doi: 10.17221/881/2014-PSE

Environmental impact of the Al smelter on physiology and macronutrient contents in plants and Cambisols

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ABSTRACT

At present, a serious problem is the loss of soil nutrients in forest ecosystems with acidic atmospheric deposition and heavy metal contamination, which can have negative impact on plant growth. The objective of the research was to verify, whether different distance (1.5 and 18 km) from Al smelter Žiar nad Hronom (Slovak Republic) affects physiology and macronutrient contents (Ca, Mg, K, Na) in plant leaves and Cambisols of the nudal beech forests in Slovenské stredohorie Mts. In the surface of humus horizons significantly lower the amount of Ca_{tot} was found close to the smelter (stress stand); in Aoq soil horizons up to 60–76% less Na_{tot}, Mg_{tot} and Ca_{tot} was accumulated compared to control stand. Available forms of soil macronutrients were higher in the control stand and compared with stress stand, differences were significant for Ca and Mg. In plant leaves somewhat higher macronutrient contents were found in stress stand, with the exception of Ca. In relation to the physiological characteristics environmental impact of Al smelter significantly influenced photosynthesis of beech, chlorophyll fluorescence parameter of both indicator species and calorific values of sedges in the vicinity of 1.5 km from the emission source.

Keywords: anthropogenic pollutants; acidification; leaching; immissions; physiological status

The impact of anthropogenic pollutants to forest ecosystems is still actual problem in relation to the acidification of environment. The origin of acidic components is mainly in emissions of CO, SO_2, NO_x entering the atmosphere. Acid deposition adds hydrogen ions, which displace important soil nutrients in a process called leaching. Acidic soil environment can have a negative impact on plant growth due to the deterioration of chemical, physical and biological properties of soils (Von Uexküll and Mutert 1995). Increased atmospheric CO_2 concentration alters enzymes involved in nitrogen metabolism, causing premature senescence of plants (De la Mata et al. 2013). Many studies confirm that Al smelting is a result of the pollutants emitted into the atmosphere (Vike 2005, Wannaz et al. 2012). Low concentrations of Mn, Ca and Mg in the leaves of plant species and in the organic layer of soil near a smelter in Norway were recorded by Løbersli and Steinnes (1988). Fritze et al. (1989) reported a clear decreasing gradient in exchangeable Ca, Mg, K and Mn concentrations in the organic layer with decreasing distance to the smelter at Harjavalta. Decline in soil organic matter and available nutrients indicate the serious facts on evaluation and extension of soil degradation processes during the last period in Slovak Republic (Kobza and Gašová 2014). In Žiar nad Hronom territory (Central Slovak Republic) a greater environmental pollution occurred in the past (F, Hg, As, Al). The introduction of new technology of Al production in 1996 represented a decline in emissions of fluorine from 319.5 t to 91.5 t, but emissions of CO, SO_2, NO_x substantially in-

Supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and Slovak Academy of Science, Grant No. VEGA 2/0027/13 and by the Scientific Grant Agency of the Ministry of Education, Youth and Sports of the Czech Republic, S grant.

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creased as well (emissions of CO from 959.6 t in 1995 on 11 171.4 t in 1996). Emission of pollutants for the year 2010 represented (t/year): 47.1 particulate matters, 1309.9 sulphur dioxide, 519.6 oxides of nitrogen, 35.5 of total organic carbon and 13 472.2 of carbon monoxide (http://www.air.sk/). CO in 2010 compared to 1996 increased by 17.1%. At present Al smelter Žiar nad Hronom is among the top 20 polluters in Slovak Republic and its share of pollutant emissions for the year 2010 represented: 2.29% – particulate matters, 2.10% – SO_2, 1.49% – NO_x, 10.37% – CO (Report 2010).

Pollutants are brought into soil by means of atmospheric precipitation, changing its chemistry, consequently there is a deficiency of nutrients due to an increased leaching of bases from the sorption complex of soil, which weakens plants. Therefore, the objective of the study was to evaluate the environmental impact of Al smelter on (1) physiological status, (2) calorific values and (3) macronutrient content (Ca, Mg, K, Na) in plant leaves and Cambisols of nudal beech forests.

MATERIAL AND METHODS

Study sites. The study period covered the years 2012–2014. The research was performed on two monitoring plots situated at different distances from the emission source – Al smelter Žiar nad Hronom. Monitoring plot (MP) Žiar nad Hronon (stress stand) is located at a distance of 1.5 km from the emission source; Ecological Experimental Station (EES) Kremnické vrchy Mts (control stand), 18 km from the emission source. Description of the nudal beech forests and climatic characteristics of the study sites are presented in Table 1. There is mono-dominating *Fagus sylvatica* L. species. In the synusia of undergrowth of both phytocoenoses, mesotrophic herb species dominate, which is characteristic for forest type group *Fagetum pauper* (Zlatník 1976).

Soil analysis. Soil samples were obtained by random sampling on an area 400 m^2 within each monitoring plots. Surface humus samples (Oo) were samped from the plot 33.33 × 33.33 cm in triplicate from each studied stand. Organic-mineral soil samples were taken from 0–10 cm thick Aoq horizon. Values of soil reaction were determined potentiometrically by a digital pH meter Inolab pH 720 (Weilheim, Germany). Concentrations of Ca_{tot}, Mg_{tot}, K_{tot}, Na_{tot} in soil samples were extracted with *aqua regia* using atomic absorption spectrometry (GBC SensAA, Braeside, Australia). N_{tot} and C_{tot} content was determined by NCS analyzer type FLASH 1112 (Hanau, Germany). Available forms of macronutrients were extracted according to the Mehlich-2 (AES-ICP, LECO ICP-3000).

Analysis of plant species. On monitoring plots (400 m^2), leaves of beech (from the bottom third of the tree crown) and sedges were sampled in the first half of July 2012. The gas exchange – rate of

Table 1. Description of the nudal beech forests

Monitoring plot		MP Žiar nad Hronom	EES Kremnické vrchy Mts.
Emission source (km)		1.5	18.0
Geographical coordinates		48°32'N, 18°51'E	48°38'N, 19°04'E
Altitude (m)		450	470
Climatic region[1]		moderately warm (M)	
Climatic subregion[1]		moderately warm, moderately humid, hilly land or highlands (M3) July ≥ 6°C, summer days < 50, moisture index Iz = 0–60	
Mean annual precipitation totals (mm)[1]		700–800	700–800
Mean annual air temperature (°C)[1]		7–8	6–7
Stand age		90	110
Parent rock		rhyolitic tuff, tuffite	andesite tuffaceous agglomerates
Soil subtype		Stagnic Cambisol	Andic Cambisol
0–10 cm	pH_{H_2O}	4.6–4.7	5.8–6.3
	C/N	14–19	9–15

[1]according to Miklós (2002). MP – monitoring plot; EES – ecological experimental station

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photosynthesis (P_n), rate of transpiration (E), stomatal conductance (g_s) and the intercellular CO_2 concentration (c_i) were measured on the upper surface of leaves (the middle part of the leaf blade) *in situ* using the portable gas exchange system LCpro+ (ADC BioScientific Ltd., Hoddesdon, UK). Measurement time was set according to Tucci et al. (2010). The physiological characteristics were measured under adjusted light and temperature conditions, the irradiance was 650 μmol/m^2/s of photosynthetically active radiation, the temperature in the measurement chamber was 25°C, the CO_2 concentration was 420 ± 35 vpm (μmol/mol), the air flow rate was 205 ± 30 μmol/s and the duration of the measurement of each sample was 20 min after the establishment of steady-state conditions inside the measurement chamber. The value of VSD (vapour pressure deficit) was 0.85 ± 0.15 kPa. The minimum Chl fluorescence (F0) and the maximum Chl fluorescence (F_m) were also measured *in situ* with the portable 1 Chl fluorometer ADC:OSI 1 FL (ADC BioScientific Ltd., Hoddesdon, UK) with 1 s excitation pulse (660 nm) and saturation intensity 3000 μmol/m^2/s after 20 min dark adaptation of the leaves. The maximum quantum efficiency of photosystem II (PS II) was calculated according to Genty et al. (1989). The efficiency of excitation capture by open PS II reaction centres (F_v/F_m) can routinely be used to estimate changes in the quantum efficiency of non-cyclic electron transport. Maximum PS II photochemical efficiency (F_v/F_m) was evaluated with the measurement of gas exchange simultaneously.

Plant samples were dried at 85°C for 48 h and homogenised with a Fritsch planetary micro mill (< 0.001 mm). The energy value in phytomass (J/g of dry matter) was determined using an adiabatic calorimeter IKA C-4000 (software C-402, Heitersheim, Germany, DIN 51900). Ash content was determined gravimetrically at 500°C. Concentrations of Ca_{tot}, Mg_{tot}, K_{tot}, Na_{tot} were extracted with *aqua regia* using atomic absorption spectrometry (GBC SensAA, Braeside, Australia).

Data analysis. Analyses were made with the use of a statistics program Statistica 9 software (Tulsa, USA) and the variability of measured characteristics between monitoring plots was tested by ANOVA model and Fisher-*LSD* test.

RESULTS AND DISCUSSION

Soil analysis. Soil reaction of Cambisols on studied plots is acidic to slightly acidic (Table 1) and with increasing distance from the emission source it is increased (from pH_{H2O} values 4.6–4.7 to 5.8–6.3). In soil horizons of the control stand (EES Kremnické vrchy Mts) the values of C/N ratio are lower (9–15) and closer to the source of emissions (MP Žiar nad Hronom) they increase to the value 14–19. The content of total macronutrients in the surface humus of beech stands was relatively fluctuated. The least varied the content of Mg_{tot} (*CV* 7.6%), the most the content of Ca_{tot} (*CV* 41.6%), both in the stress stand. In the surface of humus horizon a higher amount Ca_{tot} was found in the control stand and compared with the stress stand, the difference was significant (ANOVA: $F_{(1, 13)}$ = 19.329, P = 0.0007) (Figure 1). Content of Mg_{tot} and K_{tot} was higher closer to the smelter and only K_{tot} value differed significantly from value in the control stand (ANOVA: $F_{(1, 13)}$ =

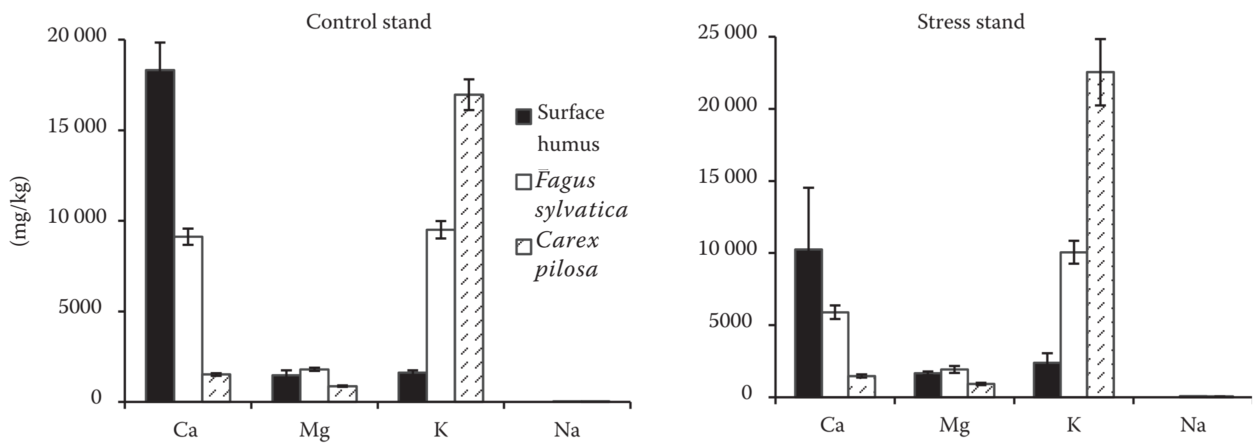

Figure 1. Macronutrient contents in surface humus and plant leaves of the beech stands. Data are means ± SE

doi: 10.17221/881/2014-PSE

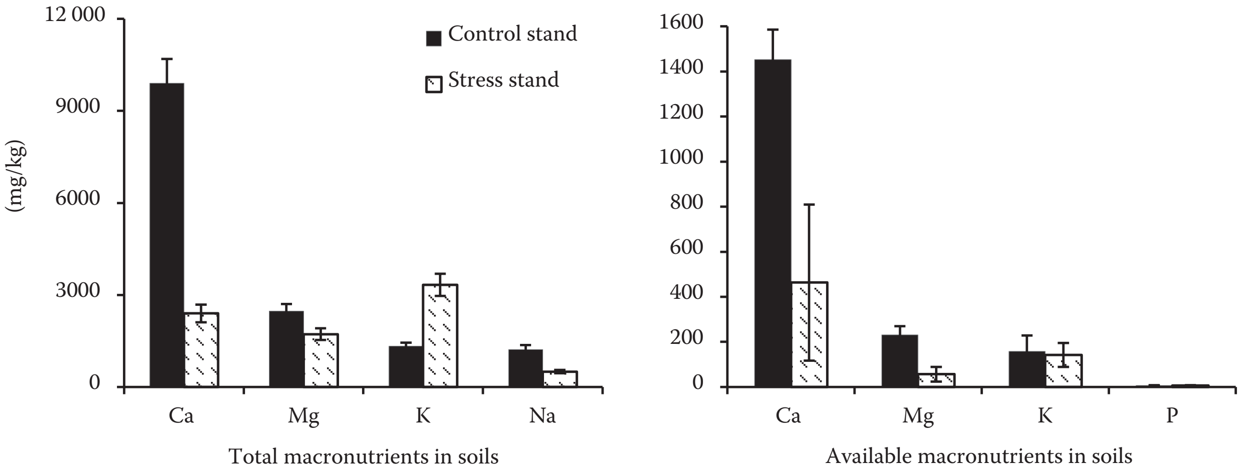

Figure 2. Macronutrient contents in organo-mineral soil horizonts of the beech stands. Data are means ± SE

8.480, P = 0.0121). In Aoq soil horizon more of total Ca_{tot}, Mg_{tot} and Na_{tot} were accumulated in the control stand (Figure 2). In the stress stand Ca_{tot} value in soil reached only approximately 24%, Mg_{tot} 30% and Na_{tot} 40% from values in the control stand. On the other hand, approximately 60% more K_{tot} was accumulated in Cambisol on plot with high immission load. Higher contents of available macronutrients were recorded in Aoq soil horizons of the control stand and compared with stress stand difference was significant for Ca (ANOVA: $F_{(1, 4)}$ = 21.325, P = 0.0099) and Mg (ANOVA: $F_{(1, 13)}$ = 35.795, P = 0.0039). Variability of compared files was somewhat higher in beech stand close to the smelter (Figure 2).

The results show that Cambisol in the control stand contained higher concentrations of macronutrients. Up to 76% less Ca was accumulated in Cambisol close to the smelter. Washout of Ca from the soil may be accelerated especially by acidic atmospheric deposition. Stagnic Cambisol in Žiar nad Hronom has consistently increased humidity due to stagnation of rainfall and occasional supply of slope water and at a depth greater than 30–40 cm, soil has signs of oxidation-reduction processes. By imissions acidified soil environment in Žiar nad Hronom (pH_{H2O} 4.6–4.7 in 0–10 cm) points to oligo-mesotrophic conditions. This fact is in agreement with the data of Maathuis (2009) who states that leaching of soils may lead to deficiency in Ca content, a condition that is accelerated by lower soil pH. Increased concentration of K_{tot} in Aoq layer of stress stand can be reasoned by the low adsorption ability and easy leachability through the soil profile (between horizon of surface humus and Aoq horizont the difference was 28%) supported by acidic atmospheric deposition. Results show that both total and available contents of Ca and Mg were washed out from Aoq horizons close to the smelter, evidenced by the several fold lower values compared with the control stand. Hüttl and Schaaf (1995) state, that acid and increased N deposition in forest ecosystem may cause a reduction in soil alkalinity (Mg, Ca, K).

Macronutrients in plant species. In plant samples, the levels of K are the highest among all studied elements (Figure 1). Ca contents are considerable, too, especially in the leaves of *F. sylvatica*. Regarding Mg, assimilatory organs of beech accumulated higher amount of element than the organs of sedges, in both stands. In general, in the stress stand we observed somewhat higher values of macronutrients in plant leaves, with the exception of Ca. The best Ca accumulator on both plots was beech (transfer coefficient (TC) > 1).

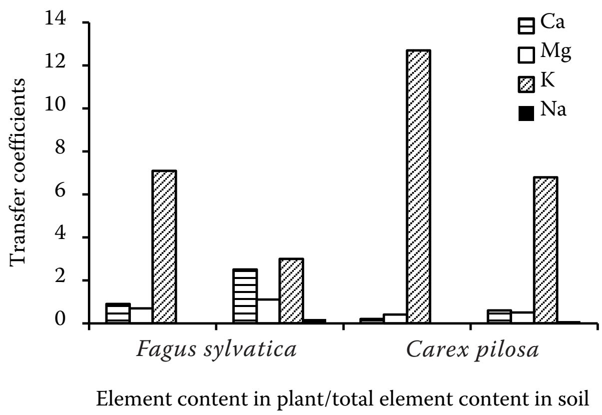

Figure 3. Transfer coefficients of plant species of the beech stands

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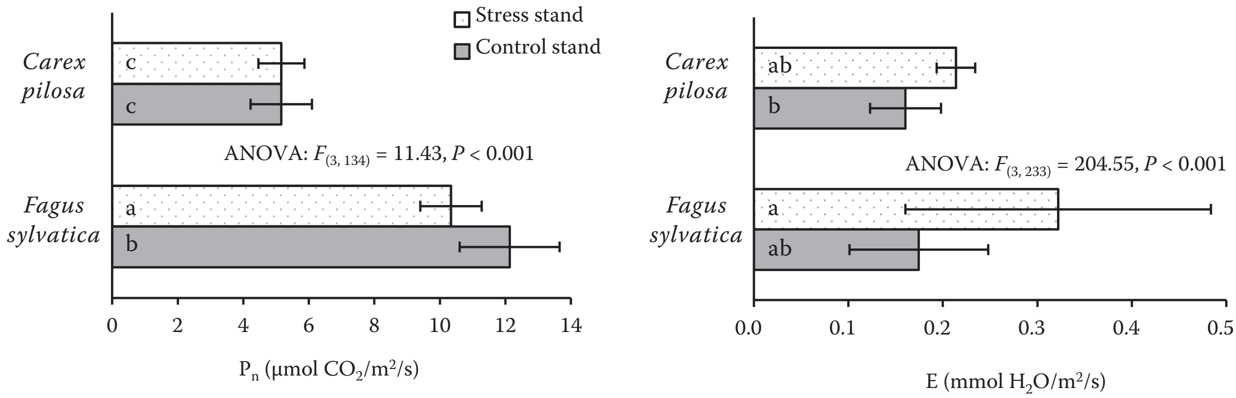

Figure 4. Photosynthetic rate (P_n) and transpiration rate (E) of plant leaves of the beech stands. No significant differences for values with the same letters. Data are means ± SE

The higher TC of Mg (TC 1.1) was found only for *F. sylvatica* growing close to the smelter. The relatively low TC of Na was observed for plants growing on both plots (Figure 3). Ca contents of studied plants decreased towards the smelter. Saison et al. (2004) showed that Ca concentrations in shoots of *Thlaspi caerulescens* were also decreased in conditions of polluted areas. In general, Ca on the studied plots prevailed in beech leaves, whereas in sedges lower values were found several times. Reason may also be that many plants from order *Fabales* can receive more Ca and store it in the cell juice. Mg in the studied plants was taken in lower amounts than Ca, resulting in a higher Ca:Mg ratios (stress stand 1.6–3.1). In the polluted areas from southern Poland, Kapusta et al. (2006) state the shoot Ca:Mg value in *Moehringia trinervia* from 3.3–7.7.

Gas-exchange parameters. On the studied plots assimilatory organs of beech showed higher rate of photosynthesis compared to the sedges (Figure 4). A significant decline (P < 0.001) of P_n was observed for beech on plot closer to the emission source. According to Woo (2009) beech belongs to the woody species sensitive to air pollution which may be reflected in the change of photosynthesis. Measured values of transpiration rate revealed an increase in this parameter for plants growing on plot situated closer to the emission source (Figure 4). Significantly differed only transpiration of beech in the stress stand opposite to sedges in the control stand (P < 0.001). Transpiration rate was increased with the impact of air pollutants in our experiment. These conclusions are not in agreement with the results of Wang et al. (2011), where atmospheric pollutants exerted only minor effects on transpiration of six urban tree species in Beijing. We had a similar situation when evaluating the stomatal conductance (Figure 5). Although higher g_s was found in leaves of both species close to the smelter, only assimilatory organs of sedges showed significant differences between plots

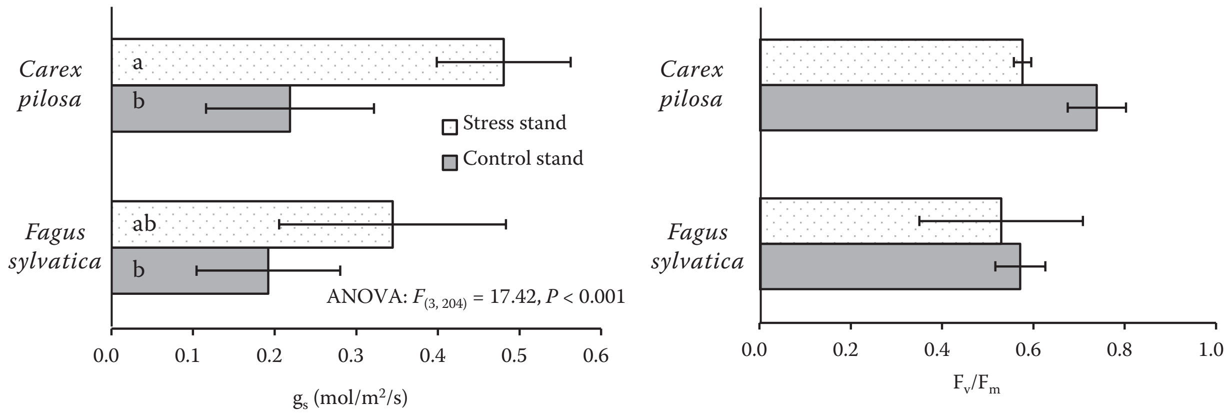

Figure 5. Stomatal conductance (g_s) and maximum PS II photochemical efficiency (F_v/F_m) of plant leaves of the beech stands. No significant differences for values with the same letters. Data are means ± SE

doi: 10.17221/881/2014-PSE

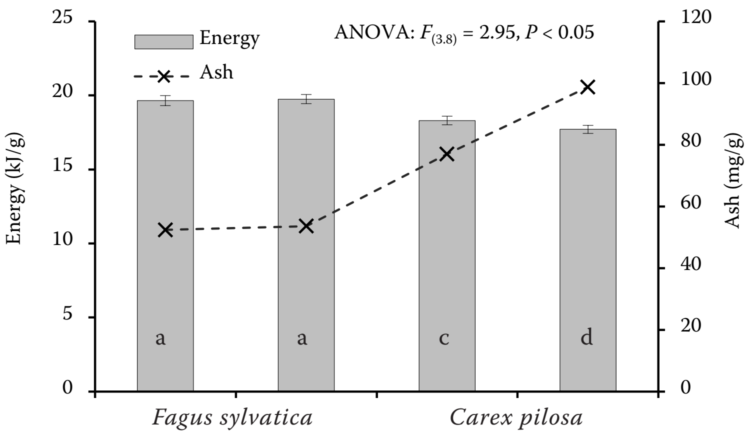

Figure 6. Energy and ash content of plant leaves of the beech stands. No significant differences for values with the same letters. Data are means ± SE

(P < 0.001). Higher values of F_v/F_m were found for plant species growing in the control stand (Figure 5.). Reduction of F_v/F_m between plots was higher in *C. pilosa* (by 22%) compared to *F. sylvatica* (by 7%). Maxwell and Johnson (2000) state, that in the case of C3 plants, photosynthesis cycle as a 'normal' is the range from 0.79–0.84. Parameter F_v/F_m was lower (< 0.6) for plant species growing on air pollutants loaded plot, which is in accordance with the results of Arena et al. (2014). Ibaraki and Murakami (2007) state that stress conditions reduce F_v/F_m and the efficiency of photosynthesis. Study of physiological parameters measured in tree foliages sampled in the vicinity of an Al production facility in Patagonia showed that air pollutants had a significant relationship with chlorophyll products of plants (Wannaz et al. 2012).

Energy and ash accumulation. Sedges growing close to the smelter reacted more sensitively on the influence of immission load (Figure 6). *C. pilosa* species revealed lower energy value and differed significantly between plots (P < 0.05). Lower calorific value of sedges in stress stand may be related with their unbalanced macronutrient contents (K:Ca + Mg ratio was several times higher than the optimal value). According to Majkowska-Gadomska et al. (2014), the K:Ca + Mg ratio is considered as an important indicator of the nutritional value of plants. Ash from plant biomass stimulates microbial activities and mineralization in the soil by improving both the soil's physical and chemical properties (Berg 2000). The results show that sedges growing close to the smelter contained by 22% more ash than in the control stand. In the case of beech difference between stands was minimal (2.3%).

In conclusion, air pollutants from Al smelter had a significant influence on lower Ca content in the surface humus and Na, Mg, Ca concentrations in Aoq soil horizons at a distance of 1.5 km compared with forest stand away from the emission source (18 km). In relation to the physiological parameters measured in plant leaves air pollutants significantly affected the rate of photosynthesis of beech, calorific values of sedges and chlorophyll fluorescence parameter of both studied plants.

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Received on November 11, 2014
Accepted on January 20, 2015

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