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DISTRIBUTION AND CYCLING OF NUTRIENTS IN A MOUNTAIN FIR ECOSYSTEM IN CENTRAL GREECE

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Abstract

The distribution and cycling of nutrients were examined in a mature Bulgarian fir forest (*Abies borisii-regis* Mattf.) in the area of Karpenisi, Central Greece. More specifically, the current and second year concentrations of Ca, Mg, K, N, P, S, Fe, Mn, Cu and Zn in bulk deposition, throughfall and litterfall in the fir needles and fluxes were determined. In addition, their total amounts were measured in the standing and ground vegetation as well as in soil up to 80 cm. It was found that the throughfall deposition was a significant source of S and K. The foliar, woody and rest fractions of litterfall were 71, 19 and 10 % of the total litterfall, respectively. Among all the ecosystem components, the highest nutrient quantities were found in the mineral soil, forest floor, trunk wood, trunk bark and canopies of the fir trees. The trunk bark proved an appreciable pool for P and S. In order to calculate the mean residence time of nutrients in the forest floor, througlfall and litterfall fluxes were taken as input. It was found that the mean residence times of nutrients in forest floor followed the order Fe>Mn>Zn>Mg>Cu>P>N>Ca>K>S. According to nutrient concentrations ranges in conifer needles and soils, the fir forest is in a very good condition with regard to nutrient status. Consequently, all the environmental parameters measured in the forest can serve as a comparison reference level for other (mature) mountainous *Abies* forests in Europe.

Key words: forest floor, litterfall, macronutrients, micronutrients, precipitation, throughfall deposition.

Introduction

Fir (*Abies* species) forests, especially silver fir (*Abies alba* Mill.), Greek fir (*Abies cephalonica* Loudon) and Bulgarian fir (*Abies borisii-regis* Mattf.), are sensitive to environmental changes (Potocic et al. 2005). Fir is predominantly a mountain species. In warm climate areas, it moves to higher altitudes. In a mountainous area in the Czech Republic Mikulenka et al. (2020) found that low temperature and frost were limiting factors of radial growth for silver fir. Macias et al. (2006) studied its growth the Main Range in the Pyrenees and southern peripheral ranges. They found that the radial growth of the fir trees was constrained by water stress during the summer before the next growth period. In the early 1970s, fir was the first species to show symptoms of a strange forest disease in Northern Europe (Krause et al. 1986). That disease was related to Mg deficiency and increased Al concentration in soil solution. Species of the fungus *Armillaria* were commonly observed on dead silver fir trees (Oliva and Colinas 2007) in Spain, whereas *Heterobasidion annosum* was found to cause increased mortality in fir forests of the area of Tuscany in Italy (Certini et al. 2000). In Greece, there was extensive necrosis of fir trees (Greek and Bulgarian firs) in the late 80's. That was due to drought, which brought about an outbreak of the secondary bark-boring beetles (Markalas 1992). Certini et al. (2000) argued that the importance of soil was somewhat neglected with regard to fir decline because the pathogen attacks were more severe in sites where soil was shallow or infertile. For these reasons, there is some research on fir nutrition although not as much as on other conifers. Novotný et al. (2010) presented data with the nutrient concentrations in the needles of silver fir grown in the Bohemian Forest in the Czech Republic and Szymoura (2009) dealt with the nutrient concentrations in fir needles as a function of age. Comandini et al. (1998) did research with fir mycorrhiza and Berg et al. (2003) with the decomposition of fir needles in the forest floor. Up to date, no complete nutrient cycle has been studied in any of the three species of fir mentioned above. In general, for the proper management of a forest ecosystem, the study of the nutrient cycle is necessary (Kimmins 1996). The Bulgarian fir is a species native to the mountains of the Balkan Peninsula in Bulgaria, Northern Greece, North Macedonia, Albania and Serbia. It occurs at altitudes of 800–1800 m, on mountains with an annual rainfall of over 1000 mm. Some botanists consider it as a natural hybrid between silver and Greek fir. The aims of this work were to assess the nutrient status of a Bulgarian fir stand in foliage, and calculate the nutrient fluxes in precipitation and litterfall together with the nutrient stocks in the various components of the ecosystem. When comparing the results of this work with those of other ones involving firs, the authors treated the three *Abies* species as one.

Materials and Methods

Site description

The experimental plot to which the present work refers is located on the ridges of the Timfristos Mountain in Central Greece at an altitude of 1170 m, with an area of 0.27 ha and is included in a catchment area of 147 ha. The coordinates are 21°51′57" longitude and 38°52′28" latitude. The site belongs to the Intensive Monitoring Survey of ICP Forests network (UN-ICP-Forests 2020).

The average annual rainfall on the surface is 1670 mm (1997–2018). The vegetation cover consists of an even aged Bulgarian fir (*Abies borisii-regis* Mattf.) stand in good health having an average age of 100 years approximately. The ground vegetation consists mainly of ferns (*Pteridium aquilinum* L.), shrubs (*Rubus hirtus* W. & K.), herbs (*Sanicula europaea* L., *Geranium lucidum* L., *Geranium rotundifolium* L., *Luzula forsteri* Sm.) and plants from the family Gramineae such as *Melica uniflora* R. and *Brachypodium sylvaticum* H. The tree density of fir species is 299 trees·ha^{-1}, the average tree height 24.3 m and the average diameter 42.5 cm (data assessed in 2009).

The soil of the stand is clay loam; it is deep and classified as a Cambisol (WRB 2006). The average pH (determined in water in a water-soil ratio 1:5 by volume) of FH horizon was found 6.48 and that of the mineral layers ranged from 6.07 in the soil surface to 5.32 down to 80 cm depth.

Collection of precipitation

In the year 1997, deposition collectors were placed inside the plot for the assessment and chemical analysis of the bulk and throughfall deposition. More specifically, the throughfall deposition was estimated with 20 collectors placed randomly within the stand and bulk deposition with three collectors placed in a clearing about 100 m from the plot. The collectors consisted of a plastic tube with a height of 1.05 and a diameter of 0.2 m, respectively. A plastic funnel with a diameter of 0.18 m was attached to the mouth.

Every week, on the same day, samples of rainwater were collected which, after measuring the volume of water, were transported approximately once a month in sealed containers to the laboratory for chemical analysis. The data covers the period 1997–2018.

Collection of current and second year needles

Needle samples of current and second year were collected every two years in winter (dormant period) from the upper part of the crown from five dominant trees and formed a pooled sample. The collection always took place from the same trees. The two fractions of needles were dried at 80 °C for 48 h and then ground in a special mill for analysis. The data covers the period 1995–2019.

Collection of litterfall

Litterfall was collected with 10 plastic cylinders systematically placed in a straight line at a distance of 5 m from each other with a surface area of 0.242 m^2 each. A composite sample of the 10 traps in total was transferred to the laboratory at each sampling. The litterfall was separated into its fractions, i.e. foliar, woody (twigs, bark parts) and rest (fruits, lichens, mosses, insect frass) and weighed. Subsamples were ground in a ball mill for total analysis. The litterfall data covers the period 2009–2019.

Collection of soil samples and ground vegetation

Soil collection and ground vegetation was carried out by systematic sampling in 2007. For each layer of L, FH, 0–10 cm, 10–20 cm, 20–40 cm and 40–80 cm depths three replicates in space were formed. Details of the soils sampling can be found in Michopoulos et al. (2020a).

L and FH layers were weighed. The bulk density of mineral soils in all layers was measured by a cylinder 129 cm^3. The samples of FH and mineral layers passed through a 2 mm sieve.

Subsamples of L, FH and mineral soils were pulverized in a ball mill for total elemental analysis.

The ground vegetation was collected systematically with a framework having an area of 0.544 m^2. In total 10 collections took place.

Chemical analysis

The concentrations of Ca, Mg, K in deposition were measured with an atomic absorption spectrophotometer (Perkin Elmer 3110), whereas those of P, Mn, Fe, Zn and Cu with an ICP-MS instrument (Thermo iCAP Qc). The concentrations of NH_4^+-N, NO_3^--N and SO_4^{2-}-S were determined with ion chromatography. All analyses were done according to EMEP (1996).

Foliage, ground vegetation, wood and bark were digested in a mixture of HNO_3-$HClO_4$. Ca, Mg, K, Mn Fe, Zn and Cu were measured with atomic absorption spectroscopy. N was measured with the Kjeldahl method (Velp-UDK 126A) and P with the Mo blue method and a U/V spectrophotometer (Varian Carry). S was determined with a CNS analyzer (CNS analyzer, Vario MAX).

Exchangeable Ca^{2+}, Mg^{2+} and K^+ in FH and mineral soil layers were extracted with a 0.1 M unbuffered $BaCl_2$ solution and their concentrations were determined with FAAS spectroscopy. Available P in soils was extracted with a $NaHCO_3$ solution (Olsen and Sommers 1982) and its concentration was measured with the methods mentioned above. Available trace elements (Fe, Zn, Mn and Cu) in soil were extracted with DTPA (Lindsay and Norvell 1978) and their concentrations were determined with FAAA spectroscopy. Total P and S in soil samples were measured by means of the Energy Dispersive X-Ray Fluorescence (ED-XRF) method (XEROS model of the TURBOQUANT Company). The concentrations of total N and organic C in soils with the CNS analyzer mentioned above. For total metal analysis, soil samples were digested in a microwave oven with HF and *aqua regia* at a temperature range of 160–170 °C for 20 min. Concentrations of metals in the digests were determined with the ICP-MS instrument mentioned above.

Data handling and statistics

For tables 1, 2, 3 and 5 the means and coefficient of variations (percentages of the standard deviations over the averages) of the macronutrients and micronutrients in the various components of the fir forest were calculated.

Comparison of nutrient concentrations in tree needles

The nutrient concentrations in current year and second year needles were compared with a paired t-test. Before the tests were applied, the data were transformed to logarithms to be closer to normal distribution.

Fluxes in deposition and litterfall

Nutrient fluxes in the hydrological cycle for the period 1997–2018 were calculated by taking into account water volumes and nutrient concentrations. The fluxes of P and micronutrients were assessed only for the year 2013, as they were not monitored on a routine basis. This is the reason that there are no coefficients of variations for these elements.

Annual fluxes of masses and nutrients were calculated for the three fractions of litterfall, foliar, woody and rest litterfall, by multiplying nutrient concentrations times the masses of litterfall in each fraction.

Calculation of nutrient stocks in canopies, trunk wood, and bark samples

A tree with the average height and diameter was cut down and trunk and bark samples were collected to estimate density and carry out chemical analysis. The densities of wood and bark were calculated and the volume of all trees in the plot were calculated with equations (specialised for fir trees) based on the height and diameter of the trees (Apatsidis and Sifakis 1999). The equations (1–3) used were:

$$G = \frac{\pi \cdot d^2}{4} \cdot 10{,}000^{-1} \quad (1)$$

$$V_{nb} = 6.366 \cdot d^{1.76} \cdot h^{1.061} \cdot 10^{-5} \quad (2)$$

$$V_{wb} = 0.024 + 1.101 \cdot G, \quad (3)$$

where: G is basal area of the circle area of a tree trunk at DBH (m^2), V_{nb} is trunk volume with no bark (m^3), V_{wb} is trunk volume with bark (m^3), d is the tree diameter (cm), h is the tree height (m).

The mass of trees per ha was then calculated taking into account (apart from the volume) the densities of the wood and bark. For each tree, the crown mass per ha was calculated by specific equations for fir by inserting tree heights and diameters (Kittredge 1944). The equation (4) used was:

$$\lg(gf) = 2.1 \cdot \lg(d_{in}) - 0.5, \quad (4)$$

where: gf is the mass of green foliage (kg) per tree and d_{in} is the tree diameter in inches.

Finally the total crown dry mass per ha was calculated (in $kg \cdot ha^{-1}$).

Tree branches were counted and needle samples were collected from 10 branches around the perimeter of the crown so that the chemical composition of the needles would be representative. Multiplying the canopy mass by the concentration of each element yielded the total amount of each element in the canopy of the trees per ha.

Stocks of nutrients in soils

The calculation of nutrient stocks in L and FH horizons was based on masses and concentrations. The means and coefficients of variations were calculated for the three-pooled samples (three replicates). Total nutrient stocks in the mineral soil were found by adding the stocks derived from each separate layer. In each separate layer, nutrient stocks were calculated by multiplying layer masses by nutrient concentrations. The layer masses were found by multiplying layer volumes by the soil bulk densities. Coefficients of variation of total nutrients stocks were calculated by taking into account the variability of each separate layer (Miller and Miller 1988).

Nutrient residence time in forest floor

The residence time of nutrients in forest floor is calculated as the ratio of the amount of stocks of nutrients in the forest floor over the sum of the data in the fluxes of litterfall and throughfall deposition (Gosz et al. 1976). The presupposition for this equation is the equilibrium between the input and the output of nutrients. This is something that cannot always be attained. Nevertheless, by applying the equation we can have a strong indication of the residence times.

Results and Discussion

Nutrient concentrations in needles

The statistical comparison in Table 1 deals with different nutrient concentrations in needles of different ages. Ca, Fe and Mn had higher concentrations in the second year needles, whereas Mg and K had higher concentrations in the current year needles. In general, there is a decline in the mineral content of leaves with age caused by relative increase in the proportion of structural material (cell walls and lignin) and of storage compounds (e.g. starch) in the dry matter (Marschner 1989). This is a dilution effect. It does not stand for Ca, which is itself a cell structural component. In addition, it does not seem to apply for N, S and P concentrations of which do not differ significantly in the needles of different age. This means that there is ample uptake of these elements, which is called luxurious consumption (Marschner 1989).

Increase of Mn and Fe concentrations in older needles in various conifer species had also been found in an old work by Turner et al. (1977). The dilution effect should be complimented by another theory, which is the mobility of ions. Nutrient mobility, or immobility, helps us to diagnose deficiency symptoms. If the deficiency symptom appears first in the old growth, we know that the deficient nutrient is mobile. In general, when certain nutrients are deficient in the plant tissue, older leaves are able to translocate them to younger leaves (Mauseth 1998). Nutrients with this ability are mobile nutrients, and include N, P, K S and Mg. In contrast, immobile nutrients such as Ca, Fe and Mn do not have that ability because once they reach plant cells they are no longer able to enter the phloem. The fir in our work does not present symptoms of nutrient deficiency. So the dilution effect, the luxu-

Table 1. Nutrient concentrations in current and second year needles in present work and other data.

Needle age	Ca	Mg	K	N	P	S	Mn	Fe	Cu	Zn
	g·kg^{-1}						mg·kg^{-1}			
Bulgarian fir (present work)										
Current year	9.56 a (24)	1.40 a (18)	7.76 a (17)	13.6 a (11)	1.33 a (21)	1.22 a (12)	298 a (34)	94.6 a (36)	4.29 a (35)	31.8 a (41)
Second year	13.8 b (18)	1.35 b (16)	7.21 b (19)	13.6 a (12)	1.26 a (15)	1.24 a (10)	434 b (29)	115 b (37)	4.17 a (45)	29.1 a (39)
Silver fir in Spain[1]										
Current year	12.0	1.41	8.12	12.0	1.38	1.4	629	101	No data	46
Silver fir in the Czech Republic[2]										
Current year	5.43	1.97	6.20	13.9	2.8	1.35	625	54.0	No data	41.0
Greek fir in Greece[3]										
Current year	8.31	1.38	7.71	11.6	0.968	No data	126	48.5	3.33	31.8
Critical concentrations in needles in conifers										
Current year	1.7	0.6	3.0	12.0	1.40	No data	25.0	50.0	3.0	14.0

Note: coefficients of variations are in parentheses. In Bulgarian fir data in the first two rows, letters (a and b) in the same column differ for at least 0.05 probability level. Sources for the other data: [1]EC-UN/ECE-FBVA (1997), [2]Novotný et al. (2010), and [3]Michopoulos (2013).

rious consumption (in fertile soils) and the mobility concepts apply together in order to interpret results.

In terms of absolute concentrations, it can be concluded that there is no deficiency in any nutrient. Table 1 contains the average nutrient concentrations of silver fir in Spain (EC-UN/ECE-FBVA 1997) and the Bohemian Forest in the Czech Republic (Novotný et al. 2010), as well as Greek fir in Greece (Michopoulos 2013). The last row gives information on the critical nutrient concentrations for conifers derived from literature (Morrison 1974, Wyttenbach et al. 1985, Wyttenbach and Tobler 2000, Maňkovská et al. 2004, Szymura 2009). For most elements, the concentrations in Bulgarian fir needles are more similar to those in Spain. The concentrations of P in the Bohemian Forest were found rather high as the authors acknowledged.

Elemental fluxes in bulk deposition and throughfall

With the exception of both forms of inorganic N there was enrichment (ratio of throughfall/bulk deposition fluxes>1) in the throughfall fluxes for all nutrients (Table 2). It is obvious that fir needles absorbed N for their nutritional needs. This is not always the case in forests. There was N absorption in Norway spruce and mixed stands of conifers in Italy (Balestrini et al. 1998) but not in Norway spruce in Austria (Berger et al. 2008). In our work the sum of the average values of inorganic N in precipitation were 8.85 and 6.62 kg·ha^{-1}·yr^{-1} in bulk and throughfall deposition, respectively. These values are considered rather low considering that in many forest sites in Europe the throughfall deposition fluxes of N range between 15–20 kg·ha^{-1}·yr^{-1} (Michel et al. 2020). According to Dise and Wright (1995), the inorganic N fluxes in throughfall must be greater than 10 kg·ha^{-1}·yr^{-1} to start causing a nutrient cycle problem.

Despite the low values of inorganic N, the fluxes of -S in the fir stand are rather high (Table 2) taking into account that the value of 8 kg·ha^{-1}·yr^{-1} is a threshold sign for human activities for most European forests (Michel et al. 2020). The throughfall fluxes are considered more important that the bulk ones because the enrichment in them is mainly due to dry deposition which in turn is due to anthropogenic sources (Johnson 1984). In the 1980s far higher fluxes of SO_4^{2-}-S ranging from 15 to 54 kg·ha^{-1}·yr^{-1} had been observed in

Table 2. Average values of nutrient fluxes and height in bulk and throughfall deposition in the period 1997–2018.

Ca	Mg	K	SO_4^{2-}-S	NH_4^+-N	NO_3^--N	P	Mn	Fe	Cu	Zn	Height,
kg·ha^{-1}·yr^{-1}											mm
Bulk deposition											
21.4	2.36	7.36	14.0	4.61	4.23	1.24	0.137	0.189	0.316	0.019	1670
(41)	(35)	(55)	(20)	(44)	(32)						(17)
Throughfall deposition											
28.6	5.40	46.6	18.8	3.39	3.23	0.992	0.188	0.424	0.0264	0.0598	1372
(24)	(18)	(31)	(26)	(47)	(34)						(18)

Note: coefficients of variations are in parentheses. Fluxes of P and micronutrients were calculated only for the year 2014.

Austrian forests (Berger et al. 2008). The excess SO_4^{2-}-S fluxes in the fir area could be ascribed to fossil fuel consumption for heating purposes of the local population. Temperatures are very low in winter.

The bulk deposition of P in the fir stand was in the range of 0.05–1.7 kg·ha^{-1}·yr^{-1} that characterizes its inputs from the atmosphere (Newman 1995). There was absorption of P from needles as the throughfall fluxes were lower than those in the bulk deposition (Table 2). Belyazid and Belyazid (2012) argued that absorption or leaching depends on the growing period, microbial activity in the canopy and species.

The fluxes of Ca and Mg in throughfall deposition are considered high according to Michel et al. (2020) which set the thresholds 10 and 3 kg·ha^{-1}·yr^{-1} for Ca and Mg, respectively. The enrichment of deposition with the last two elements can be due to Sahara dust often settled on Greek lands. Among all metals, the highest enrichment was observed for K. This is something common for forests as throughfall is the main path towards forest floor for this element, exceeding even litterfall (Parker 1983).

With regard to micronutrients, there was enrichment in the three of them with the exception of Cu (Table 2). According to McColl (1981), the enrichment of Fe and Zn is only due to dry deposition, whereas for Mn exudation from leaves and bark can be a significant factor. In a mixed forest of Norway spruce and beech with 709 mm of annual rain height Fišák et al. (2006) found enrichment in throughfall only for Mn (0.460 kg·ha^{-1}·yr^{-1}), whereas Zn and Fe had a flux of 0.053 and 0.154 kg·ha^{-1}·yr^{-1} respectively.

Litterfall

Littefall is the main path through which the forest soil is enriched with nutrients. Monitoring it over time is essential to assess the health of forest ecosystems as abrupt changes in litterfall fluxes are equivalent to changes in the abiotic and biotic environment (Pedersen and Hansen 1999). Fluctuations in the masses of litterfall productions are strongly related to weather conditions (Finer 1996). The variability of 19 % for the foliar fraction mass (Table 3)

Table 3. Average fluxes of nutrients in the three fractions of litterfall in the period 2009–2019.

Ca	Mg	K	N	P	S	Mn	Fe	Cu	Zn	Mass,
kg·ha^{-1}·yr^{-1}										t·ha^{-1}·yr^{-1}
Foliar litterfall										
67.8	5.75	12.4	48.3	3.27	4.92	1.78	2.32	0.040	0.15	3.88
(22)*	(21)	(34)	(29)	(46)	(31)	(27)	(51)	(92)	(44)	(19)
Woody litterfall										
16.6	1.03	1.58	10.8	0.700	1.29	0.215	0.869	0.008	0.041	1.02
(73)	(75)	(73)	(89)	(93)	(80)	(84)	(102)	(98)	(118)	(65)
Rest litterfall										
5.38	0.784	2.45	7.52	0.610	0.746	0.168	0.473	0.005	0.021	0.578
(82)	(71)	(105)	(83)	(86)	(78)	(83)	(79)	(87)	(90)	(73)

Note: coefficients of variations are in parentheses.

is low if we take into account the 40 % coefficient of variation found in the foliar litterfall mass of Scots pine monitored over 24 years (Kouki and Hokkanen 1992).

When studying litterfall, researchers must pay attention to the climatic variables and single events, which could affect fluxes for example storms (Portillo-Estrada et al. 2013). Johnson and Turner (2019) stressed the importance of including catastrophic events such as wildfire, insect attacks, hurricanes, etc. in nutrient cycling studies. In our plot, no extreme event was observed in the 11 years of monitoring. There were some winters with heavy snow but they did not affect the overall variability of foliar biomass. The other two fractions did not have low variability and this fact is worth studying. Probably the slightest change of environmental parameters can affect their production. Cole and Rapp (1981) recorded elemental fluxes of litterfall for many forest stands. All quantities of N, Ca, Mg, K and P in the Bulgarian fir stand are considered large in relation to most of the forest species recorded by the above researchers apart from those in the litterfall of *Picea abies* (L.) Karst. stands grown on deep soils in Sweden and Germany. Mass percentages of the three litterfall fractions calculated from Table 3 were 70.7 % foliar, 18.7 % woody and 10.6 % rest litterfall. For the elements Ca, S and Fe the woody fraction proved appreciable. The rest litterfall fraction was lower in quantities than the other two. However, it should not be underestimated because some parts of it are more decomposable than the previous two fractions.

Biomass allocation and nutrient stocks in tree parts

From Table 4 it appears that the largest amounts of elements are accumulated in the trunk wood and trunk bark. The biomass allocation followed the sequence: trunk wood>trunk bark>branches>canopy>twigs. For some important macronutrients (N, P, S) and micronutrients (Mn, Zn) the bark is more important source than the trunk wood despite the larger mass of the latter due to the higher elemental concentrations in comparison with the trunk wood. Adhikari et al. (1995b) found higher stocks in all elements in the trunk wood of silver fir in a high altitude forest of Central Himalaya. That forest had a higher tree number per ha (355) in comparison to 299 in our work and higher vegetation biomass (454 $t \cdot ha^{-1}$) (Adhikari et al. 1995a) in comparison to 356 $t \cdot ha^{-1}$ in the fir stand in our work (Table 4).

The highest number of trees the more the nutrient stocks in trunk wood in even aged stands because there is no much variation in tree diameters and heights. The elements contained in the trunk and bark are relatively inactive. They re-enter the cycle of elements with the fall and decay of the trees. However, if the trees are cut down and removed, these elements are lost from the ecosystem forever. In addition, if the canopy of the trees is also removed, nutrient deficiency problems may appear in the forest. In a mixed oak site, Johnson et al. (2016) found that whole tree harvesting affected the concentrations of exchangeable Ca and Mg in soils after some years. The last component in biomass and nutrient stocks is the ground (understory) vegetation. The stocks of nutrients (Table 4) in comparison with the other components is low but its role is important in retaining nutrients within the ecosystem. This occurs during the decomposition of organic matter. The elements are released in inorganic form and the ground vegetation with its rich root system absorbs them and thus pre-

Table 4. Stocks of nutrients and biomass dry weights in the tree components and ground vegetation.

Component	Ca	Mg	K	N	P	S	Mn	Fe	Cu	Zn	Bio-mass, t·ha-1
	kg·ha-1										
Canopy	324	26.8	122	294	25.7	25.3	8.83	3.28	0.091	0.030	20.2
Twigs	104	8.83	72.6	79.9	1.08	7.07	7.18	4.69	0.070	0.444	11.7
Branches	136	8.67	43.3	32.6	4.64	4.58	5.62	2.11	0.104	0.347	34.7
Trunk wood	350	40.0	175	360	4.00	4.74	5.74	20.0	0.581	1.21	250
Trunk bark	292	18.8	36.8	599	36.1	13.6	19.2	3.72	0.274	1.56	39.1
Ground vegetation	4.33	1.34	8.64	9.34	1.037	1.012	0.083	0.206	0.003	0.020	0.418

vents them from leaching. Xie et al. (2019) found that the understory plants affected the relationship between litter and soil in Chinese fir plantations.

Concentrations and stocks of nutrients in soil

The nutrient concentrations in Table 5 are usually those to assess the fertility of soils. There are thresholds values for this purpose. It must be taken into account that these values were derived for agricultural soils and the extrapolation to forest soils should be held with caution. According to BAI (1984) all concentrations for exchangeable cations (Ca, Mg, K), organic C and Kjeldahl N are well above the deficiency limits with the exception of available P in the mineral soil layers. An adequate concentration for Olsen P is considered 11–25 mg·kg^{-1}.

The pH range in the soil of the fir stand (6.48 to 5.32) is ideal for P availability. However, even in the first mineral layer (0–10 cm) the P concentration is low. The latter does not depend on forest types because low concentrations of P in mineral layers in comparison were found in other forest soils as well (Michopoulos et al. 2020b). It seems that the humus layer plays an important role in supplying P for the uptake. The humus contribution is complimented with the re-translocation capacity trees have to transfer nutrients to new tissues before abscission.

The C/N ratio calculated from Table 5, ranges from 18.9 in the FH layer to 11.2 in the 40–80 cm mineral one. The fact that we have *Abies* sp. and no other conifer in the stand is the explanation of the relatively low C/N ratio. Cools et al. (2014) found a strong dependence of it and tree species in the European forests. Among all coniferous stands, only 34 % had C/N ratio lower than 25. However, one should not overestimate its role with regard to organic matter decomposition. Michopoulos et al. (2020a) found that a maquis stand in Greece with a higher ratio of C/N in L soil layer than L layer of the fir plot in the present study had a faster decomposition rate due to higher ambient temperatures. So abiotic environmental factors can have a predominant role.

There are not many works concerning the stocks of nutrients in forest soils. Eriksson and Rosen (1994) found lower stocks of macronutrients in the forest floor in a 35–40-years-old forest stand of silver fir in Sweden. For example, the N stock was 844 kg·ha^{-1} in the forest floor and 5000 kg·ha^{-1} in the mineral soil down to 95 cm depth. In our work, we

Table 5. Concentrations and stocks of nutrients in the organic soil horizons and mineral soil as well as residence times (years) of nutrients in the forest floor.

Exchangeable cations, total C and N as well as available P and micronutrients in five soil layers

Layer	Ca	Mg	K	N	P	C	Mn	Fe	Cu	Zn
	cmoles$_c$·kg^{-1}			g·kg^{-1}	mg·kg^{-1}	g·kg^{-1}	mg·kg^{-1}			
FH	52.6	4.00	1.09	12.2	30.5	230	370	133	1.45	18.5
	(9.4)	(7.2)	(23)	(13)	(6.0)	(14)	(5.7)	(12)	(4.9)	(15)
0–10 cm	15.6	1.63	0.599	3.31	5.26	51.2	151	54.4	0.358	1.38
	(16)	(9.2)	(20)	(16)	(28)	(20)	(15)	(25)	(20)	(54)
10–20 cm	8.97	1.32	0.593	2.45	2.68	33.6	116	45.3	0.383	0.483
	(18)	(1.8)	(23)	(9.4)	(14)	(10)	(14)	(5.0)	(32)	(18)
20–40 cm	5.65	1.18	0.55	2.12	2.90	27.5	92.5	41.5	0.575	0.275
	(9.3)	(11)	(16)	(4.4)	(36)	(3.5)	(28)	(4.2)	(15)	(16)
40–80 cm	2.28	1.13	0.29	1.35	6.3	15.3	65.0	32.9	0.438	0.175
	(25)	(17)	(28)	(15)	(37)	(19)	(37)	(0.54)	(12)	(0.0)

Stocks of nutrients in the forest floor and mineral soil

Layer	Ca	Mg	K	N	P	S	Mn	Fe	Cu	Zn
	t·ha^{-1}								kg·ha^{-1}	
L+FH	1.34	0.419	0.568	1.091	0.110	0.0973	0.144	2.036	1.87	9.13
	(4.6)	(10)	(9.9)	(11)	(5.2)	(7.9)	(4.6)	(15)	(7.2)	(5.6)
0–80 cm	15.5	42.3	57.2	9.77	3.748	1.309	4.278	239	131	519
	(5.1)	(1.8)	(1.9)	(5.4)	(1.8)	(3.2)	(18)	(2.8)	(5.1)	(4.0)

Residence times of nutrients in the forest floor in years

Layer	Ca	Mg	K	N	P	S	Mn	Fe	Cu	Zn
L+FH	11.4	32.3	9.02	14.9	19.7	3.78	61.2	498	24.7	33.6

Note: coefficients of variations are in parentheses.

found 1091 kg·ha^{-1} in the forest floor and 9770 kg·ha^{-1} N in the mineral soil (80 cm depth) (Table 5). This difference stresses the importance of the maturity of stands with regard to the total nutrients pool. To the best of our knowledge, there is no information in literature for micronutrients stocks in forest soils. The high amounts of Fe and Mn were expected, as mineral oxides are abundant in soils. The other two micronutrients Cu and Zn were in small amounts. The mineral soil contains the largest amounts of nutrients (Table 5) but the forest floor is the most active layer of soil in terms of microbial activity. It has to be mentioned that of the large amounts of elements in the mineral soil layers only a small percentage is available for plants. This is not necessarily bad for the ecosystem because the essentials elements are not in the risk of leaching. However, climate change can increase temperatures and thus accelerate organic matter decomposition and organic N mineralization.

That will be a constant point of alert in the future.

Residence time of nutrients in the forest floor

The calculation of this parameter is of great importance because, as mentioned above, the forest floor is the most active biological pool of forest soils. Table 5 shows the length of time of the various elements in the forest floor. It can be seen that S and K have the shortest residence time and Fe has the longest one. The high amounts of both S and K in throughfall deposition contributed to their short residence time. Iron forms strong bond with the soil organic matter and for this reason its residence time is high. Cole and Rapp (1981) quoted the mean residence time of five macronutrients in the forest floor of 13 temperate coniferous sites in the world. The N (17.9 years) and P (15.3 years) were similar to those found in our work (Table 5). There was an appreciable difference for the residence times of Ca, Mg and K, which was higher in the fir plot. This must be related with the nature of the parent material among the various forest sites. There has not been any information on S and micronutrients.

Conclusions

The Bulgarian fir under consideration is in good nutritional condition judging from foliar and soil analysis. In contrast to other nutrients, P concentrations were low in the mineral soil but this does not seem to be a problem because its availability in the humus layer and the re-translocation capacity that trees have fully cover P needs. Sulphate S fluxes in throughfall are high and thus they shorten the residence time of this element in the forest floor. The highest stocks of nutrients were in the mineral soil, forest floor, trunk wood and trunk bark as well as foliage canopy. Trunk bark was a large pool for N, P and S. This finding is important to consider (especially for P) when a logging plan is applied. It is recommended that the logging remnants should stay in the forest to enrich the forest floor. The high amounts of N in the mineral soil can be a point of alert for climate change as mineralization of organic N can be increased due to a rise in ambient temperature. The shortening of the residence time of this element in the forest floor can be an indication of that change. The fir plot in our work can serve as a reference level for comparison under the presupposition that we have mature and mountainous *Abies* species.

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