Lesn. Cas. For. J. 62 (2016) 77–88
DE GRUYTER OPEN
DOI: 10.1515/forj-2016-0008
Lesnícky časopis - Forestry Journal
http://www.nlcsk.sk/fj/
ORIGINAL PAPER

Ozone phytotoxicity in the Western Carpathian Mountains in Slovakia

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Abstract
In this work, the response of temperate coniferous forests to ozone air pollution (O_3) in the mountain environment of the High Tatra Mts. (Western Carpathians) was analyzed. The modelling of stomatal O_3 flux is a complex method for the estimation of phytotoxicity of O_3 pollution to forest vegetation. Stomatal flux-based critical levels (*CLef*) for effects of O_3 on radial growth take into account the varying influences of O_3 concentration, meteorological variables, soil properties, and phenology. The application of the model DO_3SE (Deposition of Ozone for Stomatal Exchange) at five experimental plots with altitudes varying from 810 to 1,778 m a.s.l. along vertical and spatial profile in the High Tatra Mts. revealed the high phytotoxic potential of O_3 on spruce forests during the growing season 2014. The accumulated stomatal O_3 flux above a threshold of Y (1 nmol m^{-2} s^{-1}), i.e. POD_1 (Phytotoxic Ozone Dose) ranged from 13.6 mmol m^{-2} at the Kolové pleso site (1,570 m a.s.l.) to 16.2 mmol m^{-2} at Skalnaté Pleso site (1,778 m a.s.l.). *CLef* for POD_1 (8 mmol m^{-2}) recommended for the protection of spruce forests were exceeded at all experimental plots from early July. Similarly, AOT40 index suggests vulnerability of mountain forests to O_3 pollution. AOT40 values increased with altitude and reached values varying from 6.2 ppm h in Stará Lesná (810 m a.s.l.) to 10.7 ppm h at Skalnaté Pleso close to the timber line (1,778 m a.s.l.). Concentration-based critical level (*CLec*) of 5,000 ppb h was exceeded from June to August and was different for each experimental site.

Key words: mountain forests; Phytotoxic Ozone Dose$_Y$; DO_3SE model; stomatal conductance; stomatal ozone flux

Editor: Bohdan Konôpka

1. Introduction

Ozone levels in Europe are rather high to jeopardize human health and vital growth of vegetation (WHO 2008; Paoletti 2014; Monks et al. 2015). Relevant reduction of O_3-precursors emissions in Europe (Vestreng et al. 2004) tends to decrease O_3 maxima and increase annual averages at both urban and rural sites (Paoletti et al. 2014) due to less O_3 titration by reduced NO_x emissions. The ozone levels are increasing in cities and decreasing at Mediterranean remote sites (Sicard et al. 2013). However, cumulative indices such as SOMO35 and AOT40, i.e. 5,000 ppb h (Directive 2008/50/EC) indicate that rural highland sites of Europe are more vulnerable to health and environmental risks associated with perpetual O_3 exposure than urban lowland areas (Bičárová et al. 2013). Concentration-based critical level (*CLec*) of AOT40 for forest ecosystems is regularly exceeded in almost whole territory of Slovakia (Pavlendová 2008) as well as in the Czech Republic (Hůnová & Schreiberová 2012; Hůnová et al. 2016). At high-altitude stations, the background O_3 levels (chronic exposure) are higher, and higher O_3 concentrations are observed at night (Sicard et al. 2009). Acute exposures are characterized by high O_3 concentrations for a relatively short time period, within hours or days that lead to visible foliar injury (Schaub et al. 2010; Sicard et al. 2011). Chronic exposures involve lower concentrations that persist or recur over a period of weeks or months (Grulke et al. 2007). Mountains can act as cold-traps for long-range transport of atmospheric pollutants. The mechanism of transport of pollutants through the atmosphere and accumulation in the mountain environment were well described in literature (Steinbacher et al. 2004; Sicard et al. 2009, 2011; Monks et al. 2015). For example, there is evidence of accumulation of persistant organic pollutants (POPs) in the mountainous environment (Hageman et al. 2015). The highest deposition fluxes of organochlorine compounds (OCs) were found at high-altitude European sites, especially at Skalnaté Pleso in the High Tatra Mts. (Arellano et al. 2015).

Tropospheric ozone acts as a phytotoxin which produces an oxidative stress in plants. The phytotoxic nature of O_3 can impair forest productivity by both favouring stomatal closure and impairing stomatal control. High O_3 concentrations reduce carbon assimilation in trees while this reduction is more related to stomatal O_3 deposition than to O_3 concentration (Fares et al. 2013). The scientific community is moving toward an evaluation of the ozone risk based on stomatal O_3 fluxes (Matyssek et al. 2007; UN-ECE 2010; Mills et al. 2011; Büker et al. 2012). Tracking of stomatal O_3 uptake by vegetation required more comprehensive methods than the evaluation of O_3 concentration data alone. Multiplicative models of stomatal conductance, such as the DO_3SE (Deposition of Ozone and Stomatal Exchange), have been suggested as a basis for calculating the hourly O_3 flux resulted to the Phytotoxic Ozone Dose (POD_Y) (Emberson et al. 2000). For forest trees, stomatal flux-based critical levels (*CLef*) of POD_Y were derived for effects on changes in annual increments in the whole tree biomass. These critical levels can be used to refer adverse health effects of O_3 on

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relevant ecosystem services provided by forest trees, e.g. production of roundwood, C sequestration, soil stability and flood prevention (Mills et al. 2011). Main problem is that present exposure-based standards for protecting vegetation from ozone (O_3) do not reflect the actual field conditions. Recent knowledge resulting from epidemiological assessment of forest responses to O_3 showed that a risk assessment based on POD_Y and on real plant symptoms is more appropriate than the concentration-based method and developed the new flux-based critical levels *CLef* for forest protection against visible O_3 injury (Sicard et al. 2016).

Previous studies concerning the problems of air quality pointed to the high level of ozone air pollution in the Western Carpathian Mts. that is comparable with the most polluted regions in Europe (Bytnerowitz et al. 2004; Bičárová et al. 2013; Hůnová et al. 2016). Formation of O_3 in mountain regions of Slovakia is substantially influenced by long-range transport of O_3 precursors and their interaction with local components from both antropogenic and biogenic sources (Bičárová et al. 2005). It can be expected that high chronic O_3 exposure and O_3 uptake by vegetation may impair the vitality of forests, especially in wet and cold climate conditions of highland areas.

The aim of this work is to quantify phytotoxical ozone dose for coniferous forest species, especially Norway spruce (*Picea abies* L. Karst) in the mountain environment of the High Tatra Mts. (Slovakia). Stomatal O_3 fluxes and POD_1 are calculated by DO_3SE model for five experimental sites situated along spatial and vertical profiles from 810 to 1,778 m a.s.l. during the vegetation season 2014. The results are intendend to support new complex approach in research of adverse impact of O_3 pollution on forest vegetation based on modelling of stomatal O_3 flux. This new approach may improve still prevalently used O_3 concentration based method associated with AOT40 indicator for the protection of vegetation and forests. Presented research can provide many results useful for the wide scientific community (in environmental and forest science, physiological and biological research, ecological modelling etc.). Research activities and field measurements are part of the ongoing project MapPOD (Mapping of Phytotoxic Ozone Dose in the Forest Environment of the High Tatra Mts.) which focuses on assessment of potential O_3 risk to mountain forests in Slovakia.

2. Material and methods

2.1. Study area

The High Tatra Mts. are located in the northern part of Slovakia on the border with Poland (Fig. 1). Region of interest represents the highest part in the whole Carpathian Mountains. The elevation of the main mountain chain of the High Tatra Mts. varies from about 2,000 m a.s.l. (saddles) to 2,654 m a.s.l. (the highest peak). Temperate coniferous forest with Norway spruce (*Picea abies* L. Karst.) is the dominant vegetation type up to 1,500 m a.s.l. From the other tree species occur European larch (*Larix decidua* Mill.), Scots pine (*Pinus sylvestris* L.) and Grey alder (*Alnus incana* L. Moench). The higher part of the valley (subalpine) is almost completely covered by Dwarf pine (*Pinus mugo* Turra).
In order to model O_3 fluxes, the O_3 concentrations, meteorological and environmental parameters were measured at 3 experimental sites situated in the south aspect: Stará Lesná – SL, Štart – STA, Skalnaté Pleso – SP (Table 1, Fig. 1). On the north side of the High Tatra Mts., in the vicinity of Tatranská Javorina municipality, the other 2 experimental sites (Podmuráň – PDM and Kolové pleso – KP) are located. On the south side, the massive rocky branches separate numerous glacial valleys including Skalnatá dolina area. Due to strong rain-shadow effect the climate of south-facing Skalnatá dolina area is slightly warmer and significantly drier

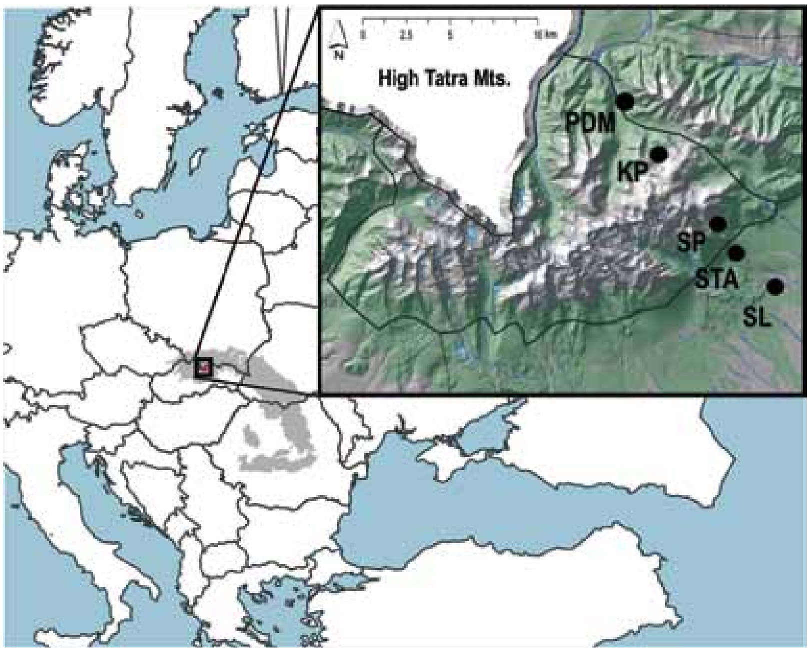

Fig. 1. The geographical position of the High Tatra Mts. in the Carpathian Montane Forests and location of the experimental sites (SL – Stará Lesná, STA – Štart, SP – Skalnaté Pleso, KP – Kolové pleso, PDM – Podmuráň).

Table 1. Experimental sites description (CODES used in relation to Fig. 1).

Transect Aspect	Experimental site CODE	GPS Latitude Longitude	Altitude m asl	Vegetation zone	Group of forest type	Tree species composition	Geological subbase	Soil type	Soil texture	$AT_{1961-90}$ °C	$P_{1961-90}$ mm
South transect Skalnatá valley area	Stará Lesná SL	49°09'08'' N 20°17'19'' E	810	Fir–beech (5th)	*Pineto-Piceetum*	Norway spruce, Birch, Scots pine, European larch, Grey alder	Fluvioglacial	Gleyic Cambisols	Silt loam medium coarse	5.4	740
	Štart STA	49°10'30''N 20°14'48'' E	1,150	Spruce–Fir–Beech (6th)	*Sorbeto Piceetum Lariceto piceetum*	spruce, larch, pine, fir, maple	Granodiorite	Cambic Podzols	Sandy loam coarse	4.0	981
	Skalnaté Pleso SP	49°11'21'' N 20°14'02'' E	1,778	Mountain pine (8th)	*Mugethum acidifilum*	Mountain pine	GranodioriteGranite	Skeli-Dystric Leptosols	Sandy loam coarse	0.8	1,220
North transect Tatr. Javorina area	Podmuráň PDM	49°15'00'' N 20°09'25'' E	1,100	Spruce (7th)	*Sorbeto Piceetum Acereto Piceetum*	spruce, fir, rowan, beech, maple	Granodiorite Fluvioglacial	Cambic Podzols	Loam medium	3.8	1,250
	Kolové pleso KP	49°13'22'' N 20°11'27'' E	1,570	Mountain pine (8th)	*Mugethum acidifilum*	Mountain and swiss pine, spruce	Granodiorite	Skeli-Dystric Leptosols	Silt loam medium coarse	2.0	1,493

Used data sources:
1 – forestry databases of National Forest Centre in Zvolen (soil, geological and typological maps, Forestry GIS-databases).
2 – climate data provided by Slovak Hydrometeorological Institute for the reference period 1961–1990 and Climate Atlas of Slovakia (SHMI 2015).
3 – soil units according to WRB Soil Classification System (WRB 2015, FAO).
4 – forest typology and edaphic-trophic units based on Zlatník's geobiocenological school (Zlatník 1976).
Abbreviations: AT – air temperature; P – precipitation.

compared to north part of the High Tatra Mts. (Table 1). On the contrary, the climate of the north-facing Tatranská Javorina area is cold and very wet with long-term mean annual temperatures around 3.8 °C and rainfall total of 1,250 mm at the altitude of 1,100 m a.s.l. The meteorological observation during the last two decades revealed moderate warming and increasing rainfall amounts (SHMI 2015).

In recent decades, the area of interest was affected by large-scale disturbances in connection with the adverse effects of climate change. The extreme weather conditions more frequently observed in the recent years (drought, heat waves, snow cover decline etc.) contributed to the massive bark beetle outbreaks (*Ips typographus*) in forest stands weakened by abiotic destructive factors as windstorm, fire, flooding, long-range transport of air pollutants etc. (Mezei et al. 2014; Nikolov et al. 2014).

2.2. Meteorological and ozone data

The basic meteorological variables (such as air temperature, relative humidity, wind speed, wind direction, solar radiation and precipitation) were continuously monitored at all experimental sites using automatic weather stations (EMS Brno CZ; Physicus, s. r. o. SK). The measuring interval of meteorological data was set on variable time step (starting from 10 seconds up to 5–10 minutes) and average data were consequently stored every 10 to 30 minutes into the central datalogger of the weather station.

Ozone concentration data were measured at five experimental sites using the ozone analyzers based on the well established technique of absorption of UV light at 254 nm. At three experimental forest sites (Stará Lesná – SL, Skalnaté Pleso – SP, Podmuráň – PDM), the analyzers manufactured by Horiba (APOA360 Ambient Ozone Monitor) and Thermo Electron Environmental (49C Ozone Analyzer) were used. The more remote experimental sites where the electricity was unavailable (Štart – STA, Kolové pleso – KP) were equipped by Ozone Analyzer Monitor M106-L (2B Technologies, Inc.) and powered by solar energy. The ozone data in default ppb units were measured in 6–10 second interval and hourly averages were stored into the datalogger. For purposes of this study, the hourly meteorological and O_3 concentration data from the period of April to October of the year 2014 were processed and analysed.

2.3. DO_3SE model

The multiplicative deposition DO_3SE model has been developed to estimate the risk of O_3 damage to the European vegetation and it is capable of providing flux-modelling estimates according to UN-ECE LRTAP methodologies for effects-based risk assessment (Pihl-Karlsson et al. 2004; Emberson et al. 2007; Karlsson et al. 2007; Tuovinen et al. 2007).

Meteorological data, O_3 concentration and plant-specific characteristics (e.g. physiological and phenological) are three basic groups of input data that enter into the model for the estimation of O_3 flux to the vegetated surfaces (Büker et al. 2012). The stomatal conductance (G_{sto}) is one of the most important and key parameters of the DO_3SE model. The detailed description of the algorithm of G_{sto} calculation is given in the manual for modelling and mapping of the critical level exceedance (UN-ECE 2004).

The stomatal flux of O_3 (*Fst*) is modeled using an algorithm incorporating the effects of meteorological conditions (air temperature, vapour pressure deficit, light); soil and plant water (soil water potential, available water content); plant phenology and O_3 concentration on the maximum stomatal conductance measured under the optimal conditions. *Fst* is the instantaneous flux of O_3 through the stomata pores per unit projected leaf area (PLA) and refers specifically to the sunlight leaves at the top of the canopy. As there is strong biological support for the use of a threshold to represent the detoxification capacity of the trees (Karlsson et al. 2007), the expert judgement was used to set Y to 1 nmol m^{-2} PLA s^{-1} for the forest trees (Mills et al. 2011). The model calculation of the stomatal flux is based on the assumption that the concentration of O_3 (nmol m^{-3}) at the top of the canopy c (z1) measured in the tree height (z1) represents a reasonable estimate of O_3 concentration at upper surface of the laminar layer. Stomatal O_3 flux *Fst* (nmol m^{-2} PLA s^{-1}) is given by (UN-ECE 2004):

$$Fst = c(z1) * Gsto * (rc / (rb + rc)) \quad [1]$$

where *Gsto* is the stomatal conductance for O_3 (m s^{-1}), *rb* and *rc* are the quasi-laminar resistance and the leaf surface resistance (s m^{-1}), respectively. *PLA* is the abbreviation of Projected Leaf Area.

The stomatal conductance can be calculated as:

$$G_{sto} = g_{max} * f_{phen} * f_{light} * max\,\{f_{min}, (f_{temp} * f_{VPD} * f_{SWP})\} \quad [2]$$

where g_{max} is the species-specific maximum stomatal conductance (mmol O_3 m^{-2} PLA s^{-1}), f(phen, light, min, temp, VPD, SWP) are the parameters determining the effect of the environment and phenophase on the stomatal conductance. The detailed description of the algorithm and derivation of the physical relationships for the final calculation is given in the manual for modelling and mapping of *CLef* level exceedance (Mills et al. 2011).

The phytotoxic ozone doses (POD_Y) is the accumulated value of the stomatal fluxes that exceed the threshold Y nmol m^{-2} s^{-1} during the vegetation season. It is calculated according to the formula:

$$POD_Y = \Sigma(1; n)\,[Fst - Y] \quad [3]$$

for $Fst \geq Y$ with the accumulation of the hourly stomatal O_3 flux during the whole vegetation season (defined for the tree species and year of the assessment). *Fst* is the hourly mean stomatal O_3 flux (nmol m^{-2} s^{-1}) and *n* is the number of hours within the accumulation period. The threshold Y is defined as species-specific, the actual value for forest trees is proposed to 1 nmol m^{-2} PLA s^{-1}, the *CLef* of POD_Y is proposed to be 8 mmol m^{-2} PLA for spruce (evergreen coniferous) with expected biomass increment reduction of 4 and 2% respectively (Mills et al. 2011).

Besides POD_Y, the exceedance of *CLec* of exposition index AOT40 was calculated for all experimental sites. The AOT40 for forests is the accumulated excess of the hourly ozone concentrations above 80 µg m^{-3} between 8:00 and 20:00 CET over the period April–September (Directive 2008/50/EC). This indicator quantifies only the ozone exposure, i.e. not the effective ozone uptake by (and therefore the damage caused to) vegetation. In this study, AOT is the sum of the concentrations over the threshold value *X* calculated for the daily hours during the vegetation season according to the equation:

$$AOTX = \Sigma\,(1; n)\,[C - X] \quad [4]$$

for $C \geq X$, where *C* is the hourly mean O_3 concentration (ppb), *n* is the number of daily hours in the accumulation period, and *X* is the threshold value for forest ecosystems being 40 ppb. *CLec* of AOT40 was set to 5,000 ppb h (Directive 2008/50/EC). In the past, the value 10,000 ppb h was used. The exceedances of *CLef* for POD_1 and *CLec* for AOT40 are calculated for the main tree species Norway spruce (*Picea abies* L. Karst.).

The parameterisation of DO_3SE model reflects the recommendations in different scientific papers, the generic values are also given in manual ICP Modelling and Mapping (UN-ECE 2010), for some of them it is possible to assess by field measurement to be species specific and also site specific. More specific and detail information about model parametrisation is included in the Appendix.

3. Results

3.1. Meteorological data and weather conditions

Information on the development of meteorological parameters is important not only for the interpretation of the measured ozone data but also as key input into the model of stomatal ozone fluxes. In the High Tatra Mts., growing season 2014 (GS 2014) started after the snowmelt (March/April) and depending on the altitude continued until the late autumn (October/November). The statistical characteristics of the hourly weather data measured at the selected field sites in the High Tatra Mts. from April to October 2014 are included in the Table 2. The mean air temperature varied in interval from 7.5 to 12.0 °C and reached maxima up to 30 °C. Values were in line with the normal course of climate data (Fig. 2). The calculated values of the vapour pressure deficit (VPD) were under the limit level (VPD_min, 3.00 kPa) for the minimal stomatal conductance (Fig. 2) that illustrates the favourable air humid conditions for the stomatal flux. The precipitation sums varied between 918 and 1,370 mm depending on the altitude of the site (Table 2). During the given GS period, the extraordinary weather events occurred. In May there was intensive heavy rain for two days and there fell about 100–200 mm. The windstorm at high altitudes (the maximum observed gust has achieved value of 42 m s^{-1}) resulted in flooding and forest windfall, especially in the NW area above the Podmuráň experimental site (PDM). On the other hand, the SE foothill area was affected by an exceptional long dry event in June. A rainless or light rain period lasted 38 days from 22th May to 28th June with a very low precipitation sum of 19 mm at the Stará Lesná experimental site. The next wet event started on 29th June and continued for the next 34 days. During this period, the total amount of precipitation reached a high value of 295 mm. July was a very wet month with a mean monthly temperature slightly above normal in the High Tatra Mts. as well as in whole territory of Slovakia. The weather at the end of summer and during autumn was relatively normal without unusual events. Frequently, the mean hourly wind speed values were up to a level of 5 m s^{-1} (Fig. 2), median ranged from 0.7 to 1.9 m s^{-1} (Table 2). For GS period, the sums of global radiation varied between the values from 542 kWh m^{-2} measured in the NW area (Kolové pleso) to 848 kWh m^{-2} observed in the SE area (Stará Lesná). The mean air pressure varied from 82.3 to 92.4 kPa and corresponded to the altitudinal position of the experimental sites.

3.2. Ozone data

The mean O_3 values at the study sites aggregated over GS 2014 fluctuated from 30.9 to 44.1 ppb (Table 3). Prevailing humid weather in the summer of 2014 influenced the O_3 formations in the atmospheric boundary layer, therefore the O_3 concentrations for GS 2014 was relatively low. According to data from the Slovak air quality monitoring network (SHMI and ME SR 2015), the mean O_3 concentrations for GS 2014 were lower then those in GS 2003 when the summer O_3 event occurred (Bičárová et al. 2005) likely due to the heatwave and extraordinary drought in Europe (Fiala et al. 2003). Generally, by many physiological studies it was approved that the light causes plant stomata to open and darkness to close. At the sites under the altitude of 1,600 m a.s.l., the mean O_3 concentrations during the hours of sunlight (i.e. between 07–17 h, when global radiation >50 W m^{-2}) were higher about 30–90% than O_3 mean concentrations during the night and weak sunlight hours (18–06 h). These results suggest relevant stomatal O_3 uptake into forest vegetation during daylight hours. On the contrary, at the high altitude site of Skalnaté Pleso (1,778 m a.s.l.) the values of ozone concentrations were higher by approximately 1.7 ppb during the nights in comparison to the sunlight part of day. Nevertheless, the mean O_3 values for both sunlight and night part of day at this site exceeded a level of 40 ppb. Maximal hourly O_3 concentrations occurred at sites on the northern slope (75.7 – 88.0 ppb) were higher in comparison with sites on the southern slope (70.5 – 78.1 ppb). Lower O_3 maxima on south-facing slope may be associated with large deforestration and reduction of biogenic O_3 precursors after wind disaster (Bičárová et al. 2015).

3.3. Plant-specific parameters and POD_1

The descriptive statistics of *Gsto* data estimated by DO_3SE model for all 5 experimental sites in the High Tatra Mts. during GS 2014 are included in Table 4. The modeled *Gsto* values reached maxima up to 115 mmol m^{-2} s^{-1}. Over the GS 2014, *Gsto* mean ranged between 21 and 28 mmol m^{-2} s^{-1}, during the sunlight hours (07–17 h) mean values were nearly twice higher. Night-time mean *Gsto* did not exceed level of 10 mmol m^{-2} s^{-1}. As the growing season of 2014 was mostly humid the impact of water stress on plant stomatal conductance was minimal with the exception of June at the foothills represented by the Stará Lesná site. Generally, the stomatal conductance gradually increases as the temperature increases reaching a peak and then gradually declines as the temperature increases beyond the optimum, whilst the stomatal conductance increases rapidly as light levels increase, reaching a maximum at relatively low light levels and maintaining that maximum as light level increase further (UN-ECE 2004).

DO_3SE model estimation of *Fst* for the experimental sites in the High Tatra Mts. (Table 5) showed that the mean *Fst* values for GS 2014 were over the threshold value Y of 1 nmol m^{-2} PLA s^{-1}. Nearly twice higher mean *Fst* calculated for the sunlight part of a day (07–17 h) suggests intensive stomatal O_3 uptake to the forest vegetation during the photosynthetic process. The elevation profile of mean values of O_3, *Gsto* and *Fst* (Fig. 3) illustrates great increase of O_3 concentration with altitude that is in contrast to slightly decrease of *Gsto* and nearly unchanged *Fst*.

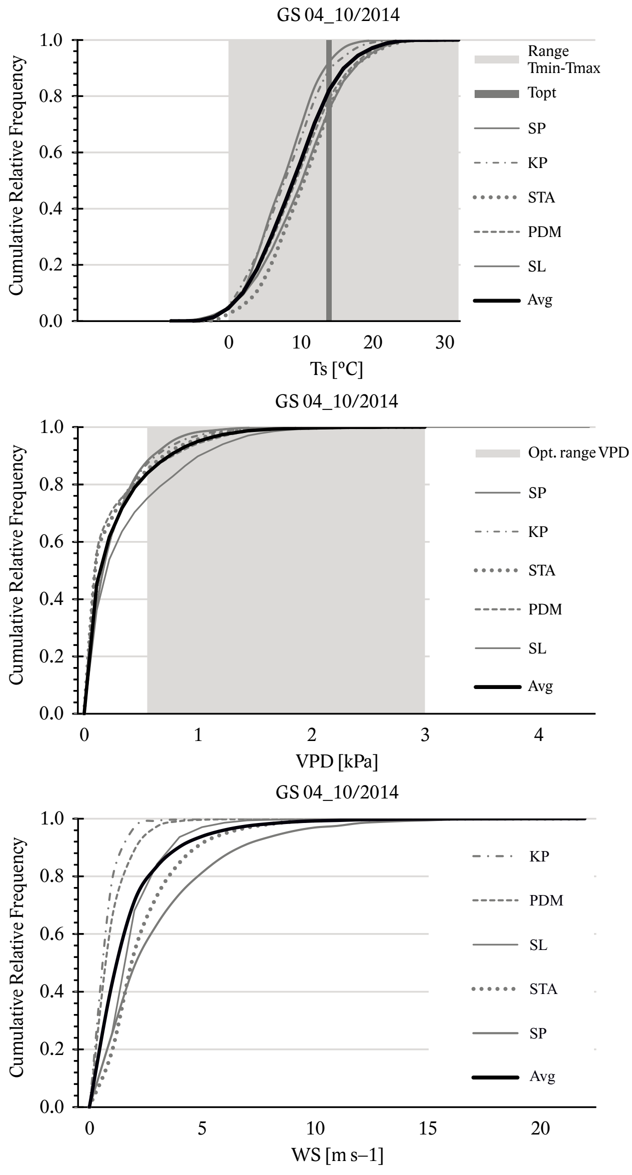

Fig. 2. Cumulative frequency distribution of hourly mean air temperature (Ts), vapour pressure deficit (VPD) and wind speed (WS).

Table 2. Statistics of hourly meteorological data measured at experimental sites for growing season (GS), April – October 2014.

Experimental plot Altitude	SL 810 m asl	STA 1,150 m asl	SP 1,778 m asl	PDM 1,100 m asl	KP 1,570 m asl
		Meteorological variables			
Air temperature – Ts [°C]					
Minimum	−2.9	−3.6	−5.6	−4.0	−3.5
Maximum	28.4	27.2	21.8	26.5	24.9
Median	12.2	10.5	7.6	9.5	7.8
Mean	12.0	10.5	7.5	9.4	7.9
Standard deviation	5.8	5.3	4.6	5.8	5.0
Vapour Pressure Deficit – VPD [kPa]					
Maximum	2.536	2.153	1.560	2.466	2.217
Median	0.174	0.071	0.151	0.079	0.140
Mean	0.342	0.209	0.228	0.232	0.231
Standard deviation	0.386	0.302	0.227	0.327	0.262
Precipitation – P [mm]					
Sum for GS period	749.1	917.6	1,286.0	1,337.0	1,370.6
Median	342.7	377.2	624.2	779.3	760.2
Mean	382.5	438.9	643.5	717.6	696.0
Standard deviation	252.5	306.4	427.2	437.6	460.5
Wind speed – WS [m s^{-1}]					
Maximum	13.7	16.1	20.6	8.6	6.0
Median	1.5	1.9	2.0	0.7	0.7
Mean	1.9	2.4	3.0	1.0	0.8
Standard deviation	1.3	1.9	2.8	0.8	0.5
Global radiation – R [kW m^{-2}]					
Sum for GS period	848	552	744	657	542
Monthly maximum	156	100	140	119	106
Median	120	78	117	95	77
Mean	121	79	106	94	77
Standard deviation	35	22	28	22	21
Air Pressure – Pa [kPa]					
Minimum	90.9	87.1	80.8	87.7	82.8
Maximum	93.8	90.1	83.6	90.6	85.3
Median	92.4	88.7	82.4	89.1	84.1
Mean	92.4	88.7	82.3	89.2	84.1
Standard deviation	0.5	0.5	0.5	0.5	0.4

Table 3. Statistics of hourly O_3 data for growing season (GS), April – October 2014.

Experimental site Altitude	SL 810 m asl	STA 1,150 m asl	SP 1,778 m asl	PDM 1,100 m asl	KP 1,570 m asl
		O_3 concentration (0–23 h) [ppb]			
Minimum	4.4	3.2	10.6	2.0	5.9
Maximum	77.1	70.5	78.1	88.0	75.7
Median	30.5	31.1	44.3	29.5	33.0
Mean	30.9	31.7	44.1	29.5	33.7
Standard deviation	12.8	11.5	8.2	15.8	11.1
Sunlight daily (07–17 h)					
Minimum	6.1	7.1	14.9	4.4	10.1
Maximum	77.1	70.5	78.1	88.0	75.7
Median	38.0	37.1	43.5	40.2	39.1
Mean	37.4	36.6	43.2	39.1	39.5
Standard deviation	10.8	10.8	8.4	13.0	9.6
Night and weak sunlight hours (18–06 h)					
Minimum	4.4	3.2	10.6	2.0	5.9
Maximum	65.6	62.6	70.8	73.4	63.6
Median	23.5	26.5	45.1	17.4	27.7
Mean	25.3	27.5	44.9	21.4	28.8
Standard deviation	11.8	10.4	8.0	13.2	9.8

Table 4. Statistics of stomatal conductance G_{sto} data estimated by DO_3SE model for growing season (GS), April – October 2014.

Experimental site Altitude	SL 810 m asl	STA 1,150 m asl	SP 1,778 m asl	PDM 1,100 m asl	KP 1,570 m asl
Stomatal Conductance G_{sto} [mmol m^{-2} s^{-1}]					
All daily hours (0–23 h)					
Maximum	115	114	114	115	112
Median	0	0	0	0	0
Mean	28	22	23	24	21
Standard deviation	35	32	34	34	32
Sunlight daily hours (07–17 h)					
Maximum	115	114	114	115	112
Median	59	43	44	50	40
Mean	53	44	45	49	43
Standard deviation	34	34	38	35	36
Night and weak sunlight hours (18–06 h)					
Maximum	99	82	83	79	76
Median	0	0	0	0	0
Mean	7	4	6	4	4
Standard deviation	16	12	15	11	10

Table 5. Descriptive statistics of stomatal *Fst* flux of O_3 estimated by DO_3SE model for growing season (GS), April – October 2014.

Experimental site Altitude	SL 810 m asl	STA 1,150 m asl	SP 1,778 m asl	PDM 1,100 m asl	KP 1,570 m asl
		Stomatal O_3 flux *Fst* (nmol m^{-2} PLA s^{-1})			
All daily hours (0–23 h)					
Maximum	5.80	5.78	6.42	6.83	6.06
Median	0.00	0.00	0.00	0.00	0.00
Mean	1.30	1.18	1.29	1.25	1.14
Standard deviation	1.56	1.55	1.72	1.69	1.58
Sunlight daily hours (07–17 h)					
Maximum	5.80	5.69	6.42	6.83	6.06
Median	2.80	2.55	2.62	2.94	2.49
Mean	2.45	2.26	2.35	2.53	2.24
Standard deviation	1.43	1.55	1.76	1.70	1.68
Night and weak sunlight hours (18–06 h)					
Maximum	5.42	5.78	5.69	4.55	4.75
Median	0.00	0.00	0.00	0.00	0.00
Mean	0.32	0.27	0.39	0.17	0.21
Standard deviation	0.81	0.78	1.04	0.50	0.59

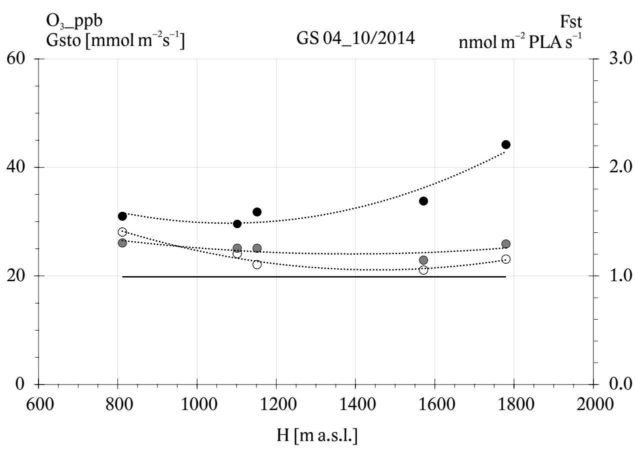

Fig. 3. Altitudinal relation of O_3 concentration (ppb), stomatal conductance (Gsto_mmol m^{-2} s^{-1}) and stomatal flux (Fst_nmol m^{-2} s^{-1}) in the High Tatra Mts. averaged for GS 2014 (0–23 hours).

The model estimates for both AOT40 (Fig. 4) and POD_1 (Fig. 5) for Norway spruce (*Picea abies* L. Karst) indicate the exceedance of *CLec* as well as *CLef* at all experimental sites in the High Tatra Mts. during GS 2014. Index AOT40 was increasing with the altitude and reached the values from 6.2 ppm h in Stará Lesná (810 m a.s.l.) to 10.7 ppm h at Skalnaté Pleso near the timber line (1,778 m a.s.l.). The critical threshold (*CLec* of 5,000 ppb h) was exceeded at each considered sites in different date. First it was at the Skalnaté Pleso site in the first half of June due to a generally higher O_3 concentration for the higher altitude position. At the beginning of August, index AOT40 was above *CLec* at all sites. POD_1 reached values from 13.6 mmol m^{-2} PLA at site Kolové pleso (1,570 m a.s.l.) to 16.2 mmol m^{-2} PLA at Skalnaté Pleso (1,778 m a.s.l.). The critical level *CLef* of 8 mmol m^{-2} PLA recommended for the spruce protection was exceeded at all experimental plots during July, in around half of the growing season 2014.

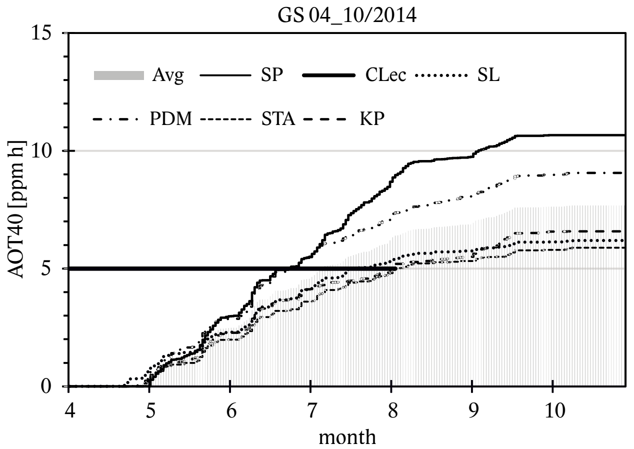

Fig. 4. Accummulated ozone exposure index AOT40 [ppm h] and the concentration-based critical level (*CLec*) for effects of ozone on forests at experimental sites in the High Tatra Mts. during GS 2014.

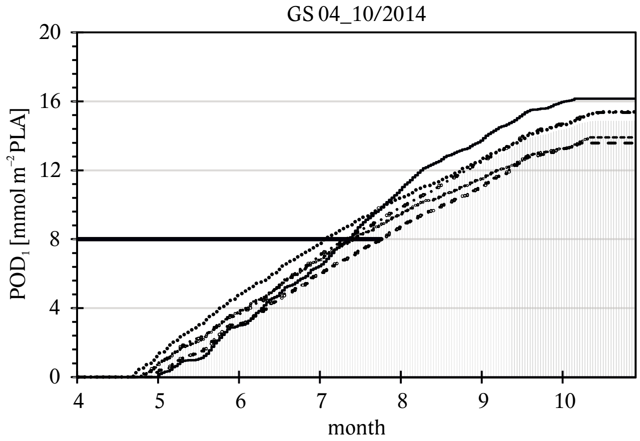

Fig. 5. Cumulative stomatal flux of ozone POD_1 [mmol m^{-2} PLA] and stomatal flux-based critical level (*CLef*) for effects of ozone on forests at experimental sites in the High Tatra Mts. during GS 2014.

4. Discussion

Phytotoxic effects of O_3 on forest vegetation are hardly distinguishable by direct methods. Based on recent epidemiological studies, Norway spruce is not clearly affected by visible O_3 injury (chlorotic mottling on the needles) and may be classified as an O_3-tolerant species (Nunn et al. 2002; Sicard et al. 2016). Critical levels of ozone concentrations could be described in different ways including concentration-based *CLec* for AOT40 and stomatal flux-based *CLef* for POD_Y that considers the stomatal conductance as the main control driver of O_3 uptake by plants. Stomatal flux-based approach has not been applied yet in assessment of O_3 impact on forest vegetation in Slovakia, mainly due to the extensive requirement of direct measurements and model input data. The presented results of pilot O_3 measurements and model outputs of POD_1 and AOT40 in the High Tatra Mts. achieved for the growing season of 2014 indicate vulnerability of forest vegetation to chronic and long-term exposure of O_3 pollution in the Western Carpathian Mts. Our results are consistent with the findings of many previous research studies conducted in surrounding countries. For example, in the medium altitudes of forested mountains in Central Europe (in the Jizerské hory Mts.), the O_3 exposure is also relatively high and comparable with the polluted sites in Southern Europe and in the higher altitudes (Hůnová et al. 2016). On the contrary, some areas of the Carpathian Mountains, in Romania and parts of Poland, as well as the Šumava and Brdy Mountains in the Czech Republic are characterized by low European background O_3 concentrations (summer season means of 30 ppb). Other parts of the Carpathians, particularly the western part of the range (Slovakia, the Czech Republic and Poland), some of the Eastern (Ukraine) and Southern (Romania) Carpathians and the Jizerske Mountains have high O_3 levels with the peak values >100 ppb and seasonal means of 50 ppb (Bytnerowicz et al. 2004). In the Czech Republic, the O_3 flux over a Norway spruce forest was measured by the gradient method and the results showed that the total deposition and stomatal uptake of O_3 significantly decreased the net ecosystem production (Zapletal et al. 2011).

As shown in our results, mean O_3 concentrations are high enough to effective O_3 uptake through stomata of coniferous trees supported by colder and wetter mountain climate favourable for open stomata processes. Both, simple concentration-based AOT40 and complex stomatal flux-based POD_1 values exceeded critical levels during growing season. AOT40 more reflects increase of O_3 concentration with altitude while POD_1 in relation to *Gsto* and *Fst* takes into account meteorological conditions. The main difference between AOT40 and POD_1 was found in the date (month) of exceedance of critical levels, particularly at site Skalnaté Pleso where the *CLec* value was exceeded in June (at the earliest date) and the *CLef* value was exceeded later in July 2014.

As confirmed by many researches, the high mountain regions are especially susceptible to the deposition of many industrial and agricultural pollutants undergoing atmospheric transport, through a process called orographic cold trapping (Hageman et al. 2015; Arellano et al. 2015). The influence of long-range transport of air pollutants on O_3 concentration in the High Tatra Mts. was noticed e.g. during unusual drought and heatwave event in summer 2003 (Bičárová et al. 2005), when the values of O_3 were significant higher then those observed within this study in wet GS 2014. The accumulated stomatal O_3 uptakes calculated by model DO_3SE exceeded *CLef* during the growing season 2014 (April-October) and indicate the risk of O_3 injury to spruce forest in the High Tatra Mts. Based on our results, the application of DO_3SE model in the High Tatra Mts. seems to be appropriate tool for monitoring of chronic O_3 exposure, O_3 deposition and stomatal O_3 uptake to forest vegetation.

Innovative epidemiological assessment of forest responses to O_3 reflecting flux-effect relationships includes species-specific *CLef* for forest protection against visible O_3 injury (Sicard et al. 2016). New *CLef* for the forest protection against the visible O_3 injury was calculated for O_3 highly sensitive conifer *Pinus cembra*. In this case, the proposed value of *CLef* 19 mmol m^{-2} represents the value POD_0 accumulated for hours with a non-null global radiation (Sicard et al. 2016). However, visible injuries on the needles of many conifer species, like Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), are rare and cannot yet be reliably associated with O_3 in the field (Günthardt-Goerg 2001).

Currently the main tree species of interest in our research are Norway spruce (*Picea abies* L. Karst.), mainly for its economic relevance in the model area as well as the Mountain pine (*Pinus mugo* Turra), creating a timberline in the High Tatra Mts. Another ecologically valuable and endemic tree in the Tatra Mountains is Swiss stone pine (*Pinus cembra* L.) that occupies specific, relatively small areas close to the alpine tree line and is highly protected in the whole Tatra National Park. Therefore, in the next years the research priorities linking to study of O_3 effect on forest vegetation in the High Tatra Mts. will be focused on biomonitoring of conifer pine species, particularly *Pinus cembra* and *Pinus mugo*.

5. Conclusions

In recent decades, the considerably and progressive deterioration of forest health status in the Tatra National Park in Slovakia was observed. Synergy of biotic and abiotic disturbances has caused the degradation of the living forest, disruption of ecological relations and other functions of the forest environment. This study presents the results of the phytotoxic ozone doses (POD_1) modeling for Norway spruce forests in the High Tatra Mts. – the highest part of Western Carpathians. The DO_3SE model outputs for the growing season 2014 indicate an excessive stomatal O_3 uptake by spruce forests at five experimental sites distributed in the altitudinal range from 810 to 1,778 m a.s.l. along the vertical and spatial profile in the High Tatra Mts. Accumulated stomatal O_3 flux i. e. POD_1 exceeded *CLef* at all considered sites during July 2014, approximately in the middle of considering growing season. Potential detrimental effect of O_3 is shown also by AOT40 index that exceeded *CLec* differently for each experimental site from the half of June to the end of August 2014. Both POD_1 and AOT40 show a high phytotoxic potential of O_3 pollution in the forest environment of the highest part of Carpathian Mountains. The deposition models such as DO_3SE that simulate the total and stomatal O_3 fluxes was in our study approved as an appropriate tool for the assessment of critical O_3 level exceedance and risk of secondary air pollution for the mountain forest ecosystems.

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contracts No. APVV–0429–12 and APVV–0111–10, and by the Grant Agency of the Slovak Republic (VEGA, No.2/0053/14). The authors are grateful to the Slovak Hydrometeorological Institute for providing of meteorological and EMEP data. The development of DO_3SE model interface has been made possible through funding provided by the UK Department of Environment, Food and Rural Affairs (Defra) and through institutional support provided to the Stockholm Environment Institute from the Swedish International Development Agency (Sida).

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Appendix – Supplementary Information to paper

Details to section: Material and methods

Model parametrisation of input variables is performed by creation of DO_3SE model project. For each experimental site, creation of new project is needed e.g. Appendix 1 includes input parameters for Norway spruce forest in Stará Lesná. The structure of model project consists of ten items explained in next paragraphs.

[1] **The model introduction** is related to the opening of a new or selected project that could be modified according to the location properties, vegetation type, environmental interactions, growing season, and phenology.

[2] The input dataset format processed the CSV data file, including the hourly values of **O_3 concentration and meteorological variables** as specified in the Table 1 and with respect to the required units. The Vapour Pressure Deficit (VPD, kPa) was calculated from the air temperature and relative humidity measurements. Where O_3 and meteorological data were missing for periods of several hours, data gaps were filled using a linear interpolation between adjacent data points.

[3] **The location properties** cover the geographical coordinates and typical soil texture (Appendix 1): silt loam (medium coarse), sandy loam (coarse) and loam (medium) where the soil resistance term to water vapour flow (*Rsoil*) is 200 s m^{-1}. *Rsoil* is a complex function of the vertical soil water distribution. An important feature of evaporation from soil is a fast reduction due to the drying of the uppermost soil layer after rainfall. For a fully wet soil *Rsoil* value is equal to 100 s m^{-1} (Grünhage & Haenel 2008).

[4] **Measured data** were optimised and recalculated for individual heights of O_3 and wind speed measurements. For forests, O_3 concentrations must often be derived from measurements made over grassy areas or other land-cover types. O_3 measured at variable heights over land-use were used to estimate the O_3 concentration at a referenced height by application of the gradient profile appropriate for the desired land use (UN-ECE 2004). Soil water measurement depth (d, 0.5 m) allows the model to calculate soil water data for a particular depth which can then be compared to the real-world data.

[5] **Vegetation characteristics** were linked to the following parameters: Canopy height (h, 20 m); Rooth depth (dr, 1 m); Leaf dimension (Lm, 0.05m); Albedo (0.12); Species specific maximum stomatal conductance (gmax, 125 mmol O_3 m^{-2} PLA s^{-1}); Sun/shade factor (1); Receptor specific value (fmin, 0.16); External plant cuticule resistance (Rext, 2,500 s m^{-1}); Threshold Y for POD_Y (1.0 nmol m^{-2} s^{-1}); Closed stomata conductance (Gsto0, 30,000 µmol m^{-2} s^{-1}); Species-specific sensitivity to An (m, 16.83); Maximum catalytic rate at 25 °C (Vcmax, 30 µmol m^{-2} s^{-1}); Maximum rate of electron transport at 25 °C (Jmax 60, µmol m^{-2} s^{-1}).

[6] **The environmental response** includes: A parameter related to the function f_{light} and the photosynthetic photon density (ligh_a, 0.010); Minimum temperature (T_min, 0 °C); Optimum temperature (T_opt, 14 °C); Maximum temperature (T_max, 35 °C); Vapour Pressure Deficit for maximal stomatal conductance (VPD_max, 0.50 kPa); Vapour Pressure Deficit for minimal stomatal conductance (VPD_min, 3.00 kPa); Critical daily VPD sum (VPD_crit, 1,000 kPa); Soil water potential for minimal stomatal conductance (SWP_min, –0.50 MPa); Soil water potential for maximal stomatal conductance (SWP_max, –0.05 MPa).

[7] **The model option** allows an alternate choice of different methods for calculating the same factors. For the simulation in this work, the following ones were selected: Multiplicative stomatal conductance model; Estimated leaf temperature; Not used the fO_3 method in the calculation of leaf Gsto; Linear (SWP_min, SWP_max) fSWP calculation; Use of supporting interface fSWP for calculating the effect of soil water availability on stomatal conductance; Steady-state method of Leaf Water Potential calculation – the steady state model controls water flux on an hourly time-step using an estimation of LWP based on the daily SWP and plant transpiration of the previous hours (Büker et al. 2012).

[8] **The season** was set on the duration of Growing Season (GS). Duration of GS from the start (SGS) to the end (EGS) estimated according to the latitude function with respect to the forest vegetation. Leaf Area Index at SGS (LAI_a, 3.5 m^2 m^{-2}); First mid-season LAI (LAI_b, 4.0 m^2 m^{-2}); Second mid-season LAI (LAI_c, 3.8 m^2 m^{-2}); Leaf Area Index at EGS (LAI_d, 3.5 m^2 m^{-2}); Period from LAI_a to LAI_b (LAI_1, 25 days); Period from LAI_c to LAI_d (LAI_2, 30 days); Stem Area Index calculation for forest.

[9] **Phenology** is focused on the configuration of the *Fphen* function. For the forests species, the *fphen* parameterisation is based on data describing the increase and reduction in *Gsto* with the onset and end of the physiological activity (CLRTAP 2004). We assumed that *fphen* was 1 throughout the growing season, i.e. the POD_Y accumulation period. *Fphen* at SGS (fphen_a, 0.0); First mid-season *Fphen* (fphen_b, 1.0); Second mid-season *Fphen* (fphen_c, 1.0); Third mid-season Fphen (fphen_d, 1.0); *Fphen* at EGS (fphen_e, 0.0); Period from fphen_a to fphen_b (fphen1, 0 days); Parameters of SWP limitation are set to 0, the model reverts to a simpler version.

[10] **Leaf phenology** (*Leaf fphen*): the calculation is the same as of *Fphen*.

Appendix 1. Input parameters using for model calculation of POD_1 for Norway spruce forest at Stará Lesná experimental site during growing season 2014.

DO_3SE model: INPUT parameters			
Location properties		Measurement data	
Latitude	49.15	O_3 measurement height-recalculated [m]	20
Longitude	20.28	O_3 measurement canopy height [m]	20
Elevation [m a.s.l.]	810	Wind speed measurement height- recalcul. [m]	20
Soil texture	Silt loam (medium coarse)	Wind speed measurement canopy height [m]	20
Rsoil [s/m]	200	Soil water measurement depth ([m]	0.5
Environmental response		Vegetation characteristics	
light_a	0.01	Canopy height [h, m]	20.00
T_min ºC	0.00	Root depth (root, m)	1.00
T_opt ºC	14.00	Leaf dimension [Lm, m]	0.08
T_max ºC	35.00	Albedo (fraction)	0.12
VPD for max.g [VPD_max, kPA]	0.50	gmax [mmol O_3/m^2 PLA/s]	125.00
VPD for min.g [VPD_min, kPA]	3.00	Sun/shade factor (fraction)	1.00
SWP for min.g [SWP_min, Mpa]	−0.50	fmin (fraction)	0.16
SWP for max.g [SWP_max, Mpa]	−0.05	External plant cuticule resistance [Rext, s/m]	2500.00
Model options		Threshold Y for PODy [nmol/m^2/s]	1.00
Stomatal conductance model	Multiplicative	Closed stomata conductance [Gsto0, umol/m^2/s]	30000.00
Leaf temperature calculation	Estimate	Species-specific sensitivity to An [m, dimensionless]	16.83
fO_3calculation	Not used (f3=1)	Maximum catalytic rate at 25 ºC [Vcmax, umol/m^2/s]	30.00
Soil water influence on Gsto	Use fSWP	Maximum rate of electron transport at 251C [Jmax, umol/m^2/s]	60.00
LWP calculation	steady-state	fphen	
fSWP calculation	Linear	fphen_a	0.0
Season		fphen_b	1.0
SGS/EGS method	Latitude function	fphen_c	1.0
Star of growing season SGS	112	fphen_d	1.0
End of growing season EGS	291	fphen_e	0.0
LAI at SGS [LAI_a, m^2/m^2]	3.5	fphen_1	0
First mid-season [LAI_b, m^2/m^2]	4.0	fphen_limA	0
Second mid-season LAI [LAI_c, m^2/m^2]	3.8	fphen_2	200
LAI at EGS [LAI_d, m^2/m^2]	3.5	Fphen 3	200
Period from LAI_a to LAI_b [LAI_1, days]	25	fphen_limB	0
Period from LAI_c to LAI_d [LAI_1, days]	30	fphen_4	0
SAI calculation	Forest	Leaf fphen calculation	Same as Fphen

Explanatory note:
DO_3SE model parametrisation for interfaced version (DO3SE_INTv3.0.5) developed by the Stockholm Environment Institute, Available at: www.sei-international.org/do3se.