Environ Monit Assess
DOI 10.1007/s10661-011-2515-7

Status of the Southern Carpathian forests in the long-term ecological research network

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Received: 11 July 2011 / Accepted: 28 December 2011

Abstract Air pollution, bulk precipitation, throughfall, soil condition, foliar nutrients, as well as forest health and growth were studied in 2006–2009 in a long-term ecological research (LTER) network in the Bucegi Mountains, Romania. Ozone (O_3) was high indicating a potential for phytotoxicity. Ammonia (NH_3) concentrations rose to levels that could contribute to deposition of nutritional nitrogen (N) and could affect biodiversity changes. Higher that 50% contribution of acidic rain ($pH<5.5$) contributed to increased acidity of forest soils. Foliar N concentrations for Norway spruce (*Picea abies*), Silver fir (*Abies alba*), Scots pine (*Pinus sylvestris*), and European beech (*Fagus sylvatica*) were normal, phosphorus (P) was high, while those of potassium (K), magnesium (Mg), and especially of manganese (Mn) were significantly below the typical European or Carpathian region levels. The observed nutritional imbalance could have negative effects on forest trees. Health of forests was moderately affected, with damaged trees (crown defoliation >25%) higher than 30%. The observed crown damage was accompanied by the annual volume losses for the entire research forest area up to 25.4%. High diversity and evenness specific to the stand type's structures and local climate

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Published online: 11 January 2012

conditions were observed within the herbaceous layer, indicating that biodiversity of the vascular plant communities was not compromised.

Keywords Air pollution · Climatic conditions · Atmospheric deposition · Drought · Forest health · Biodiversity · Tree growth

Introduction

Forest ecosystems provide socio-ecological and economic benefits indispensable for life quality at global, regional, and local levels. Forest ecosystem services can be maintained by ensuring its appropriate health status, stability, and sustainability through proper forest management. However, climate change, air pollution, and forest land-use changes are important destabilizing factors of forest ecosystems composition, structure, and functions (ICP-Forests 2010b).

In Europe during 1970–1980, most countries reported the presence of numerous types of damage in forests caused by unspecified factors. The rapid development of damage symptoms and their spatial distribution and independent occurrence affecting various forest species has been described as the "unknown decline of the forests syndrome" (ICP-Forests 1997, 2006a), meaning that research results could not explain all aspects of this phenomenon due to the complexity of multiple biotic and abiotic factors (ICP-Forests 2010b). However, in areas near industrial air pollution sources, forest ecosystems decline has been often attributed to the harmful effects of atmospheric pollutants. In this context there has been a need for better understanding of multiple interrelationships between long-range trans-boundary air pollution and the main ecosystem components and processes.

Most hypotheses on the causes of different types of injury, such as physiological and mechanical, have been interpreted as an expression of a lack of resilience of the entire ecosystem, with air pollution being considered as a facilitating, accompanying, or even a mitigating factor. However, there is still insufficient knowledge of the normal functioning of forest ecosystems to understand the causes of forest decline and deterioration of forest health (Lorenz et al. 2004).

Environmental pollution, climate changes, and various biotic and abiotic factors that cause the decline of forest ecosystems have been evaluated in different national and international studies of individual trees, stands, and forest ecosystems as undivided growth dynamics (Badea and Neagu 2011). However, all these stress factors, mainly anthropogenic, are characterized by a more intense dynamic than the natural adaptation processes of forests, because trees as living organisms have a slow ability to adapt to changes in environmental conditions. Increasing anthropogenic influences on the environment, especially pollution loads, have caused negative changes in natural ecosystems, such as biodiversity decline or reduced productivity (Shparyk and Parpan 2004).

There is clear evidence that during the past century ambient ozone (O_3) concentrations in the northern hemisphere have significantly increased due to increased anthropogenic emissions of nitrogen oxides and volatile organic compounds that are O_3 precursors (Volz and Kley 1988). The present background O_3 concentrations have already reached phytotoxic levels in many parts of the world, and it is predicted that by 2050 about 50% of global forests will experience negative O_3 effects (Fowler et al. 1999). At present, ambient O_3 is the most important phytotoxic air pollutant for forest vegetation in Europe, including tracts of the Carpathian Mountains, while nitrogen and sulfur oxides (NO_x and SO_x) at concentrations harmful to forest vegetation rarely occur (Bytnerowicz et al. 2005). However, combined effects of O_3, sulfur dioxide (SO_2), and nitrogen dioxide (NO_2) could have negative effects on some forest stands in the western Carpathians (Muzika et al. 2004). In addition, high levels of nitrogen (N) and sulfur (S) deposition occur widely across Europe, particularly in its central part, including the Carpathians, and may cause acidification and N enrichment of forest ecosystems (ICP-Forests 2010a). Ammonia (NH_3) is one of the main drivers of atmospheric N deposition to forests and other ecosystems with its effects increasing over time (Erisman et al. 2008).

High levels of O_3 and other phytotoxic pollutants, as well as N and S deposition at the levels found in the Carpathian Mountains, may cause negative effects on forest health status and biodiversity, including visible leaf injury, losses in stand growth and productivity, as well as higher sensitivity to biotic and abiotic stressors (Bytnerowicz et al. 2005; Silaghi et al. 2011). Consequently, secondary stresses such as the increasing rate of bark beetle attacks or changes in nutritional status of forest soils caused by acidic precipitation may contribute to the worsening condition of forest stands.

Spatial and temporal distribution of air pollutants vary significantly due to physiographic differences, such as altitude, and environmental changes, including climate change and human activities. Long-term monitoring activities of O_3 and other phytotoxic pollutant concentrations, as well as dry and wet atmospheric deposition (bulk deposition), are necessary in order to understand the nature and future risks to forest ecosystems. In the Romanian Carpathian Mountains, the effects of air pollution on forest ecosystems were studied on an international network of long-term ecological research (LTER) sites. The Bucegi Natural Park in the Bucegi Mountains located in the southern Carpathian Mountains was chosen as one of the sites because it has important scientific value for the entire Carpathian Mountains, as well as for the Romanian Carpathians. This is intended as a long-term investigation of the effects of air pollution on forest ecosystems in Bucegi Natural Park. It was expected that the Bucegi forests would have a "normal" environmental, nutritional, forest health and growth status, as shown in different other research conducted in Romanian Carpathians (Bytnerowicz et al. 2005).

The general objective of these research and monitoring activities in the Romanian Carpathians Mountains is to determine the level of air pollution and its potential effects on forest ecosystems status and biodiversity, and its connection with the effects of climate change in Bucegi Natural Park. The specific objectives of this paper are: (a) to assess the spatial and temporal distribution of selected air pollutants (O_3 and NH_3); (b) to determine precipitation and throughfall acidity and chemical composition in selected forest sites; and (c) to evaluate forest health status, biodiversity, growth of trees, and soil condition affected by the air pollution and other risk factors.

Materials and methods

Study area

The Bucegi Mountains are located in the southern Carpathians in Romania and have an area of 32,498 ha with more than 60% forest cover. Natural reserves cover 8,216 ha, of which 4,997 ha are in the administrative territory of Prahova County, 1,575 ha in Dambovita County, and 1,644 ha in Brasov County, representing around 25% of Bucegi Natural Park (RNP-Romsilva 2010). The vast richness and diversity of the Park's vegetation, many endemic species, and unique plant associations provide high scientific value. This diversity was the main reason for assigning Natural Park status to the Bucegi Mountains, aiming to preserve natural landscapes and specific biocenoses of these mountains.

The development of multidisciplinary studies for the purpose of long-term research of forest ecosystems under the influence of air pollution and climate change required an establishment of an LTER network representative of the entire study area and its rich diversity of the forest ecosystems. Thus, forest ecosystems and their accessibility, topography, altitude and exposition, and air pollution by O_3 and NH_3 were investigated.

In 2006, a monitoring network of 10 uniformly distributed LTER sites located in forest zones with elevations ranging between 800 and 1,700 m was established (Fig. 1). Each forest ecosystems category (conifers, broadleaves, and mixed forests) was represented at two to three LTER sites. Research activities conducted within the network are presented in Table 1 (Gol Alpin location was selected only for air quality measurements).

Methodology

After identifying and selecting representative forest ecosystems category on maps and in the field, ten permanent plots (LTER sites) with their subsequent subplots were established and spatially positioned using a global positioning system. At a distance of 30 m of the plot center, four permanent subplots (PSPs) were arranged in cardinal directions crosswise, as well as one in the center of the LTER sites, in homogeneous stand conditions (Lorenz et al. 2004).

The research area of each site was 0.7 ha. It contained five circular PSPs of 500 m^2 each in which annual assessments of forest health, periodic measurements of dendrometric characteristics (species, Diameter at Breast Height, height, Kraft class, quality class; Dobbertin and Neumann 2010; Eichhorn et al. 2010), and seasonal vegetation biodiversity assessments were conducted (Fig. 2). In a buffer zone close to the permanent subplots, destructive sampling (increment cores, foliar samples, soil samples) and atmospheric deposition and soil solution sampling were carried out. Crown condition was assessed annually in 2006–2009 during July to August (Badea et al. 2004; Bytnerowicz et al. 2005; Neagu and Badea 2008). Each year, all the trees of the PSP areas

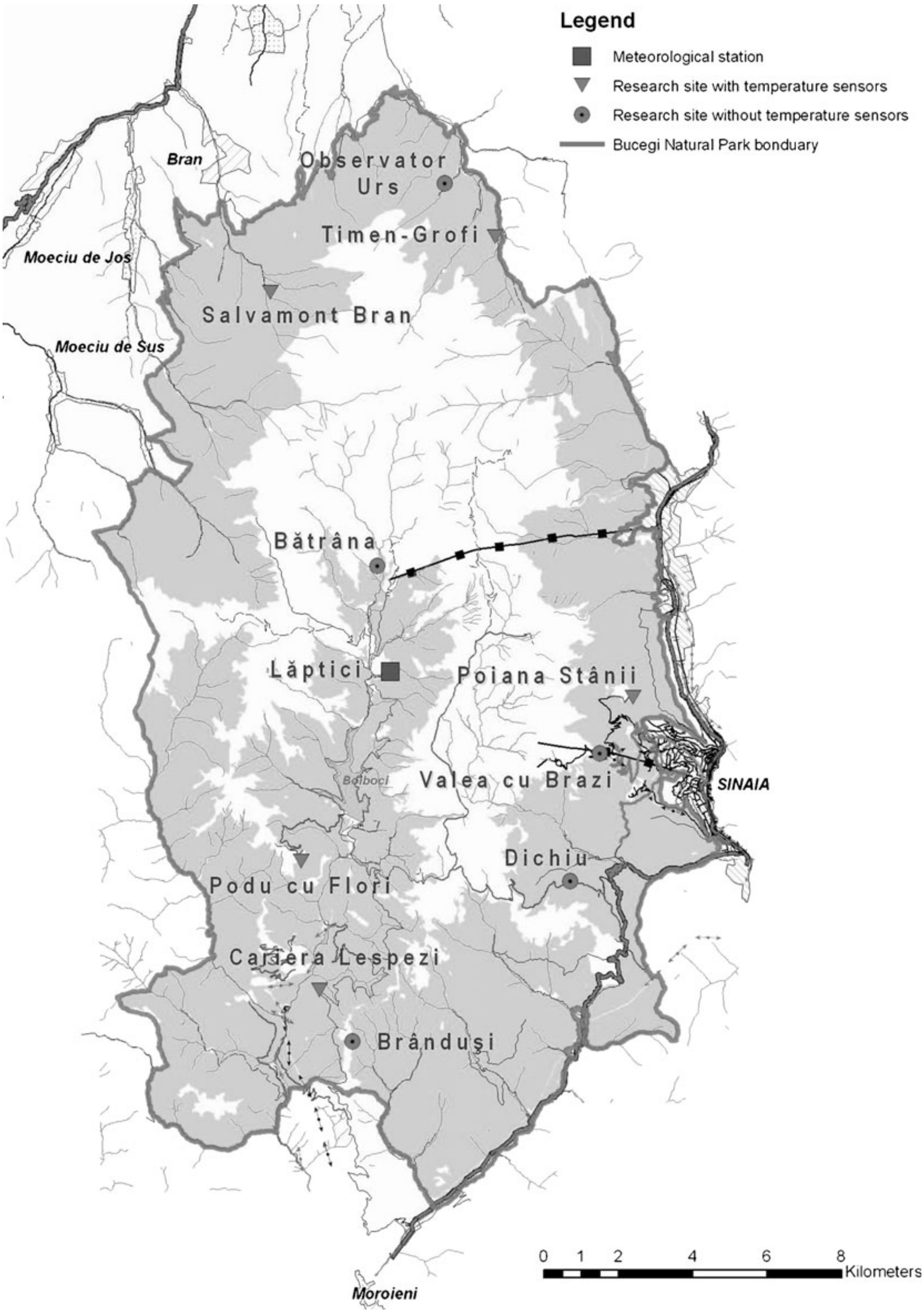


Fig. 1 Long-term ecological research (LTER) network in Bucegi Natural Park

Table 1 Research activities performed in the long-term ecological research (LTER) sites in the Bucegi Mountains, Romania, 2006–2009

LTER locations	Altitude a.s.l. (m)	Main species	Growth and yield	Crown condition	Soil condition	Analysis of needles and leaves	Deposition (bulk and throughfall)	Soil solution	Biodiversity	Air quality
1. Salvamont Bran	1250	*Picea abies*	✓	✓	✓	✓	✓	✓	✓	✓
2. Observator Urs	930	*Picea abies, Fagus sylvatica, Abies alba*	✓	✓	✓	✓			✓	✓
3. Timen-Grofi	1000	*Picea abies*	✓	✓	✓	✓			✓	✓
4. Poiana Stanii	1300	*Fagus sylvatica*	✓	✓	✓	✓	✓	✓	✓	✓
5. Valea cu Brazi	1450	*Picea abies*	✓	✓	✓	✓			✓	✓
6. Dichiu	1250	*Fagus sylvatica*	✓	✓	✓	✓			✓	✓
7. Brânduşi	1750	*Picea abies*	✓	✓	✓	✓			✓	✓
8. Cariera-Lespezi	1480	*Fagus sylvatica*	✓	✓	✓	✓			✓	✓
9. Podu cu Flori	1750	*Picea abies*	✓	✓	✓	✓	✓	✓	✓	✓
10. Bătrana	1700	*Picea abies*	✓	✓	✓	✓			✓	✓
11. Gol Alpin	1950	–								✓

All the research activities started in 2006

located in Kraft classes I, II, and III (predominant, dominant, and codominant) were evaluated according to the ICP Forests methodology (ICP-Forests 2006b). Dendrometric measurements were taken during the vegetation season according to the methodological manual developed under this research project (Badea et al. 2008). Phytosociological (plant community) data were recorded for each permanent plot twice over the growing season (spring and summer) using the Braun Blanquet's method (Grodzinska et al. 2004; Badea 2008; Vadineanu et al. 2008). Increment core samples were taken from 20–25 trees located in the buffer zone of each site, both for main living tree species and for the 0–1 (defoliation ≤25%) and 2–3 (defoliation >25%) defoliation group classes.

In mixed stands consisting mainly of Norway spruce (*Picea abies*), European silver fir (*Abies alba*), and European beech (*Fagus sylvatica*) the increment cores were taken from 10–15 trees of each main species. Based on radial increment and a single periodic measurement of trees, the average annual volume growth and yield (Giurgiu 1979; Leahu 1994; Giurgiu et al. 2004) as well as losses due to the effects of different stress factors (air pollution, climatic changes) were determined. The average annual increment (the average tree ring width) was determined for all living trees (defoliation classes 0–3), for healthy trees (defoliation group classes 0–1), and for damaged trees (defoliation group classes 2–3) of individuals of similar age at each site and for the entire network for the main species (*P. abies*, *A. alba*, and *F. sylvatica*). In order to obtain statistically significant results, at each site at least ten dominant or codominant trees were core sampled at 1.3 m height for each species and defoliation group classes. The data processing and interpretation was performed according to Badea et al. (2008).

Calculation of the normal (theoretical) growth was made assuming that all trees were healthy (defoliation classes 0–1), by inferring the growth of healthy trees to the damaged ones (defoliation classes 2–3), taking into consideration the corresponding DBH.

The growth losses are computed based on the assumption that the damaged trees (defoliation classes 2–3), in 'normal' conditions, would have been healthy and would have had similar axiological behavior with the healthy ones (Badea and Neagu 2011). This assumption does not take into consideration the growth losses that occurred before the study period (the last 10 years), which could have an accumulated effect. In

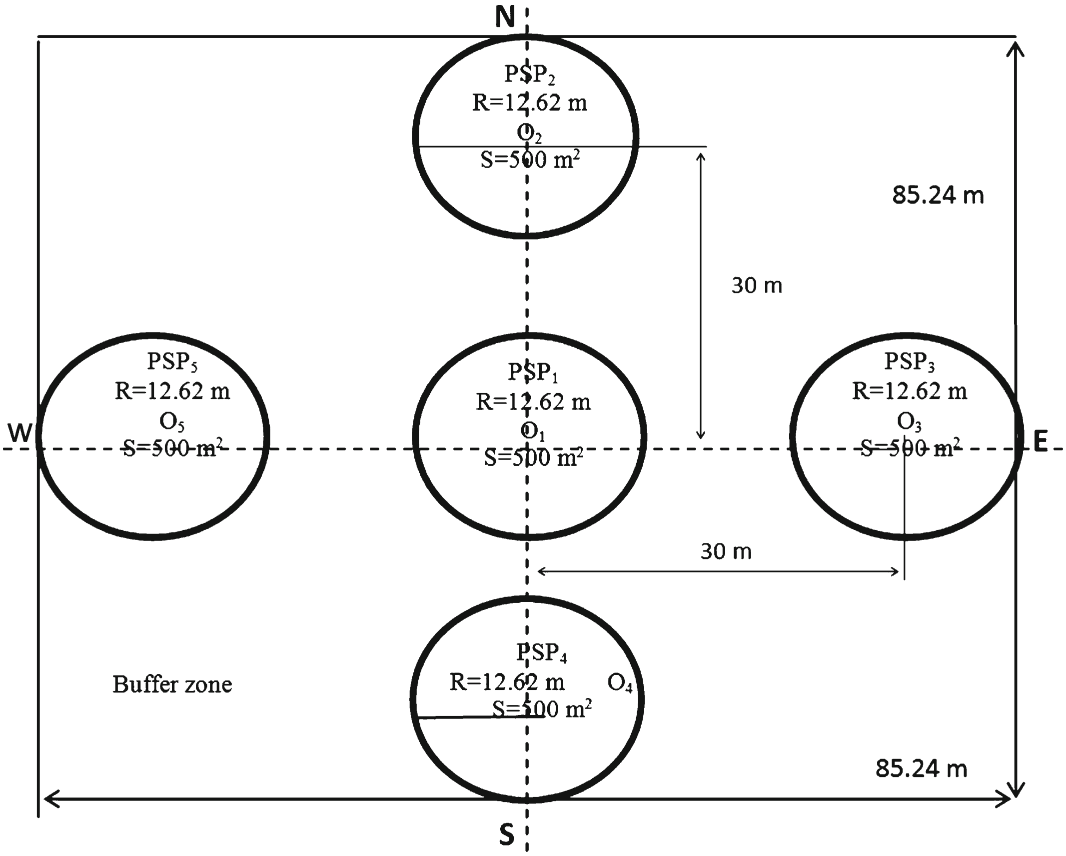


Fig. 2 Design of study site and spatial distribution of circular permanent subplots (PSP) for forest vegetation assessment

2007, to assess forest soil condition, several soil profiles were excavated for mineral and organic layers sampling at all LTER sites (Geambasu and Danescu 2008). The morphological, physical, mechanical, and chemical properties of forest soils were analyzed at the Chemistry Laboratory of Forest Research and Management Institute ICAS Bucharest.

Foliar samples for analysis of the nutritional status of trees were harvested by main species (*P. abies*, *A. alba*, *Pinus sylvestris*, and *F. sylvatica)* from eight trees of each species in each site's buffer zone. For conifers (spruce, fir, pine), foliar samples were collected in April 2007 and for beech in August 2007 (Blujdea and Ionescu 2008). The *P. sylvestris* and *A. alba* foliage samples for chemical analysis were collected only from single locations. The population of Scots pine (*P. sylvestris*) at the Timen-Grofi site was unique in the specific composition of that stand and poorly represented. For *A. alba*, samples were collected at the Observator Urs site, where this species was well represented in the stand composition. Foliage of *F. sylvatica* was collected in two locations, Poiana Stanii and Cariera-Lespezi. The chemical analyses of foliar samples were performed according to the methodology described by Mankovská et al. (2004).

Close to the LTER plots in locations of optimal exposure to incoming air masses, concentrations of O_3 and NH_3 were monitored during the growing seasons (15 May to 15 October) of the 2006–2009 study. Passive samplers for O_3, NH_3, and NO_2 (Ogawa and Co., USA, Pompano Beach, Florida) were placed in protective caps and hung on wooden stands at ~2 m aboveground. Each O_3 sampler (Koutrakis et al. 1993) contained two replicate cellulose filters coated with nitrite, which is oxidized by O_3 to nitrate. Nitrate was extracted from passive samplers with ultrapure water, and its concentrations were determined with ion chromatography (Dionex, Model DX 600, Dionex Co., USA, Sunnyvale, CA). Based on comparisons with collocated UV absorption active O_3 instruments, the nitrite formation rates and O_3 concentrations were calculated (Bytnerowicz et al. 2008a). Each NH_3 sampler (Roadman et al. 2003) contained two replicate filters coated with citric acid that in the presence of NH_3 is converted to ammonium citrate. Ammonium from filters was extracted in ultrapure water and its concentrations were determined colorimetrically with TRAACS 2000 Autoanalyzer (Bran Luebbe, 611 Sugar Creek Road, Delavan, WI 53115), and ambient concentrations were calculated based on comparison with collocated annular denuder systems (Bytnerowicz et al. 2010). Each NO_2 sampler contained two replicate cellulose filters coated with triethylamine that captures NO_2 as nitrite that is extracted in water and determined with ion chromatography (Dionex, Model DX 600). Concentrations of NO_2 were calculated based on collocated NO_2 real-time monitors (Monitor Labs) chemiluminescence analyzers. Passive samplers were collected monthly, sealed in plastic containers and ziplock bags, and immediately shipped for chemical analyses. Concentrations of NO_2 were also determined and were presented with the preliminary O_3 and NH_3 results for the 2009 season by Badea et al. (2011).

Bulk deposition (open field and throughfall) was collected at three plots (Salvamont Bran, Poiana Stanii, and Podu cu Flori). Precipitation samples were collected both during the growing season (15 May to 15 October) and during the dormant period (15 October to 15 May). To minimize chemical contamination of the samples, special precautions were taken, especially rinsing all equipment after each collection. Using different analytical methods (ion chromatography, colorimetry, conductometry), a set of parameters like pH, conductivity, alkalinity, and potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), ammonium N (N-NH_3), chlorine (Cl), nitrate N (N-NO_3), sulfate S (S-SO_4) were determined Barbu and Iacoban (2008).

A meteorological station was installed in a representative location (Laptici) near the Bătrana site (Fig. 1) in order to measure air temperature, air humidity, precipitation, and wind parameters. Additional air temperature and humidity data loggers were set up inside representative forest stands.

Forest health status was assessed annually, during the 15 July to 31 August period, which corresponds to the maximum physiological activity of the trees. Crown condition and mechanical damages of trees were assessed according to the methodological manual (Badea 2008). Statistical analysis of data was made with the SPSS software, using correlation, linear regression (simple and multiple) and ANOVA analysis (mean comparison method used in Tukey's test).

Results and discussion

Air chemistry

In the Bucegi Mountains during the 2006–2009 growing seasons, both spatial and temporal trends of ambient O_3 distribution showed high variability (Table 2, Fig. 3). Ranges of the monthly average O_3 concentrations for individual locations were similar for 2006, 2007, and 2009 (20.7–61.6 ppb, 23.0–66.8 ppb, and 19.2–67.0 ppb, respectively), but were more variable in 2008 (13.5–80.0 ppb). Seasonal averages for various sites varied between 22.5 ppb (Observator Urs in 2009) and 57.4 ppb (Podu cu Flori in 2007), and large differences between the sites (Table 2) and times of the season (Fig. 3) were determined. Highest O_3 concentrations typically occurred in the middle of summer (mid-June to mid-August), with the lowest values after the photochemical smog season in mid-September to mid-October (Fig. 3). Considering that O_3 is a secondary photochemical pollutant, its higher concentrations in the middle of summer can be explained by high temperature and solar radiation (Finlayson-Pitts and Pitts 2000) The determined seasonal means of 42.5–47.2 ppb in 2006–2008 were higher than those determined in the Romanian Carpathians in the 1997–1999 period (39–42 ppb), while the 2009 mean of 40.0 ppb was in the range of those values (Bytnerowicz et al. 2004).

The O_3 levels determined in the Bucegi Mountains were slightly higher than those at the Retezat National Park in the southern Carpathians (Bytnerowicz et al. 2005). During the study period, ambient O_3 concentrations increased in the Bucegi Mountains with altitude up to ~1,500 m, and then decreased as the altitude increased to ~1,750 m (Badea et al. 2011). Results of the multiple linear regression analysis for each exposure period of the 2006–2009 growing seasons showed that altitude accounted for 49% of the variation of ozone concentrations, and mean temperatures corresponding to each exposure period during the 2006–2009 growing seasons explained another 18.5% of ozone variation. Therefore, the altitude increase and temperature together accounted for 67.5% of the observed O_3 changes.

Table 2 Summary statistics for ozone concentrations (ppb) measured as integrated monthly values (15 May–15 October), presented as seasonal means with standard deviation (in parentheses), and ranges of concentrations

Location	2006	2007	2008	2009
1. Salvamont Bran	38.7 (6.3), cd, 31.3–48.6	42.6 (7.6), abc, 32.5–51.1	39.5 (9.3), 24.0–48.9	36.2 (4.3), bcd, 31.1–40.7
2. Observator Urs	25.1 (3.9), e, 20.7–31.1	29.2 (6.2), c, 23.0–36.2	26.3 (7.8), 13.5–33.9	22.5 (3.0), d, 19.2–25.7
3. Timen-Grofi	33.0 (5.1), de, 28.0–41.1	35.9 (6.9), bc, 27.7–43.0	32.8 (8.4), 18.5–39.7	29.3 (3.9), cd, 24.2–32.8
4. Poiana Stanii	43.7 (4.5), bc, 38.2–50.7	48.1 (6.6), ab, 36.2–51.7	42.6 (10.6), 24.5–51.4	40.1 (3.7), abc, 34.6, 42.9
5. Valea cu Brazi	48.7 (4.3), abc, 43.4–54.9	50.6 (8.3), ab, 38.7–57.8	47.2 (11.0), 28.0, 55.1	44.3 (4.9), abc, 37.5–48.9
6. Dichiu	45.4 (4.3), abc, 40.8–52.2	47.8 (8.3), ab, 35.0–54.6	43.7 (9.6), 27.7–52.9	38.4 (5.2), bc, 30.8–42.5
7. Brandușі	50.5 (5.7), ab, 42.9–58.8	53.7 (7.4), a, 41.7–61.2	48.8 (23.0), 24.0–71.7	48.7 (6.8), ab, 40.4–57.0
8. Cariera-Lespezi	45.7 (3.6), abc, 40.3–49.8	48.2 (10.0), ab, 38.1–61.4	42.6 (18.8), 21.6–67.2	42.0 (7.7), abc, 32.6–51.4
9. Podu cu Flori	54.6 (5.2), a, 47.2–61.6	57.4 (9.0), a, 42.7–66.8	50.7 (23.9), 22.3–80.0	54.6 (10.2), a, 42.1–67.0
10. Bătrana	54.0 (4.5), ab, 47.4–59.5	57.5 (8.0), a, 43.9–64.5	49.0 (20.9), 24.3–74.3	41.2 (9.7), ab, 29.4–53.1
11. Gol Alpin	48.7 (5.6), abc, 42.7–54.4	48.3 (7.3), ab, 37.8–55.1	44.4 (8.0), 30.4–50.3	42.2 (5.5), abc, 34.5–47.3
P value for "between sites" comparison	<0.05	<0.05	0.322	<0.05
All sites	44.4 (9.0), 25.1–54.6	47.2 (8.6), 29.2–57.5	42.5 (7.4), 26.3–50.7	40.0 (8.7), 22.5–54.6
P value for "all sites" comparison	0.336	0.336	0.336	0.336

Different letters following mean and S.D. indicate significant differences between monthly mean ozone concentrations measured at different monitoring sites at a specified *P* value

The average monthly or seasonal O_3 concentrations found in the Bucegi Mountains should not be considered toxic to the investigated tree species (Skärby and Karlsson 1996; Bytnerowicz et al. 2005), although effects on sensitive understory plant species (although no visible injury were observed) cannot be ruled out (Manning and Godzik 2004). In order to be more specific about potential O_3 phytotoxic effects, real-time information on O_3 concentration (hourly values) is needed. This is because the toxicity of the pollutant

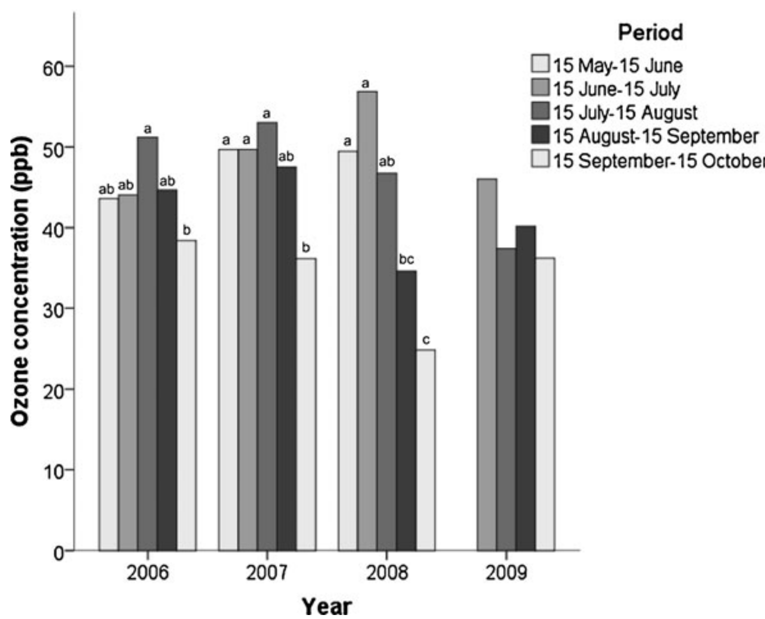


Fig. 3 Comparisons of mean O_3 concentrations (ppb) for each exposure period during each year from 2006–2009 period. Different letters set as labels to each column indicate significant differences between exposure periods at $P<0.05$

increases with the occurrence (absolute values and frequency) of its peak values (Musselman et al. 2006). Although the highest O_3 seasonal means were recorded in 2007, that does not mean that the phytotoxic O_3 effects were also the highest. That potential could have been lower due to the fact that in 2007 ambient temperatures were very high (often over 35°C). This in turn promotes closure of stomata to reduce water transpiration and consequently O_3 intake when its ambient concentrations are the highest (noon, early afternoon) (Matyssek et al. 2007).

Ambient NH_3 concentrations showed high spatial and temporal variability (Table 3; Fig. 4). Ranges of monthly average NH_3 concentrations were similar for 4 years of the study: 0.40–3.80, 0.02–3.31, 0.20–4.60, and 0.10–2.64 μg/m^3, respectively, for 2006, 2007, 2008, and 2009. In 2006 and 2007, the highest seasonal averages occurred in Bătrana (2.46 and 1.78 μg/m^3, respectively), while in 2008 and 2009 no significant differences between the sites were determined (Table 3). Seasonal averages for various sites varied between 0.63 μg/m^3 at Gol Alpin in 2007 to 2.46 μg/m^3 at Bătrana in 2006, and except for rare peaks >4.0 μg/m^3 in 2008, most seasonal values were <2.0 μg/m^3 (Table 3). For the entire area, in 2006, 2007, and 2009 there were no significant differences in NH_3 between monitoring periods and concentrations generally stayed <1.5 μg/m^3. However, from 15 May to 15 June 2008 the entire area experienced a high NH_3 episode with an average of 3.1 μg/m^3 (Fig. 4). The spikes in NH_3 concentrations were probably caused by intensive tourist activities, grazing, forest operations (cuttings), or increased biological activity (peat lands, insect outbreaks' control activities).

In general, seasonal means of NH_3 concentrations monitored in the Bucegi Mountains were lower than the levels found in the Retezat Mountains (Bytnerowicz et al. 2005) or in other Carpathians regions. These levels are similar to those found in the Canadian Rocky Mountains (Legge and Krupa 1989) and in the Eastern Sierra Nevada, California (Bytnerowicz and Fenn 1996). The measured concentrations were below phytotoxic NH_3 levels (Bytnerowicz et al. 1998) and are not expected to provide substantial amounts of dry-deposited nitrogen to forest (Gessler and Rennenberg 1998).

Nitrogen dioxide (NO_2) concentrations were measured only in 2006 and 2007. In general, the monthly averages were low (below 4 μg/m^3) in most locations. Ranges of NO_2 concentrations were between 0.8 and 1.70 μg/m^3 in 2006 and between 1.90 and 3.80 μg/m^3 in 2007. Such values are low and typical for remote

Table 3 Summary statistics for ammonia concentrations (μg/m^3) measured as integrated monthly values (15 May–15 October), presented as seasonal means with standard deviation (in parentheses), and ranges of concentrations

Location	2006	2007	2008	2009
1. Salvamont Bran	0.82 (0.46), b, 0.40–1.60	0.99 (0.27), ab, 0.59–1.26	1.60 (0.95), 0.90–2.94	1.73 (0.38), 1.38–2.12
2. Observator Urs	0.80 (0.12), b, 0.60–0.90	0.84 (0.56), ab, 0.02–1.55	1.40 (0.91), 0.56–2.91	1.14 (0.70), 0.10–1.50
3. Timen-Grofi	0.80 (0.17), b, 0.50–0.90	1.03 (0.26), ab, 0.59–1.25	1.68 (1.65), 0.60, 4.60	1.80 (0.48), 1.13–2.26
4. Poiana Stanii	0.66 (0.11), b, 0.50–0.80	0.78 (0.27), ab, 0.47–1.19	1.86 (1.33), 0.88–4.14	1.73 (0.62), 1.26–2.64
5. Valea cu Brazi	0.74 (0.15), b, 0.50–0.90	0.60 (0.12), b, 0.48–0.77	1.40 (1.35), 0.19–3.68	1.98 (0.32), 1.79–2.45
6. Dichiu	0.86 (0.29), b, 0.50–1.30	1.01 (0.37), ab, 0.68–1.59	1.73 (0.59), 1.06–2.44	1.65 (0.31), 1.28–2.00
7. Branduşi	1.48 (0.68), ab, 0.50–2.20	1.02 (0.29), ab, 0.77–1.51	1.69 (1.35), 0.78–4.03	0.82 (0.50), 0.18–1.21
8. Cariera-Lespezi	1.36 (0.63), ab, 0.602.30	0.72 (0.60), ab, 0.22–1.69	1.18 (0.35), 0.80–1.73	0.98 (0.72), 0.44–2.00
9. Podu cu Flori	0.73 (0.55), b, 0.11–0.60	1.57 (1.10), ab, 0.50–3.31	0.92 (0.80), 0.16–1.98	0.86 (0.38), 0.51–1.37
10. Bătrana	2.46 (1.28), a, 0.60–3.80	1.78 (0.76), a, 0.81–2.76	1.43 (0.95), 0.20–2.30	1.19 (0.46), 0.49–1.43
11. Gol Alpin	0.86 (0.47), b, 0.4–1.50	0.63 (0.41), b, 0.23–1.13	1.84 (1.12), 0.70–3.66	1.08 (0.74), 0.21–1.92
P value for "between sites" comparison	<0.05	<0.05	0.954	0.112
All sites	1.05 (.54), .66–2.46	1.00 (.37), .60–1.78	1.52 (.29), .92–1.86	1.36 (.42), .82–1.98
P value for "all sites" comparison	0.175	0.175	0.175	0.175

Different letters following mean and S.D. indicate significant differences between monthly mean ammonia concentrations measured at different monitoring sites at a specified *P* value

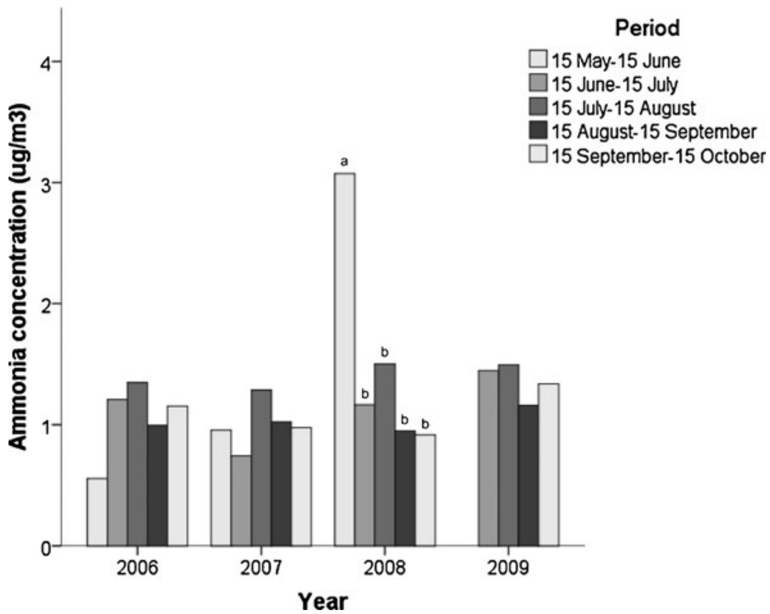


Fig. 4 Comparisons of mean NH_3 concentrations (in micrograms cubic meters) for each exposure period during each year from 2006–2009 period. *Different letters* set as labels to each column indicate significant differences between exposure periods at $P<0.05$

European mountain locations with no potential for any phytotoxic effects and minimal effect on N dry deposition given the low deposition velocity of this pollutant (Hanson and Lindberg 1991).

Additional consideration should be given to the interactive effects of various air pollutants (Muzika et al. 2004). However, considering that NO_2 and NH_3 levels were very low, and the SO_2 levels, although not measured, were probably similar to low concentrations determined in the nearby Retezat Mountains (Bytnerowicz et al. 2005), at present no serious interactive effects on trees are expected.

Precipitation chemistry

Average precipitation quantities collected between 15 May and 15 October in 2006–2009 in the LTER sites are presented in Table 4. Precipitation deposition to canopy depends mainly on the density of the stand, intensity and duration of an event, and wind speed (Kimmius 1973; Matzner 1986). The highest precipitation interception (9.08%) was recorded in the beech stand in Poiana Stanii plot and the lowest (-0.77% to -5.25%) in the coniferous stands at Salvamont Bran and Podu cu Flori. The main cause of high amounts of throughfall is frequent occurrence of fog and clouds, which very effectively deposit water droplets within the canopy (Villegas et al. 2007; Hildebrandt and Eltahir 2008). High variability of precipitation interception during the growing period between the study years was recorded. In 2008, in all plots, the open field (272.9 mm) precipitations were higher than in throughfall (249.6 mm). In 2006 and 2009, the precipitation interception rates were higher (8% and 14%, respectively) than in 2007 and 2008 (1% and 5%, respectively).

Over the period 2006–2009 the average frequencies of rainfall with pH<5.5 were higher in open field (59.4% in Poiana Stanii and 50.0% by Podu cu Flori) than those registered under the canopy (52.9% by Poiana Stanii and 47.0% by Podu cu Flori). In contrast to the other sites, in Salvamont Bran the occurrence of acid rain events was lower in open field compared to under canopy (Fig. 5).

Compared with acid rain frequencies in other Romanian intensive forest monitoring plots (ICP Forests Level II; Barbu et al. 2000; 2001) or those measured in the Retezat National Park (Bytnerowicz et al. 2005), those in the Bucegi Mountains were about two to three times and one to three times higher, respectively.

Acidity of bulk precipitation was generally higher than that of throughfall (Table 4). Comparing concentrations of acid (N, S) and alkaline (Ca, Mg) elements, as well as high values of water conductivity (salt accumulation, alkaline effects), it can be concluded that bulk precipitation in the Bucegi Mountains was

Table 4 Average concentrations of ions in bulk and throughfall precipitation samples collected during 2006–2009

Location	Pp (mm)	pH	Cond. (μS/cm)	S-SO_4 (mg/L)	Cl (mg/L)	N-NO_3 (mg/L)	N-NH_4 (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)
Bulk precipitations											
Salvamont Bran	279.9	5.02	27.12	0.83	1.77	0.28	0.61	0.23	0.31	0.09	2.55
Poiana Stanii	245.4	5.28	27.70	0.91	1.11	0.42	1.00	0.19	1.06	0.13	1.87
Podu cu Flori	151.8	5.21	29.43	0.81	0.60	0.13	0.24	0.19	0.65	0.12	2.75
Throughfall precipitations											
Salvamont Bran	294.6	5.26	38.46	1.56	0.96	0.48	1.37	0.23	2.42	0.24	2.06
Poiana Stanii	223.1	5.22	48.50	1.40	0.95	0.49	1.84	0.19	5.19	0.34	2.09
Podu cu Flori	152.9	6.11	95.15	2.93	3.40	0.39	3.58	1.89	2.89	0.45	5.81

generally acidic. Therefore, rain precipitation could contribute to the forest soil acidification process with a possible negative effect on forest health.

In open field (bulk deposition) in the 2009 growing season, the inputs range of S-SO_4 in three studied sites was wider and varied from 2 to 8 kg ha^{-1} (Badea et al. 2011). Throughfall inputs of S-SO_4 recorded values around 6 kg ha^{-1}. Compared with 2009, in 2006–2008 the inputs of S-SO_4 in the open field were variable, from 1.1 kg ha^{-1} (Podu cu Flori) to 3.7 kg ha^{-1} (Salvamont Bran) and 3.1 kg ha^{-1} (Poiana Stanii). This level of S-SO_4 shows low interaction with stand canopies, a low enrichment factor/ratio between fluxes under the canopy and in the open field, and a low pollution level of the studied area. Nitrogen inputs were very low (0.2 kg ha^{-1} to 3.5 kg ha^{-1}) and the range of N-NH_4 was higher than N-NO_3 deposition, in relation to the soil depth (Badea et al. 2011).

Throughfall had high concentrations of N-NH_4, mainly at high altitude, and bulk precipitation of N-NH_4

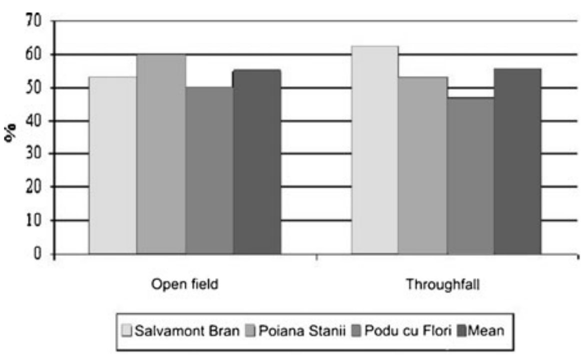


Fig. 5 Frequency of acidic rain (pH<5.5) at three research locations

contributed to 0.5 kg N ha^{-1} to 2-4 kg N ha^{-1}. In some research sites (Poiana Stanii), concentration of NH_4 in throughfall was lower than in bulk deposition, due to direct uptake of NO_3 or NH_4 by the canopy. Also, locations with low concentrations of NO_{3-} and NH_{4+} in bulk precipitation recorded insignificant amounts of these ions in throughfall, with an exception noted on Podu cu Flori, most likely due to intensive human activities (e.g., grazing of animals, tourism; Badea et al. 2011).

The S-SO_4 inputs under forest canopy (throughfall deposition) was significantly correlated with N-NO3 and N-NH_4 (Pearson correlation coefficient r_1=0.610 and r_2=0.223, respectively, for α<0.01), relation which points toward co-emissions from SO_x (mainly industry), NO_x (mainly traffic), and NH_x (mainly agriculture) in nearby industrialized areas (de Vries et al. 2003), and with S-SO_4 from bulk deposition (r=0.638, α<0.01), which is a normal relationship, although imputes in throughfall are four times higher than the ones in bulk precipitations in Podu cu Flori (Table 4) . In addition, N-NO_3 and N-NH_4 from throughfall were negatively (r=−0.285, α<0.01) and positively (r=0.221, α<0.01) significantly correlated with ambient O_3 concentration. The negative correlation between N-NO_3 and O_3 may lead to the conclusion that ozone precursors (VOC's) do not have the same source as N-NO_3 ions in depositions (nearby traffic), and are the result of long-range trans-boundary air pollution (UNECE 2004).

Nutritional status of trees

Defining nutritional status of trees in the LTER plots was done by comparing concentrations of the mineral

Table 5 Average concentrations of nutrients in the *Picea abies* foliage in Bucegi Natural Park

Location	N ($\%g\ g^{-1}$)	P ($\%g\ g^{-1}$)	K ($\%g\ g^{-1}$)	Ca ($\%g\ g^{-1}$)	Mn ($mg\ kg^{-1}$)	Zn ($mg\ kg^{-1}$)	Cu ($mg\ kg^{-1}$)	Na ($mg\ kg^{-1}$)	Mg ($mg\ kg^{-1}$)
Timen-Grofi	1.39	0.29	0.15	0.24	14.4	7.2	10.7	172.3	564.2
Observator Urs	1.24	0.21	0.13	0.26	23.4	9.8	11.0	183.6	515.9
Salvamont Bran	1.42	0.29	0.11	0.34	37.6	7.6	14.9	199.6	555.4
Valea cu Brazi	1.26	0.29	0.13	0.42	9.8	8.2	18.8	203.7	538.5
Bătrana	1.26	0.36	0.15	0.23	17.4	8.7	15.0	195.3	564.9
Podu cu Flori	1.17	0.35	0.14	0.30	48.5	7.7	28.1	245.8	524.2
Branduşi	1.23	0.29	0.12	0.24	37.5	6.8	20.9	177.2	537.3
Average	1.28	0.30	0.13	0.29	26.9	8.0	17.1	196.7	542.9

nutrient elements (total foliar form) against the average European data for the key tree species (Bauer et al. 1997; Stefan et al. 1997) and for the Carpathian Mountains (Mankovska et al. 2004). In general, levels of foliar nutrients of the studied populations of trees were not balanced, indicating their potential problems with metabolic processes, lower resistance to stressors, deterioration of tree health, and slower growth (Stefan et al. 1997).

Among the studied species, the nutritional status of *P. abies* most adequately represents forests of the Bucegi Mountains and samples from this species were collected at seven sites dispersed throughout the study area (Table 5). Compared to the normal macronutrient concentrations for this species in Europe (Bauer et al. 1997), their limit values (Stefan et al. 1997), and values previously determined in the Romanian Carpathians (Mankovska et al. 2004), the N foliar concentrations were normal, P concentrations were about twofold higher than normal, while concentrations of K, Ca, and Mg were below their normal values (about fivefold, twofold, and twofold, respectively). Concentrations of micronutrients also significantly differed from the values typically found in the Carpathian forests for this species (Mankovska et al. 2004), with very low concentrations of Mn and zinc (Zn) (10- to 15-fold and five times lower than normal values, respectively), normal copper (Cu) levels, and concentrations of Na about two times higher than normal.

The elemental ratios (in grams per gram) also suggest serious nutritional disturbances for *P. abies* in all sites (Table 6). Typically, the N/P ratio ranges between 6 and 17 (Mankovska et al. 2004), but only the trees at Observator Urs were at the typical recommended value. The recommended N/K ratio of 1.3–5 was significantly exceeded at all study sites. The N/Mg ratio did not differ much between the sites and was at the high end of the recommended limit of 8–28 (Stefan et al. 1997) but much higher than the values determined in the Romanian Carpathians (~14.5) in the late 1990s (Mankovska et al. 2004). The K/Ca ratio was at the low end of the recommended values (Stefan et al. 1997). *P. abies* needles showed a serious Mn deficiency indicated by very high values at all sites compared to the typical N/Mn ratio of 27.3 (Stefan et al. 1997) and to the average ratio of 15.2 determined in the Romanian Carpathians by Mankovska et al. (2004). This deficiency was the highest at the Timen-Grofi and Valea cu Brazi sites.

Results of elemental concentrations of *P. sylvestris*, *A. alba*, and *F. sylvatica* are presented in Table 7 and their foliar ratios in Table 8.

Similar to *P. abies*, *A. alba*, and *P. sylvestris* also had normal N and Ca concentrations, higher than normal P concentrations, and the K, Mg, Zn, and Mn concentrations were lower than recommended (Stefan et al. 1997) or typically found in the Carpathian Mountains (Mankovska et al., 2004). These general trends seen in the studied coniferous species were also determined for *F. sylvatica*, in which the N concentrations of 2.32–2.44% were typical for various European forests; however, P concentrations of ~0.3% were about two times higher than normal (Furst 2006), while concentrations of K, Mg, Zn, and Mn were lower (Bauer et al. 1997; Stefan et al. 1997) than in other Carpathian stands (Mankovska et al. 2004). These discrepancies between the study concentrations of nutrients and the recommended values for these

Table 6 Elemental ratio in *Picea abies* foliage in Bucegi Natural Park

Location	N/P (g g^{-1})	N/K (g g^{-1})	N/Mg (g g^{-1})	K/Ca (g g^{-1})	N/Mn (g g^{-1})
Timen-Grofi	4.8	9.1	24.6	0.62	967.0
Observator Urs	6.0	9.9	24.3	0.50	531.2
Salvamont Bran	4.9	12.7	25.6	0.32	378.5
Valea cu Brazi	4.4	9.4	23.4	0.31	1286.4
Bătrana	3.5	8.3	22.3	0.65	725.5
Podu cu Flori	3.3	8.6	22.3	0.47	241.7
Branduşi	4.2	10.2	22.9	0.50	326.3

species were also reflected in the nutritional ratios (Stefan et al. 1997; Mankovska et al. 2004).

Elemental foliar concentrations and ratios were similar for the compared species, which suggests that balanced nutrition resulted from cohabitation of trees in similar trophic and environmental conditions. The improper K/Ca ratio shows an abundance of calcium in substrate and of water stress at the foliar level. High differences between the N/Mn ratios in various locations could possibly be explained by high variability in various soluble forms of this mineral.

In general, several significant differences (p=0.05) were found among the nutrient mean concentrations at different locations (one-way ANOVA): Ca and Mn both for *P. abies* and *F. sylvatica*, and N, P, K, Zn, and Cu solely for *P. abies*. The cause of these differences may be a result of the distinct site conditions and stand parameters (structure, composition, age, yield class). In addition, the Pearson correlation analysis indicated a relatively high and significant correlation (p=0.05) between altitude and P concentration for both species (i.e., 0.760 for *P. abies* and 0.791 for *F. sylvatica*), and between altitude and N/P ratio, although negative (i.e., −0.873 for *P. abies* and −0.885 for *F. sylvatica*). Thus, at high altitude (over the upper vegetation limit) the health and growth of trees is expected to be reduced (Badea and Tanase 2004) due to the fact that N is less available, although P concentration is higher than in lower altitudes.

Soil condition

The soils of the Bucegi LTER sites are of the following types (according to the international WRB classification): dystric Cambisols—CMdy (Salvamont Bran, Observator Urs, Cariera-Lespezi, Branduşi), eutric Cambisols—CMeu (Timen-Grofi, Poiana Stanii, Dichiu), haplic Podzols—PZha (Podu cu Flori), entic Podzols—PZet (Bătrana), and rendzinic Phaeozems—PHrz (Valea cu Brazi).

The parent material on which these soils have developed is composed of typical Bucegi conglomerates specific to the mountainous area: micaceous sandstones, sericite–chlorite schists, limestone and limestone sandstones, conglomerate sandstones and micaschists.

The organic horizon is composed of three subhorizons, and their thickness depends on the effectiveness of the humification process. Thus, the litterfall subhorizon (OL) has a thickness between 0.8 and 2 cm,

Table 7 Average foliar elemental concentration in *Abies alba, Pinus sylvestris*, and *Fagus sylvatica* stands in Bucegi Natural Park

Species (Locations)	N (%g g^{-1})	P (%g g^{-1})	K (%g g^{-1})	Ca (%g g^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Na (mg kg^{-1})	Mg (mg kg^{-1})
Abies alba (Observator Urs)	1.31	0.25	0.17	0.53	15.1	8.3	21.4	235.4	613.8
Pinus sylvestris (Timen-Grofi)	1.82	0.27	0.15	0.23	11.5	12.2	16.2	170.1	514.5
Fagus sylvatica (Poiana Stanii)	2.44	0.30	0.12	0.38	21.3	7.0	14.1	156.5	655.1
Fagus sylvatica (Cariera-Lespezi)	2.32	0.29	0.14	0.26	37.1	7.4	17.7	159.5	527.6

Table 8 Elemental ratios in *Abies alba*, *Pinus sylvestris*, and *Fagus sylvatica* stands in Bucegi Natural Park

Species (Location)	N/P ($g\ g^{-1}$)	N/K ($g\ g^{-1}$)	N/Mg ($g\ g^{-1}$)	K/Ca ($g\ g^{-1}$)	N/Mn ($g\ g^{-1}$)
Abies alba (Observator Urs)	5.3	7.8	21.3	0.32	865.5
Pinus sylvestris (Timen-Grofi)	6.7	12.3	35.4	0.65	1586.1
Fagus sylvatica (Poiana Stanii)	8.1	20.1	37.3	0.32	1141.0
Fagus sylvatica (Cariera-Lespezi)	8.1	16.2	44.0	0.54	626.0

the fermentation subhorizon (OF) between 1.5 and 4 cm, and the humus subhorizon (OH) between 0.1 and 2 cm.

The rocky-gravel infill (5%–25%) appears on the soil profile, especially at 30–70 cm depth and the parent material (bedrock) is below 60 to 150 cm depth.

Soil texture was generally loam, sandy-loam, and loamy-sand. Structure is granular to subangular blocky, small-medium, or medium-large aggregation.

In mineral horizons, the soil is very high to high acid, whereas in the surface horizons, pH values increase with depth, becoming moderate or low acid. Only in the Dichiu site the soil is low alkaline in the first 40 cm and low acid between 40 and 125 cm depth.

In order to study the influence of atmospheric processes on soil properties, and the differences in soil chemical characteristics between sites, and especially their dominant species, a table was established (Table 9), where the soils were grouped based on the stand category that vegetates on them. Furthermore, this table comprises the main chemical elements that were analyzed on the organic horizons and on the standard depths framing the mineral horizons used in other projects (Biosoil, Futmon). It was ascertained that for each type of stand from the studied area (pure spruce stand, mixed beech-silver fir stands and pure beech stands), there is a common CMeu and CMdy soil type.

From the pH variation depicted in Table 10, it can be observed that the acidity grows from beech stands towards the spruce ones especially for the litter and in the first centimeter of the mineral soils (normally, the influence of the type of litter) but is relatively constant at higher depths. This fact demonstrates that the nature of the stand does not influence the pH at the depths >20 cm.

Thenceforth, in order to study the possible acidification of the soils from this area it is necessary to remove the influence of the type of stand (this is the reason why only the pure spruce stand and pure beech stands were taken into consideration because for the mixed stands the percentage of resinous/broad-leaved participation is important) and that of the type of soil (this is the reason why only the two soil types that appear in all the stand versions and only their mineral soil were taken into consideration). Thus, the values of the pH resulted from this method are presented in Table 11.

It can be ascertained that the pH decreases from the soil depth (where it can be influenced by the nature of the rock) towards the surface. This decrease can also be observed in the case of the first 10 cm from eutric Cambisols on pure beech stands, where the vegetation (not acid) does not influence the acidification. The decrease of these values (acidification), certifiable both for the soil types as well as for the stands, might be partially attributed to atmospheric deposition of S and N in precipitation and as dry deposition of NO_3^-, SO_4^{2-}, and NH_4^+ ions. This in turn could affect nutrient uptake and possibly contribute to the observed nutritional imbalances of the studied trees. We can make this observation without having information concerning the evolution of the pH in the same locations in different years.

Crown condition

Based on field assessments of the crown condition in the (LTER) sites in 2006–2009, the ranges of the proportion of damaged trees (defoliation classes 2–4) varied between 18.4% and 45.6% in 2006, between 11.4% and 47.5% in 2007, between 14.6% and 47.5% in 2008, and between 18.6% and 54.3% in 2009 (Table 12).

In the pure or relatively pure *P. abies* stands, the proportion of damaged trees increased in 2008 compared

Table 9 General table with the repartition of chemical properties on types of stands and standard depths

Stand type	Location	Soil type	Chemical properties	Organic and mineral fix depth (cm)						
				OL	OF	OH	0-10	10-20	20-40	>40
Pure spruce stands	Timen-Grofi	Eutric Cambisol (CMeu)	pH (CaCl2)	4.66	4.26	3.91	3.72	4.3	4.44	5.02
			organic C (g/kg)	240.4	187.86	93.07	47.33	12.06	7.77	7.54
			organic N (g/kg)	15.41	15.41	7.71	5.04	1.96	1.12	1.12
	Salvamont Bran	Dystric Cambisol (CMdy)	pH (CaCl2)	4.61	4.45	3.99	3.65	4.19	4.34	4.46
			organic C (g/kg)	247.34	190.94	66.97	60.5	28.19	21.29	6.73
			organic N (g/kg)	12.61	11.91	4.2	5.88	3.08	2.52	1.4
	Batrana	Entic Podzol (PZet)	pH (CaCl2)	4.67	4.33	3.37	3.09	3.34	3.71	4.33
			organic C (g/kg)	258.3	249.96	133.87	90.72	65.31	43.68	21.63
			organic N (g/kg)	11.91	16.1	11.2	7	3.92	2.52	1.12
	Podul cu Flori	Haplic Podzol (PZha)	pH (CaCl2)	4.83	4.43	3.52	2.99	3.27	3.7	4.01
			organic C (g/kg)	257.65	248.29	207.72	120.4	31.5	19.95	7.54
			organic N (g/kg)	12.61	15.41	16.8	8.68	2.52	2.24	1.4
	Brandusi	Dystric Cambisol (CMdy)	pH (CaCl2)	4.53	4.27	3.79	3.6	3.92	4.25	4.45
			organic C (g/kg)	253.28	240.06	198.47	149.1	34.22	17.69	7.85
			organic N (g/kg)	15.41	15.41	15.41	8.96	3.36	2.24	2.61
	Valea cu Brazi	Rendzinic Phaeozem (PHrz)	pH (CaCl2)	5.07	5.24	6.41	7.03	7.13	7.14	7.37
			organic C (g/kg)	244.58	191.54	72.54	44.02	42.92	36.77	17.46
			organic N (g/kg)	11.91	11.2	6.3	4.76	3.92	4.48	1.96
Mixed beech-silver fir stands	Dichiu	Eutric Cambisol (CMeu)	pH (CaCl2)	5.97	6.17	6.17	7.17	6.87	6.67	5.2
			organic C (g/kg)	247.72	167.27	167.27	25.87	10.56	6.55	3.25
			organic N (g/kg)	10.5	9.8	9.8	2.52	1.68	1.12	0.47
	Observator Urs	Dystric Cambisol (CMdy)	pH (CaCl2)	4.94	4.82	3.85	3.67	4.03	4.23	4.34
			organic C (g/kg)	240.74	214.78	96.24	63.57	30.28	4.58	3.13
			organic N (g/kg)	12.61	13.31	7.71	3.92	2.24	0.84	0.65
Beech stands	Poiana Stanii	Eutric Cambisol (CMeu)	pH (CaCl2)	5.94	5.63	5	5	5.14	5.34	5.93
			organic C (g/kg)	253.42	206.86	102.67	41.39	11.89	4.29	4.26
			organic N (g/kg)	14	15.41	9.8	4.34	1.68	0.84	0.84
	Cariera-Lespezi	Dystric Cambisol (CMdy)	pH (CaCl2)	5.77	5.32	4.48	4.09	4.18	4.3	4.43
			organic C (g/kg)	252.71	253.04	152.06	52.26	32.8	19.37	8.93
			organic N (g/kg)	11.2	16.8	13.31	5.6	3.64	2.52	1.68

to 2007 at the Timen-Grofi, Valea cu Brazi, Branduşi, Podu cu Flori sites, but approximately the same values were maintained in Salvamont Bran and Bătrana. The same increasing trend was observed in the case of *F. sylvatica* at the Poiana Stanii and Cariera-Lespezi sites, an exception being noticed in Dichiu and Observator Urs, where the proportion of damaged trees remained the same or significantly reduced, respectively. In this last case, *F. sylvatica* is less represented in the mixture with *A. alba* and other species.

In 2009 at the Branduşi site, a very significant increase in the percentage of damaged trees was noticed (54.3%), which was caused by windfall produced at the end of 2008. The density of the stand was very much reduced and foliar insect (*Lymantria monacha*) and bark beetle (*Ips* sp.) populations developed. At whole network level, in the same year (2009), as compared to 2008, at *F. sylvatica*, a decrease of a percentage of damaged trees was recorded (Table 12).

Table 10 Influence of stand type on chemical characteristics of soils

Organic and mineral fix depth (cm)	Stand type	pH ($CaCl_2$)	organic C (g/kg)	organic N (g/kg)
Eutric Cambisols (CMeu)				
OL	Pure spruce stands	4.66	240.4	15.41
	Mixed beech-silver fir stands	5.97	247.72	10.5
	Pure beech stands	5.94	253.42	14
OF	Pure spruce stands	4.26	187.86	15.41
	Mixed beech-silver fir stands	6.17	167.27	9.8
	Pure beech stands	5.63	206.86	15.41
OH	Pure spruce stands	3.91	93.07	7.71
	Mixed beech-silver fir stands	6.17	167.27	9.8
	Pure beech stands	5	102.67	9.8
0–10	Pure spruce stands	3.72	47.33	5.04
	Mixed beech-silver fir stands	7.17	25.87	2.52
	Pure beech stands	5	41.39	4.34
10–20	Pure spruce stands	4.3	12.06	1.96
	Mixed beech-silver fir stands	6.87	10.56	1.68
	Pure beech stands	5.14	11.89	1.68
20–40	Pure spruce stands	4.44	7.77	1.12
	Mixed beech-silver fir stands	6.67	6.55	1.12
	Pure beech stands	5.34	4.29	0.84
>40	Pure spruce stands	5.02	7.54	1.12
	Mixed beech-silver fir stands	5.2	3.25	0.47
	Pure beech stands	5.93	4.26	0.84
Dystric Cambisols (CMdy)				
OL	Pure spruce stands	4.57	250.31	14.01
	Mixed beech-silver fir stands	4.94	240.74	12.61
	Pure beech stands	5.77	252.71	11.2
OF	Pure spruce stands	4.36	215.5	13.66
	Mixed beech-silver fir stands	4.82	214.78	13.31
	Pure beech stands	5.32	253.04	16.8
OH	Pure spruce stands	3.89	132.72	9.8
	Mixed beech-silver fir stands	3.85	96.24	7.71
	Pure beech stands	4.48	152.06	13.31
0–10	Pure spruce stands	3.63	104.8	7.42
	Mixed beech-silver fir stands	3.67	63.57	3.92
	Pure beech stands	4.09	52.26	5.6
10–20	Pure spruce stands	4.06	31.2	3.22
	Mixed beech-silver fir stands	4.03	30.28	2.24
	Pure beech stands	4.18	32.8	3.64
20–40	Pure spruce stands	4.3	19.49	2.38
	Mixed beech-silver fir stands	4.23	4.58	0.84
	Pure beech stands	4.3	19.37	2.52
>40	Pure spruce stands	4.46	7.29	2
	Mixed beech-silver fir stands	4.34	3.13	0.65
	Pure beech stands	4.43	8.93	1.68

Table 11 pH variation of the soils from CMeu and CMdy categories based on depth and type of stand

Depth (cm)	Pure spruce stands		Pure beech stands	
	Eutric Cambisols (CMeu)	Dystric Cambisols (CMdy)	Eutric Cambisols (CMeu)	Dystric Cambisols (CMdy)
0–10	3.72	3.63	5.0	4.09
10–20	4.3	4.06	5.14	4.18
20–40	4.44	4.3	5.34	4.3
>40	5.02	4.46	5.93	4.43

Over the entire network for all species, the proportion of damaged trees was slightly higher in 2008 (33.9%) compared to the previous years when the values were approximately the same (30.6% in 2006 and 30.5% in 2007) and with 2009 when an improved forest health was found (percent of damaged trees was 28.0%).

Individually, *P. abies* was the least affected species, showing relative stability in the research period, with the proportion of damaged trees between 27.9% in 2007 and 31.8% in 2008 (Table 12). *A. alba* and *F. sylvatica* showed significant temporal fluctuations in the proportion of damaged trees: between 27.7% in 2009 and 41.5% in 2007 for *A. alba* and between 16.6% in 2009 and 36.6% in 2008 for *F. sylvatica*.

Evaluation of crown condition during 2006–2009 showed that the Bucegi Mountains forests were severely damaged with generally more than 20% of trees assessed at classes 2–4 for all the species (Badea et al. 2004). *F. sylvatica* was the healthiest species, followed by *P. abies*, which showed a relative stability in the study period. *P. abies* was least affected at high altitudes (over 1,500 m) where the effects of high temperature and excessive drought in the summer seasons of 2007 and 2008 were weaker than for the lower altitude species (*F. sylvatica* and *A. alba*) growing at their upper natural vegetation limit (higher than 1,000–1,200 m).

The significant fluctuation of health status recorded for *F. sylvatica* and *A. alba* may be explained by the effects of changing weather conditions, especially for *A. alba*, which is very susceptible to excessive drought and high temperatures due to its specific ecological conditions (Sofletea and Curtu 2001). These species

Table 12 Proportion of healthy trees (defoliation classes 0–1) and damaged trees (defoliation classes 2–4) for all species in the Bucegi forests in 2006–2009

Site	Main species	Group of defoliation classes 2–4 (damaged trees)			
		2006	2007	2008	2009
1. Salvamont Bran	*Picea abies*	28.9	23.5	23.0	18.6
2. Observator Urs	*Picea abies, Fagus sylvatica, Abies alba*	18.4	22.7	15.9	18.9
3. Timen-Grofi	*Picea abies*	31.6	31.7	34.4	39.3
4. Poiana Stanii	*Fagus sylvatica*	19.0	14.3	26.7	14.3
5. Valea cu Brazi	*Picea abies*	34.7	35.6	43.4	34.6
6. Dichiu	*Fagus sylvatica*	31.4	47.5	46.9	23.2
7. Brânduşi	*Picea abies*	24.0	11.4	25.0	54.3
8. Cariera-Lespezi	*Fagus sylvatica*	29.7	40.3	42.7	23.6
9. Podu cu Flori	*Picea abies*	45.6	41.1	47.5	29.6
10. Bătrana	*Picea abies*	22.3	14.0	14.6	17.6
Whole network	*Picea abies*	30.7	27.9	31.8	30.1
	Abies alba	33.3	41.5	31.8	27.7
	Fagus sylvatica	23.9	31.2	36.6	16.6
	All species	30.6	30.5	33.9	28.0

responded quickly to the amount of precipitations during the previous year's autumn and the spring of the same year (Badea 1998). Compared with the results on forest health status in the Romanian Carpathian Mountains 10 years ago (Badea et al. 2004), when the percentage of damaged trees for all species varied between 31.4% (1997) and 32.3% (1998), forest health in the Bucegi Mountains remained approximately the same (30.6% in 2006, 30.5% in 2007, 33.9% in 2008 and 28.0% in 2009). Also, compared with forest health status recorded in the Retezat Mountains in 2000–2002 and 2009, the forests of the Bucegi Mountains are more damaged (Badea et al. 2011).

The accuracy of these results is mainly influenced by the number of plots where tree condition was assessed. Thus, for forest health status in the Bucegi Mountains, the representative error ($e_{\%}$) is 17.2%, for $\alpha=0.05$. Nevertheless, the information related to tree condition is very useful in finding a trend in the dynamics of forest health at the regional level. Additionally, these results may be used at the plot (site) level to evaluate changes of various factors (air pollution, climatic parameters, precipitation chemistry) affecting forest health status and growth of trees and forest stands.

High frequency of acidic throughfall had a significant negative effect on crown condition (Pearson correlation coefficient $r=0.662$; $\alpha<0.01$). Similarly, high frequency of alkaline throughfall ($r=0.644$; $\alpha<0.01$), and high Ca concentrations ($r=0.729$; $\alpha<0.05$) also had significant effects on crown defoliation. In addition, the high frequency of acidic rain can affect soil chemistry with negative influence on the physiological processes of trees and forest stands (Edzards et al. 1997; Bytnerowicz et al. 2005).

Regarding the influence of soil solution pH on crown condition, a negative correlation was found that significantly increased with depth. Thus, up to 20 cm, Pearson correlation coefficient "r" has values of −0.687 (0–10 cm) and −0.692 (11–20 cm) with a significance level $\alpha<0.05$ and for higher depths $r=-0.742$ (21–40 cm) and $r=-0.819$ (41–60 cm) for $\alpha<0.01$. Considering that at the soil depths of 46–60-cm tree roots are characterized by high physiological activity, increasing acidity may have pronounced effects on tree health.

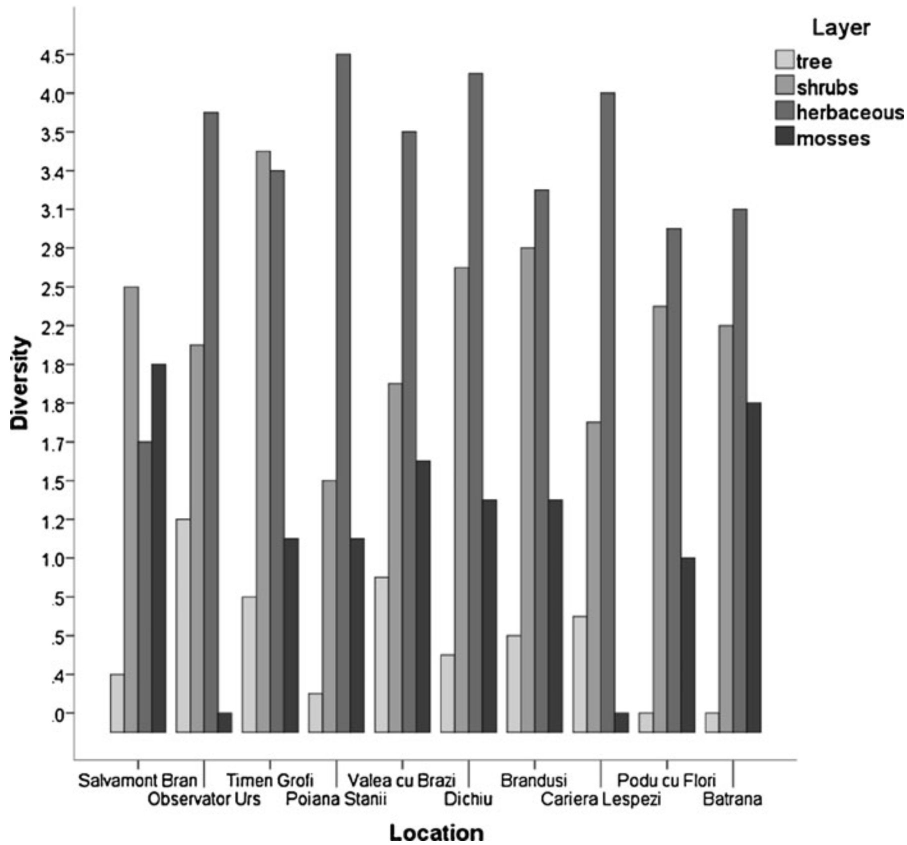
Forest health status described as mean tree crown defoliation percent within selected forest stands was insignificantly correlated with the main nutrients and with their ionic ratios. Even though the correlations were not statistically significant ($\alpha>0.05$), correlation coefficient values were positive for P, K, Ca, Mn and negative for N and for the ionic ratios (N/P, N/K, K/Ca, and N/Mn). This indicates that at higher N levels and balanced nutrition the mean defoliation and health of forest stands improve. However, higher than optimal P and Ca concentrations and a simultaneous lower than normal K, Mg, and Mn concentrations could also be responsible for worsening tree health manifested by higher defoliation.

In general, as stated above, the O_3 concentrations were too low to cause negative effects on forest health, and thus no specific O_3 injury symptoms were detected on foliage of the main tree species in the Bucegi Mountains. However, it may be expected that acidic rain events will continue to contribute to forest soil acidification with a negative effect on forest health. Also, an increase in air pollutant levels, especially the predicted increase of background O_3 levels (Fowler et al. 1999) combined with changing and variable climates, such as severe drought and high temperatures Bytnerowicz et al. (2008b), could have even more pronounced effects on forest health in the Bucegi Mountains.

Biodiversity

The composition of studied forest stands varied from the pure *P. abies* or *F. sylvatica* stands to the mixed forests of *P. abies* and *F. sylvatica*, or *F. sylvatica* with *A. alba* and other conifers (*Larix decidua* and *Picea* sp.) and broadleaves species (*Acer pseudoplatanus*, *Betula pendula*, *Sorbus aucuparia*). The number of plant species varied from 33 to 47 per studied forest stand. Mixed and pure *F. sylvatica* forests were richer both in species number and their value. Diameter and height of trees varied from site to site according to the stand type, its structure to the local environmental, and vegetation conditions. Based on inventory of species in each layer (A—trees, B—shrubs, C—herbaceous plants, D—mosses), six major plant communities were identified (Badea et al. 2011). Also, for each level (A, B, C, D), the Shannon–Wiener diversity index and Shannon evenness was determined. According to the values of this index, the lowest diversity (<2) was recorded at the tree level (Fig. 6) followed by moss layer (2–3). A high diversity was observed within the herbaceous layer (>3). A good development of herb diversity was allowed by the vertical distribution and

Fig. 6 Shannon–Wiener diversity of different vegetation layers



coverage of tree layer (Fig. 7). Vascular plant communities were characterized by a high diversity and evenness (Fig. 8). Because of its essential contribution to forest ecosystems functioning, ground vegetation structure and composition is an expression of the relationship between tree layers and environmental and vegetation conditions (Vadineanu et al. 2008).

A significant amount of aboveground biomass and nutrients are contained in the ground vegetation layer's richness and productivity (Bytnerowicz et al. 2005). High diversity and evenness was observed within the herbaceous layer, indicating that biodiversity of the vascular plant communities of the studied forest sites was substantial. All the vegetation biodiversity components of the forest ecosystems were specific to the stand type's structures and local climate conditions. Furthermore, there was no evidence of accelerated environmental modifications and significant reduction of biodiversity. Generally, plant communities play an important role as indicators of local environmental and vegetation conditions (microclimate, soil acidity, nitrogen availability) of the forest types and site types (Donita et al. 2005).

Growth

The entire LTER network of the Bucegi Mountains with an average altitude of 1,300 m had a yield class of 2.8 (medium productivity) and an average age of 90 years, which are typical to these areas for all species. The average annual volume growth over the 1996–2005 period of review was 11.1 m^3 $year^{-1}$ ha^{-1}. For the main species, the annual volume growth for *P. abies* was 14.3 m^3 $year^{-1}$ ha^{-1}, for *F. sylvatica* 9.5 m^3 $year^{-1}$ ha^{-1}, and for *A. alba* 5.3 $m^3 year^{-1}$ ha^{-1} (Table 13). The highest values of the average annual volume growth were recorded in pure stands of *P. abies* of high productivity (Salvamont Bran and Timen-Grofi) and young overstocked stands without silvicultural interventions (thinnings; Valea cu Brazi).

In cases where the main species representation was low in the composition of mixed forest stands, the annual volume growth was the lowest *(F. sylvatica* in Observator Urs, *P. abies* in Cariera-Lespezi, and *A. alba* in Dichiu). In addition, *F. sylvatica* recorded a low relative annual volume growth (7.0 m^3 $year^{-1}$ ha^{-1}) in

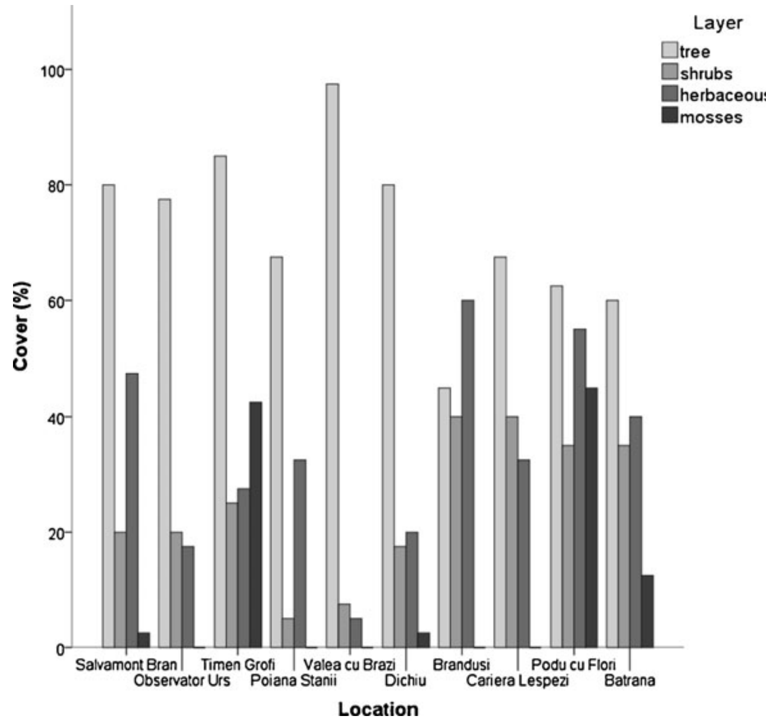


Fig. 7 Cover distribution of different vegetation layers

a pure >140-year-old forest stand (Poiana Stanii), located above the optimal altitudinal limit (above 1,300 m). In this case, age, altitude, and vegetation conditions are the main limiting growth factors. However, *F. sylvatica*

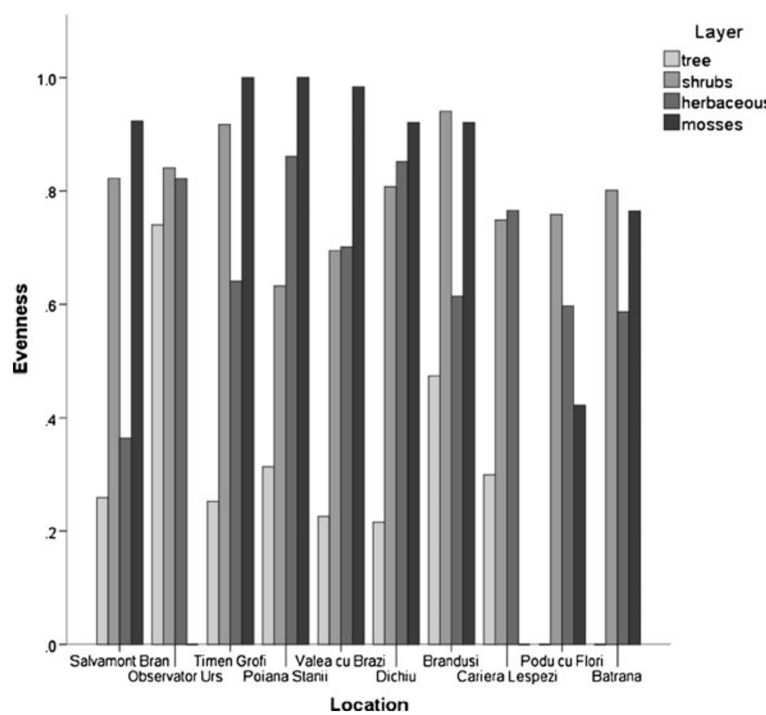


Fig. 8 Evenness of different vegetation layers

recorded higher values of annual volume growth (Dichiu and Cariera-Lespezi) in mixed stands with *A. alba* or *P. abies* as secondary species. In the mixed stands of *F. sylvatica* with conifers, the average annual volume growth per ha was between 11.7 m^3 $year^{-1}$ ha^{-1} (Observator Urs) and 18.2 $m^3 year^{-1}$ ha^{-1} (Cariera-Lespezi), confirming the structural stability and growth efficiency of these mixed stands in the mountain region (Table 13).

The annual volume was determined for defoliation group classes 0–1 and 2–4, both for individual sites and for the entire research network within the Bucegi Mountains (Table 13). Results are quite typical (Badea and Neagu 2011), both for each site and for the entire study area, demonstrating significant differences between real (I_v) and normal (I_v^1) annual volume growth per hectare. These differences (Δi_v) may be explained in terms of annual volume growth losses recorded by forest stands in real life conditions (having in their composition both healthy trees of defoliation classes 0–1 and damaged trees of defoliation classes 2–4), given the normal (theoretical) conditions (having in composition only healthy trees). These volume growth losses (%) are different from site to site and dependent on forest stand composition, age, productivity, altitude, and especially the proportion of damaged trees in each stand.

At the whole study area level, for all species, the annual volume growth losses per hectare ($\Delta i_{v\%}$) was 25.4% (Table 13) and well reflect the influence of tree condition on the bioaccumulation processes inside the forest ecosystems. Such information may be considered important for establishing the dynamics of growing stock and the allowable cutting volume. Additionally, it might be taken into consideration as a main indicator for management programs from a perspective of management and control of air pollution, pathogens, pests, and anthropogenic activities.

The variation of annual average ring width showed the typical downward increment trend of the damaged trees (defoliation >25%) compared with the healthy ones (Bytnerowicz et al. 2005; Badea et al. 2011). The average annual increment was significantly lower for damaged trees compared to the healthy trees in all sites (Fig. 9) and for each main species at the entire study network level (Fig. 10).

Table 13 Volume growth of main species and groups of defoliation classes (0–1 and 2–4) in LTER sites in Bucegi Natural Park

Location	Species	Average annual volume growth per year and per ha (m^3 $year^{-1}$ ha^{-1})				Volume growth osses	
		Total real volume growth per species	Real volume growth per species		Total normal volume growth per species	Δiv	Δiv%
			0–1	2–4		$m^3 year^{-1}$ ha^{-1}	%
Salvamont Bran	*Picea abies*	20.3	16.8	3.5	28.3	8.1	28.6
Observator Urs	*Fagus sylvatica*	5.1	4.3	0.8	5.8	0.7	12.5
	Abies alba	5.6	5.1	0.5	6.5	0.8	13.0
Timen-Grofi	*Picea abies*	27.4	20.0	7.4	39.1	11.8	30.0
Poiana Stanii	*Fagus sylvatica*	7.0	6.5	0.5	9.1	2.1	23.4
Valea cu Brazi	*Picea abies*	16.9	12.0	4.9	24.8	7.9	31.9
Dichiu	*Fagus sylvatica*	9.4	6.1	3.3	10.6	1.2	11.4
	Abies alba	4.9	2.8	2.1	6.3	1.4	22.3
Brandusi	*Picea abies*	13.2	9.9	3.3	17.1	3.9	23.0
Cariera-Lespezi	*Fagus sylvatica*	16.4	13.5	2.9	21.9	5.5	25.2
	Picea abies	1.8	1.4	0.4	2.7	0.9	34.3
Podu cu Flori	*Picea abies*	12.8	7.6	5.2	19.8	7.0	35.5
Batrana	*Picea abies*	7.7	6.1	1.6	8.6	0.9	10.6
Average	*Picea abies*	14.3	10.5	3.7	20.1	5.8	28.9
	Abies alba	5.3	4.0	1.3	6.4	1.1	17.6
	Fagus sylvatica	9.5	7.6	1.9	11.8	2.4	20.2
	All species	11.0	8.3	2.8	14.7	3.7	25.4

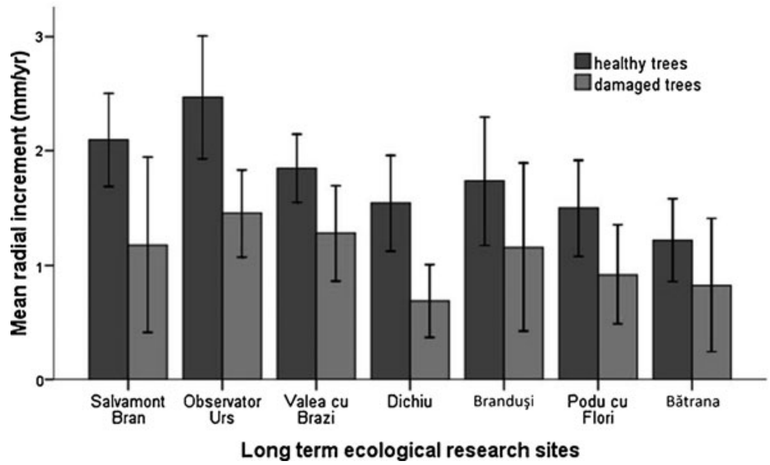


Fig. 9 Mean radial increment (*bars*) for the *Picea abies*, *Abies alba*, and *Fagus sylvatica* by defoliation group classes (0–1 and 2–3) for all studied sites in the Bucegi Mountains, with 95% confidence intervals (*lines*)

For the entire LTER network, the declining auxological (growth) tendency of the average annual radial increment for the damaged trees is clear (defoliation group classes 2–3), starting from a certain defining moment that denotes the "no turning back" point of the declining process, caused by a combination of factors such as acidic precipitation, air pollution, drought, nutritional imbalances, and other abiotic and biotic predisposing or triggering factors.

Although the correlation between measured air pollutant concentrations (O_3 and NH_3) and annual volume growth of studied stands (Badea et al. 2011) was not significant ($\alpha > 0.05$), the Pearson correlation coefficients had negative values ($r = -0.382$ for O_3 and $r = -0.273$ for NH_3, respectively). However, at higher air pollutants levels, a significant reduction in volume growth can appear (UNECE 2004). This is a hypothesis to be studied in future research, in natural ambient conditions (Manning 2005).

Conclusions

Based upon the obtained results and analysis, the Bucegi Mts. have relatively good air quality, although

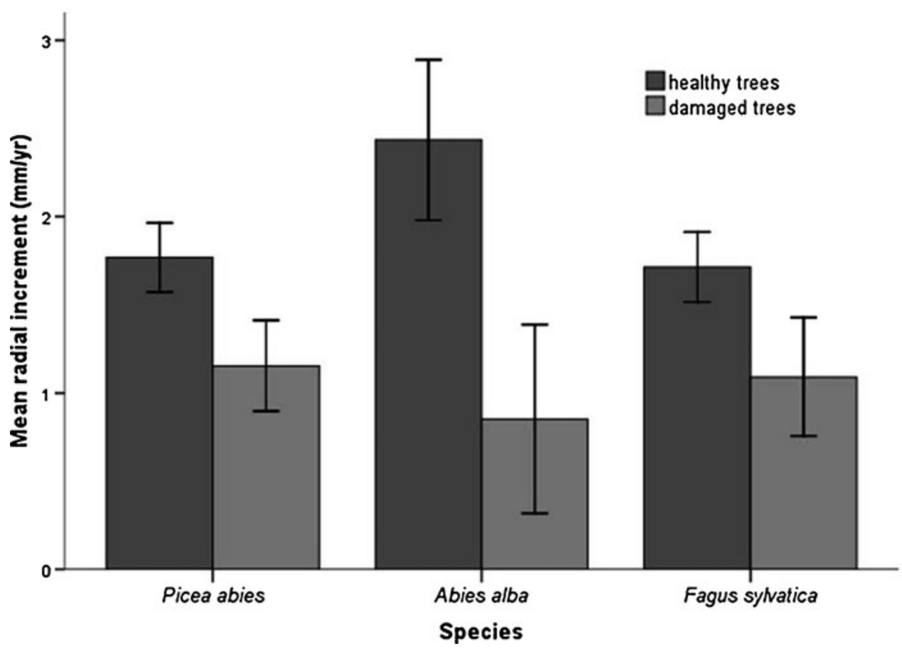


Fig. 10 Mean radial increment (*bars*) for main species by defoliation group classes (0–1 and 2–3) in the Bucegi Mountains, with 95% confidence intervals (*lines*)

in some cases, slightly high ambient O_3 and NH_3 concentrations were found.

Spatial and temporal ambient O_3 concentrations patterns are distinct, and for that manner, the ozone concentration variation could be explained by altitude up to 50%, and by mean temperature up to 20%, for each exposure period during the 2006–2009 growing seasons.

Bulk precipitation, throughfall, and soil solution were acidic in most of the studied sites. Concentrations of acidic ions (NO^-, SO_4^{2-}, NH_4^+) were below their critical limits, but could have significant long-term cumulative effects on soils and forest vegetation, especially in the context of changing climate.

The nutritional status of trees was imbalanced with higher than normal foliar concentrations of P and Ca and lower than typical concentrations of K, Mg, and Mn in all species.

There were no indications of decreased biodiversity of the forest ecosystems representative for Bucegi Natural Park. The studied plots were rich in floristically important species and had distribution of vegetation layers in accordance with their geological and ecological characteristics.

In general, forest health in the Bucegi Mountains was moderately affected. While O_3 and NH_3 had no direct effect on forest health and no specific foliar O_3-injury symptoms were detected, these pollutants together with other stressors could contribute to integrated negative stress.

Both high frequencies of acid and alkaline precipitation had significant effects on tree crown defoliation. Increased acidity of soil solution in the 40–60 cm soil layer, where root physiological activity is high, could affect nutrient uptake, tree health, and crown condition.

In general, the health of Bucegi forests was similar to the other Carpathians regions. Damaged trees grew less than healthy trees (crown defoliation ≤25%), and the differences between their mean annual volume growth was about 25%.

Acknowledgments We acknowledge financial support from the Romanian Research Agency's Excellence Research Program, in the framework of the project "Long-term effects of air pollution on selected forest ecosystems in the Bucegi Natural Park–EPAEFOR," which is an ongoing and fruitful consortium collaboration between the Forest Research and Management Institute (ICAS), USDA Forest Service, Transylvania University, Bucharest University, and National Forest Administration (Romsilva). Since 2010, this research has been conducted with the support of the European Commission and the Romanian National Forest Administration (Romsilva), under the LIFE+ program (EnvEurope project). The authors thank Ms. Laurie Dunne for technical editing.

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