnesium and sodium showed increases with depth of almost all soil profiles, as revealed by extraction with 1M NH$_4$NO$_3$ salt which corresponds to increases in pH and carbonate content with depth (Figure 2 a,b,d, example for Soils 601, 602, 603, Table 1). Pedogenic accumulation of sodium with depth of the catena may be both due to leaching of this labile cation and the presence of sodium and

![Graphs showing variation of major chemical elements along the soil profiles at different parts of the catena](image_url)

**Fig. 2.** Variation of major chemical elements along the soil profiles at different parts of the catena
other alkaline earth elements salts in the lower depths of the soil profiles. As mentioned above, the boggy conditions in the lower soil profiles of the catena may contribute to the accumulation of higher concentrations downwards the soil profiles (Popandova and Zlatareva, 2005).

In our previous study (Atanassova et al., 2009) no major changes in CEC and exchangeable cations of Ca and Mg along the soil profiles were observed, either. The reasons must be due to the different method of soil extraction and measurement used before, i.e. buffer salt exchange with K malate (pH 8.2) and titration for determination of the exchangeable Ca and Mg according to (Ganev and Arsova, 1980). In the present study we used 1M NH$_4$NO$_3$ salt extraction (Zeien and Brümmer,

Table 1
Correlation matrix

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Mn</th>
<th>K</th>
<th>Na</th>
<th>P</th>
<th>NH$_4$-N</th>
<th>NO$_3$-N</th>
<th>CEC</th>
<th>OC</th>
<th>Carb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>1</td>
<td>0.055</td>
<td>-0.202</td>
<td>-0.514</td>
<td>-0.012</td>
<td>-0.331</td>
<td>-0.39</td>
<td>-0.38</td>
<td>0.11</td>
<td>-0.369</td>
<td>0.935</td>
</tr>
<tr>
<td>Mg</td>
<td>0.055</td>
<td>1</td>
<td>-0.148</td>
<td>-0.483</td>
<td>0.659</td>
<td>-0.459</td>
<td>-0.398</td>
<td>-0.538</td>
<td>0.376</td>
<td>-0.497</td>
<td>-0.091</td>
</tr>
<tr>
<td>Mn</td>
<td>-0.202</td>
<td>-0.148</td>
<td>1</td>
<td>0.39</td>
<td>-0.172</td>
<td>0.096</td>
<td>0.404</td>
<td>0.231</td>
<td>-0.236</td>
<td>0.625</td>
<td>-0.206</td>
</tr>
<tr>
<td>K</td>
<td>-0.514</td>
<td>-0.483</td>
<td>0.39</td>
<td>1</td>
<td>-0.253</td>
<td>0.9</td>
<td>0.911</td>
<td>0.827</td>
<td>-0.047</td>
<td>0.936</td>
<td>-0.48</td>
</tr>
<tr>
<td>Na</td>
<td>-0.012</td>
<td>0.659</td>
<td>-0.172</td>
<td>-0.253</td>
<td>1</td>
<td>-0.286</td>
<td>-0.188</td>
<td>-0.279</td>
<td>0.375</td>
<td>-0.302</td>
<td>-0.189</td>
</tr>
<tr>
<td>P</td>
<td>-0.331</td>
<td>-0.459</td>
<td>0.096</td>
<td>0.9</td>
<td>-0.286</td>
<td>1</td>
<td>0.876</td>
<td>0.808</td>
<td>0.103</td>
<td>0.823</td>
<td>-0.239</td>
</tr>
<tr>
<td>NH$_4$-N</td>
<td>-0.39</td>
<td>-0.398</td>
<td>0.404</td>
<td>0.911</td>
<td>-0.188</td>
<td>0.876</td>
<td>1</td>
<td>0.918</td>
<td>0.086</td>
<td>0.916</td>
<td>-0.285</td>
</tr>
<tr>
<td>NO$_3$-N</td>
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<td>-0.538</td>
<td>0.231</td>
<td>0.827</td>
<td>-0.279</td>
<td>0.808</td>
<td>0.918</td>
<td>1</td>
<td>-0.088</td>
<td>0.798</td>
<td>-0.241</td>
</tr>
<tr>
<td>CEC</td>
<td>0.11</td>
<td>0.376</td>
<td>-0.236</td>
<td>-0.047</td>
<td>0.375</td>
<td>0.103</td>
<td>0.086</td>
<td>-0.088</td>
<td>1</td>
<td>-0.066</td>
<td>0.067</td>
</tr>
<tr>
<td>OC</td>
<td>-0.369</td>
<td>-0.497</td>
<td>0.625</td>
<td>0.936</td>
<td>-0.302</td>
<td>0.823</td>
<td>0.916</td>
<td>0.798</td>
<td>-0.066</td>
<td>1</td>
<td>-0.316</td>
</tr>
<tr>
<td>Carb</td>
<td>0.935</td>
<td>-0.091</td>
<td>-0.206</td>
<td>-0.48</td>
<td>-0.189</td>
<td>-0.239</td>
<td>-0.285</td>
<td>-0.241</td>
<td>0.067</td>
<td>-0.316</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 2
Rotated component matrix, principal component analysis with 3 components extracted, Rotation Method Varimax with Kaiser Normalization

<table>
<thead>
<tr>
<th>Component</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>-0.256</td>
<td>0.899</td>
<td>0.014</td>
</tr>
<tr>
<td>Mg</td>
<td>-0.483</td>
<td>-0.176</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>0.449</td>
<td>-0.363</td>
<td>-0.381</td>
</tr>
<tr>
<td>K</td>
<td>0.9</td>
<td>-0.349</td>
<td>-0.156</td>
</tr>
<tr>
<td>Na</td>
<td>-0.248</td>
<td>-0.223</td>
<td>0.77</td>
</tr>
<tr>
<td>P</td>
<td>0.942</td>
<td>-0.06</td>
<td>-0.03</td>
</tr>
<tr>
<td>NH₄-N</td>
<td>0.956</td>
<td>-0.188</td>
<td>-0.04</td>
</tr>
<tr>
<td>NO₃-N</td>
<td>0.884</td>
<td>-0.136</td>
<td>-0.185</td>
</tr>
<tr>
<td>CEC</td>
<td>0.204</td>
<td>0.23</td>
<td>0.824</td>
</tr>
<tr>
<td>OC</td>
<td>0.886</td>
<td>-0.251</td>
<td>-0.25</td>
</tr>
<tr>
<td>Carb</td>
<td>-0.163</td>
<td>0.949</td>
<td>-0.103</td>
</tr>
</tbody>
</table>

1989) with subsequent AAS determination leading to generally lower detectable quantities of these elements.

The major elements (nutrients) N, P, K and the micronutrient Mn, however show consistent decrease with depth (Figures 2c, d, e) which corresponds to the decrease in OC content and biological activity, i.e. points at the biogenic sources of these elements.

**Statistical analysis**

Multivariate statistical approach (Principal Component Analysis and Cluster Analysis) adopted here for data treatment, allowed the identification of three main factors (principal components) controlling chemical elements variability in the burnt soils. Interactions between elements were assessed by principal component analyses. Three principal components were identified with eigenvalues > 1 explaining 49.4 %, 18.4 % and 13.3 % respectively of the total variance (81.1 %). The correlation matrix and the components matrix are presented in Table 1 and Table 2. The data indicate that the first principle component has heavy loadings on NO₃-N, NH₄-N, OC, K and P and moderate positive loadings on Mn (0.449). The second principle component was loaded by Ca and the carbonates, implying close relationship and the third by Mg, Na and the cation exchange capacity.

The Cluster Analysis (Figure 3) revealed similar results. Groups of correlated elements were extracted from a cluster analysis performed according to average distances. The dendrogram presented in Figure 3 shows two major groups (4 subgroups in total). The more distant the parameters are, the less relation between them exists. The first main group consists of two sub-groups: available K, OC, NO₃-N, NH₄-N and P and Mn. The second main group consists of Ca, the carbonate content and Mg, Na and the CEC.

When in the PCA analysis and the Cluster analysis we added the data from the control soils, we obtained one and the same indistinguishable pattern of group linkages as with the burnt soils only, which points at the fact that similar inter-relationships between measured parameters and similar parameter groups and group linkages exist, i.e. the behaviour and origin of the measured elements is similar without major perturbations as a result of the action of fire.

The data from the principal component analysis are supported by the depth distribution of the analysed elements (Figures 2 a,b,c,d,e) indicating a decrease of N, P, K and Mn downwards the soil profiles and an increase for Ca, Mg and Na. The depth distribution points at biogenic source of N, K, P and Mn and geopedogenic source for Ca, Mg and Na.

**Conclusions**

The post fire effects on major chemical elements in mountain soils characterised as a catena sequence were investigated. The following are key findings:

- No major changes in the exchangeable basic cations were found between the surface and subsurface layers of the analysed soils of the burnt
and unburnt soils. No direct increase of bases (Ca and Mg) as a result of burning was accounted for, as there was no marked change with the subsurface and control soils.

- Mineral N, P, K and Mn contents have increased in the surface burnt soils and this increase was associated with increase of OC due to incorporation of burnt and partially burnt plant material.

- Statistical analysis including the burnt and unburnt control soils did not reveal any significant perturbations in the major relationships between the measured parameters and indicated an organic (biogenic) source for the elements N, P, K, and Mn, while Ca, Mg and Na contents were mainly related to the inorganic soil constituents (carbonates) and the physico-chemical soil characteristics, such as cation exchange capacity pointing at a geopedogenic source.

References


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Received December, 2, 2010; accepted for printing May, 12, 2011.