

Ambient ozone phytotoxic potential over the Czech forests as assessed by AOT40

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Ambient ozone (O₃) represents one of the most prominent air pollution problems in Europe. We present an analysis on O₃ with respect to its phytotoxic potential over Czech forests between 1994 and 2008. The phytotoxic potential is estimated based on the exposure index AOT40 for forests calculated from real-time monitoring data at 24 rural sites. Our results indicate high phytotoxic potential for most of the Czech Republic (CR) with considerable inter-annual and spatial variability. The highest AOT40 values were 38-39 ppm·h. The critical level for forest protection (5 ppm·h) was usually exceeded early in the growing season, generally in May. In years with meteorological conditions conducive to ozone formation, the critical level was exceeded by 5-7 folds as compared to years with non-conducive conditions; nevertheless, all sites consistently exceeded the critical level since 1994. In the extremely hot and dry year 2003, the critical level for forests was exceeded over 31 % of the Czech forested area. More research is needed to translate these exceedances into forest injury in the CR.

Keywords: Ozone, AOT40, Time trends, Spatial patterns

Introduction

Ambient ozone (O₃) has been a widely studied air pollutant for many years due to its potential toxicity for all living organisms (Felzer et al. 2007, Cape 2008, Iriti & Faoro 2008). It is an important gas playing a key role in atmospheric chemistry (Seinfeldt & Pandis 1998). It contributes to the oxidative power of atmosphere which is essential for scavenging many pollutants from the air. Moreover, due to its absorption-radiation abilities, O₃ is an important greenhouse gas (Singh & Fabian 2003, IPCC 2007). There are important mutual interactions between O₃ and climate change (Isaksen 2003), which are not fully understood yet. The urgent need to address the knowledge gaps in interactions between air pollution, climate change and forests has been recently stressed (Seringil et al. 2011, Matyssek et al. 2012).

Ozone represents one of the most promi-

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nent air pollution problems in Europe (De Leeuw & De Paus 2001, EEA 2010). Environmental O₃ quality standards are exceeded over vast areas of Europe (Horálek et al. 2007, 2009). Due to its phytotoxicity, O₃ is still considered to be the most important air pollutant for forests (Paoletti et al. 2010). Due to the fact that O₃ is a secondary pollutant formed from precursors during complex photochemical reactions and to the highly non-linear nature of O₃ chemistry, it is and will be very difficult to decrease its ambient concentrations (Seinfeldt & Pandis 1998).

Comparison of O₃ levels with those measured a century ago indicates that current levels have increased by approximately two times. European measurements between 1850 and 1900 were found to be in the range of 17-23 ppb (Bojkov 1986). Modern day annual average background O₃ concentrations over the mid-latitudes of the northern Hemisphere range between approximately 20-45 ppb, with variability influenced by geographic location, altitude and extent of anthropogenic impacts (Vingarzan 2004). Generally, three types of patterns in ambient O₃ have been apparent recently: (1) an increase in the extent of O₃ impact and the forest areas at risk; (2) a decrease in maximum 1-h O₃ concentrations, at least in the northern hemisphere countries which have introduced O₃ precursor control programs; and (3) an increase in background O₃ concentrations over much of the world (Percy et al. 2003). It is not an easy task to assess the time trends of O₃: the inter-annual variability is fairly high, so that long time series, which

mostly are not available (Jonson et al. 2006), are needed to detect trends.

In the Czech Republic (CR), ambient air pollution has been perceived as a major environmental problem since the 1950s, particularly due to extremely high emissions of SO₂ and particulate matter from large power-generating sources (Moldan & Schnoor 1992). Pollution in the form of surface O₃ was recognized as an issue as late as in the 1990s. Its levels are regularly measured within the framework of a national ambient air quality network run by the Czech Hydrometeorological Institute (CHMI) since 1993. Ozone levels are relatively high, and the limit values (EC 2008) over vast regions are frequently exceeded (Hůnová 2003). Mean O₃ concentrations during the growing season at rural sites range between 30 and 45 ppb in years with low O₃ levels (as in 2001 and 2008) and between 35 and 60 ppb in years abundant in O₃ (as in 2003). Peak 1-h mean O₃ concentrations reached 110 ppb in 2003, 90 ppb in other years (Hůnová et al. 2010).

Based on long term real-time monitoring, we present an analysis of O₃ time trends and spatial variability with respect to its phytotoxic potential over Czech forests between 1994 and 2008. Out of the two approaches (concentration-based and flux-based) developed for O₃ risk assessment by UN/ECE (2004), we used the concentration-based approach and applied the exposure index AOT40. We are fully aware of increasing number of studies promoting the flux approach as more scientifically sound (e.g., Ashmore et al. 2004, Matyssek et al. 2007, Tuovinen et al. 2009) and of numerous criticisms of AOT40 concept and robustness (e.g., Sofiev & Tuovinen 2001). Moreover, O₃ stomatal flux based indexes are reported to outperform AOT40 for explaining the biological effects such as biomass reduction and leaf visible injury (Karlsson et al. 2007). From a practical point of view, however, it is obvious that the exposure index has the advantage of relative simplicity, and in regions which are not under stress by drought - which is generally the case of the Czech mountain forests - the areas at risk indicated by exposure index and stomatal flux are not likely to differ substantially. However, even in Japan, where annual precipitation is usually very elevated, the flux approach was recommended when VPD is a limiting factor to stomatal uptake (Hoshika et al. 2011). The AOT40 has an advantage of relatively simple calculation based on ambient O₃ concentration data, while modeling of stomatal flux is much more complicated (Tuovinen et al. 2009). Modeling of stomatal flux needs O₃ concentrations and data for stomatal conductance to be measured or modeled. In case the measured data are not available (which is the case for the CR), we are likely to intro-

Tab. 1 - Sites used for the analysis ranked according to decreasing altitude.

Country	Site Name	Site Identifier (ID)	Altitude (m a. s. l.)
Czech Republic	Churanov	1	1118
	Serlich	2	1011
	Krkonoše-Rychory	3	1001
	Prebuz	4	904
	Bílý Kríž	5	890
	Rudolice v Horách	6	840
	Hojná Voda	7	818
	Sous	8	771
	Cervena	9	749
	Primda	10	740
	Svratouch	11	735
	Jeseník	12	625
	Stitná n. Vlár	13	600
	Snězník	14	590
	Kostelní Myslova	15	569
	Košetice	16	535
	Kocelovice	17	519
	Ondřejov	18	514
	Valdek	19	438
	Kučarovice	20	334
	Tusimice	21	322
	Lom	22	265
	Mikulov-Sedlec	23	245
	Studénka	24	231
Poland	Snieżne Kotły	25	1490
	Czarna Góra	26	1133
	Czierniawa	27	645
	Jeleniów	28	244
Germany	Fichtelberg	29	1213
	Carlsfeld	30	896
	Zinnwald	31	877
	Schwarzenberg	32	787

duce large uncertainties into the calculation. The shortcomings encountered in modeling O₃ flux are discussed by Tuovinen et al. (2009).

Methods

Ozone data

For our analysis, we used the data measured within the framework of the nation-wide ambient air quality monitoring network operated by the Czech Hydrometeorological Institute (CHMI). Ambient O₃ monitoring over the CR has evolved significantly since its beginning in 1993. The number of sites within this network has largely increased from an original 16 in 1993 to 55 presently covering rural, mountain and urban areas (Ostatnická 2011). The ambient O₃ concentrations were measured by real-time analyzers (Thermo Environmental Instruments TEI, M49) using UV-absorbance, a reference method in the EC (2008). Standard procedures for quality control and quality assurance (EC 2008) were applied. We only considered sites with relatively large spatial representativeness, *i.e.*, those classified as rural according to the EoI classification (EC 1997). Overall, we used 24 Czech sites. For mapping purposes,

four additional German and four Polish sites were included (Tab. 1, Fig. 1).

Exposure index AOT40Forest

We analyzed the annual trends for selected

sites representing the principal Czech mountain regions (1. Churanov - the Sumava Mts., 3. Krkonoše-Rychory - the Krkonoše Mts., 5. Bílý Kríž - the Beskydy Mts., 6. Rudolice v Horách - the Krusné hory Mts., 8. Sous - the Jizerské hory Mts., 12. Jeseník - the Jeseníky Mts.), a regional site considered to represent the CR background (16. Košetice - the Czech-Moravian Highlands), and a regional site representing the relatively warm lowlands in Southern Moravia (23. Mikulov-Sedlec). For the assessment of ambient ozone phytotoxic potential for forests, we applied the AOT40 approach (Führer et al. 1997, UN/ECE 2004). The exposure index AOT40 was calculated according to eqn. 1 (see below). For practical reasons, we considered the daylight hours between 8 a.m. and 8 p.m. Central European Time (EC 2008).

$$AOT40 = \sum_{i \in V} \sum_{j=1}^n \sum_{k \in D} (c_{ijk} - p)$$

where c_{ijk} is the ground-level O₃ concentration measured in the i -th month, j -th day and k -th hour; p is the threshold concentration (40 ppb); V is a set of the months of the growing season (April-September); D is a set of daylight hours, defined as those hours with a mean global radiation of 50 W m⁻² or greater; and n is the number of days in the month.

We carefully checked the data coverage for calculating AOT40. When all possible data were not available for calculation of the AOT40 due to monitoring gaps (Tab. 2), we used the correction factor recommended by EC (2002 - eqn. 2):

$$AOT40_{(estimated)} = AOT40_{(calculated)} \cdot a/b$$

where a is the total possible number of hours, and b is the number of measured

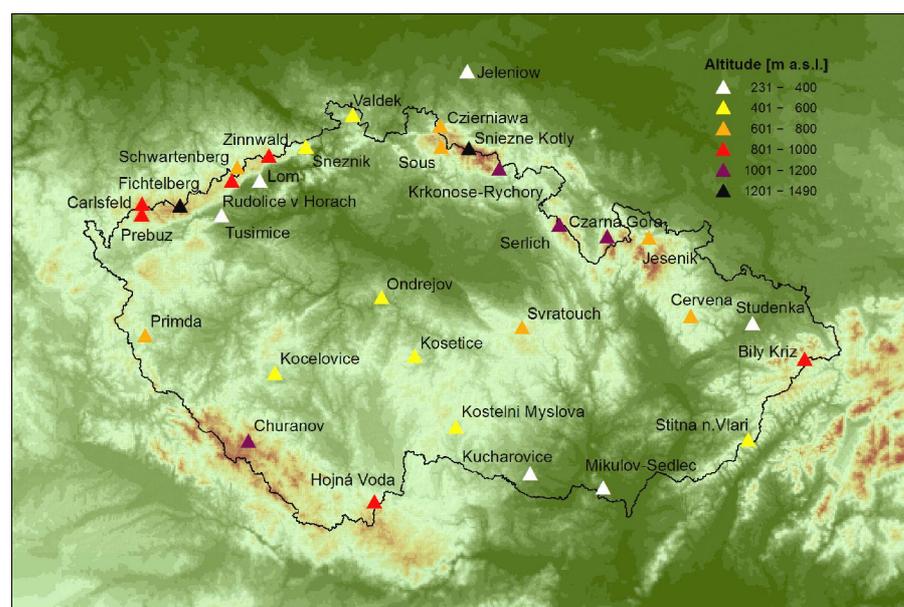


Fig. 1 - Sites with on-line monitoring of ambient ozone used for AOT40 mapping.

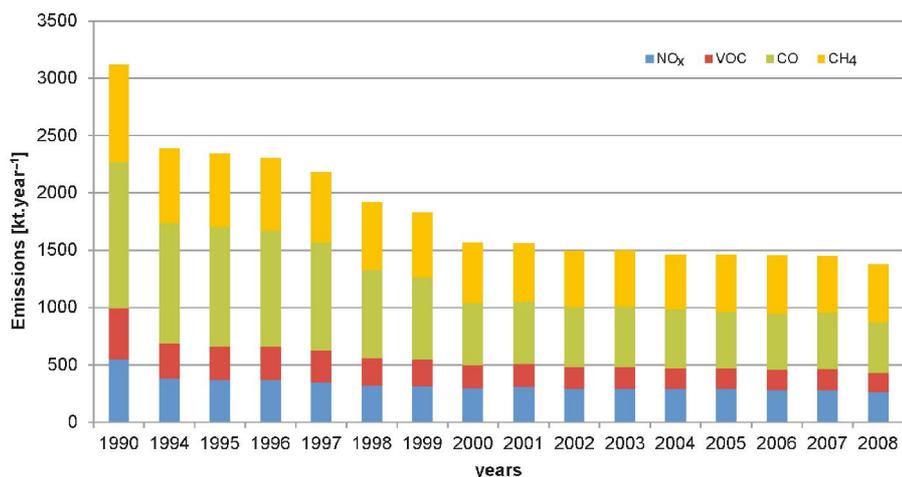


Fig. 2 - Annual emission of ozone precursors in the CR (source: CHMI).

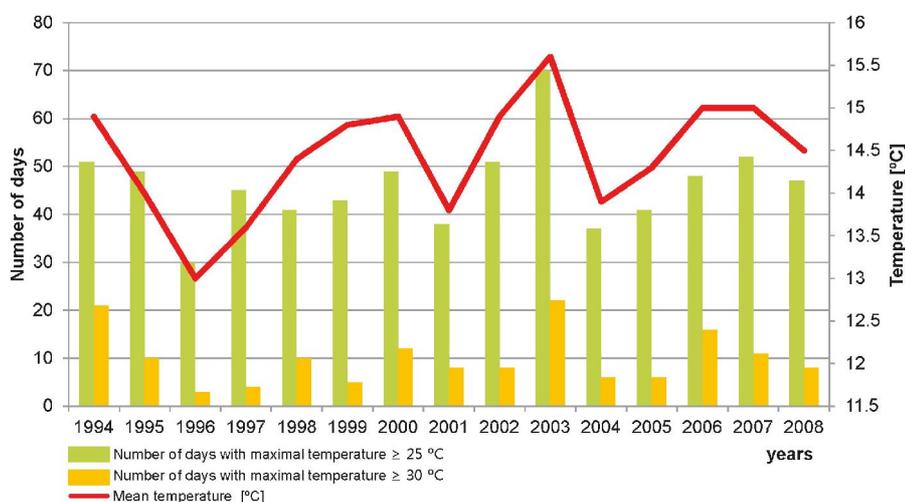


Fig. 3 - Average temperature for the CR (source: CHMI).

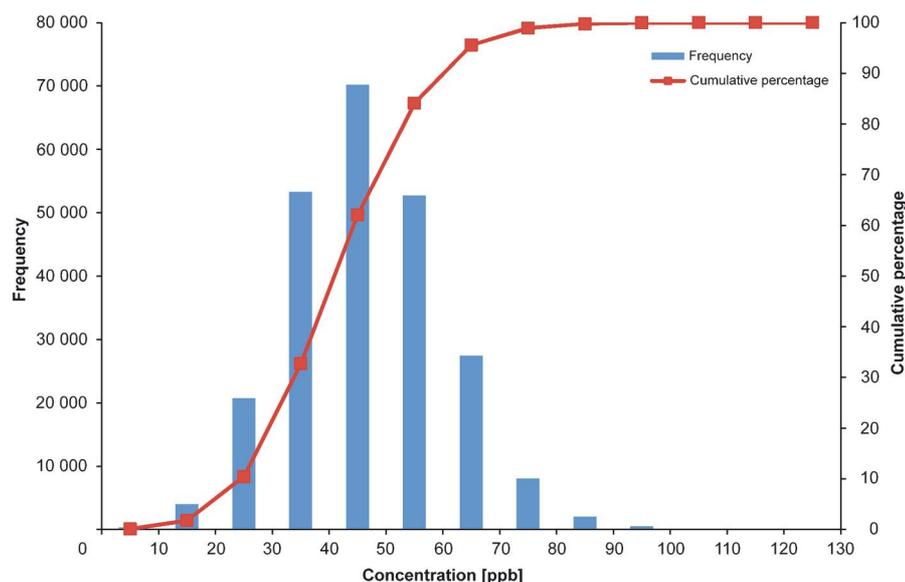


Fig. 4 - Histogram of 1-h mean O₃ concentrations at selected rural sites (indicated as 1, 3, 5, 6, 8, 12, 16, 23) in the CR, 1994-2008.

were taken from the Register of Emissions and Air Pollution Sources (REZZO), the Czech emission inventory database run by CHMI. REZZO includes information on anthropogenic sources of air pollution, both stationary (categorized as extra large, large, medium and local) and mobile (Ostatnická 2011). The data on emissions of CH₄ were taken from the National Greenhouse Gas Inventory Report (NIR) of the CR (Fott & Vacha 2011) and these include both anthropogenic and natural sources.

Temperature data

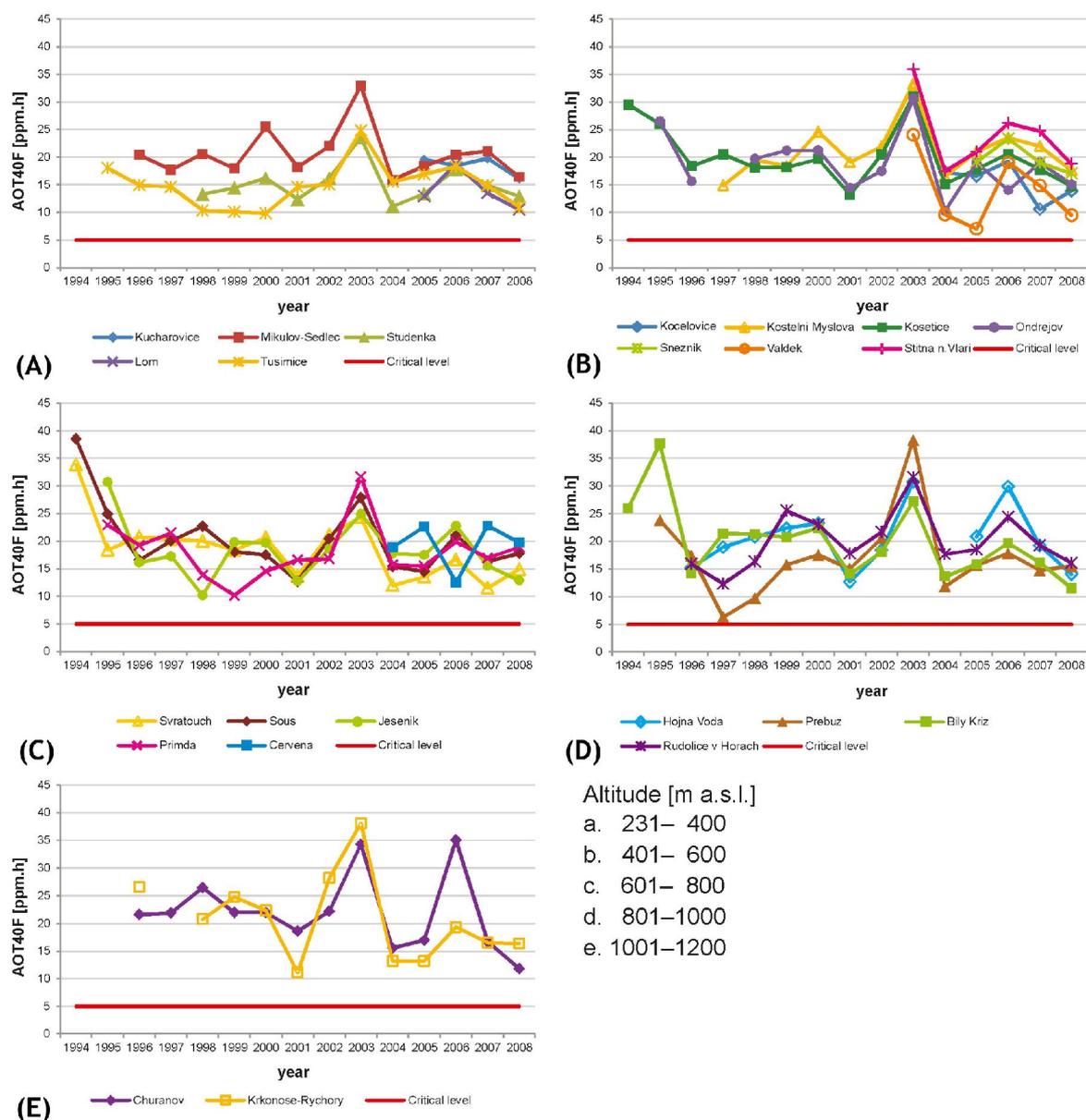
We used the data measured at climatological stations run by the CHMI. Manual climatic measurements were taken by a station thermometer in a standard thermometer screen 2 m above-ground at climatological observation times, *i.e.*, 7 a.m., 2 p.m. and 9 p.m. local mean solar time (LMST). Seasonal mean temperature was calculated based on daily mean temperatures. Daily mean temperature was calculated as an average of the temperatures at the observation times, where the evening observation was used twice. Seasonal mean temperature was calculated from all available stations which had records for the relevant year, *i.e.*, we used about 200 stations per year (Tolasz et al. 2007).

Results

Fig. 2 and Fig. 3 summarize the trends of factors which substantially influence ambient O₃ levels. Emission of O₃ precursors from Czech anthropogenic sources between 1990 and 2008 decreased by 52 % for NO_x, by 63 % for non-methane VOCs, by 65 % for CO, and by 42 % for CH₄. For the period under consideration, *i.e.*, 1994-2008, the emission of NO_x decreased by 30 %, non-methane VOCs by 47 %, CO by 58 %, and CH₄ by 23 %. Though somewhat hidden in a seasonal mean, the air temperature variability was fairly high. In 2003, for example, the temperature in the CR was 4 °C and 3.6 °C above the average in July and August, respectively.

The distribution of 1-h mean O₃ concentrations at selected rural sites (indicated as 1, 3, 5, 6, 8, 12, 16, 23 - see Tab. 1) in the CR for the period under consideration is summarized by a histogram showing that about 70 % of 1-h mean O₃ concentrations were above 40 ppb (Fig. 4). The AOT40 Forest trends for different altitudinal layers are presented in Fig. 5. The AOT40 values for Czech rural sites clearly show that the year-to-year variability was considerable. The critical level of 5 ppm·h (UN/ECE 2004) was exceeded every year at all Czech rural sites. In years with abundant O₃, the critical level was exceeded 5-7.5 times (2003). The highest AOT40 values were recorded at the Sous site (39 ppm·h in 1994), Prebuz and

Fig. 5 - AOT40 at rural sites in the CR, 1994-2008, at several altitudinal layers. Current critical level is 5 ppm·h AOT40Forest as set by UN/ECE (2004).



Tab. 4 - Average day of the year (DOY) when the critical level of 5 ppm·h was exceeded in the 1994-2008 growing seasons at selected rural sites.

Year	Site ID								Average
	1	3	5	6	8	12	16	23	
1994	-	-	5.5	-	-	-	16.5	-	10.5
1995	-	-	23.4	-	12.5	6.5	24.5	-	8.5
1996	21.4	17.4	-	27.4	21.4	26.4	2.5	28.4	26.4
1997	12.5	12.6	14.5	29.5	17.5	15.5	16.5	19.5	18.5
1998	10.5	25.5	9.5	-	8.5	21.6	12.5	10.5	20.5
1999	30.4	22.5	8.5	18.5	17.5	13.5	19.5	28.5	15.5
2000	7.5	30.4	4.5	6.5	7.5	5.5	7.5	7.5	5.5
2001	20.5	14.5	24.5	23.5	25.5	25.5	9.6	23.5	27.5
2002	9.5	7.5	14.5	14.5	12.5	17.5	17.5	21.5	14.5
2003	29.4	26.4	6.5	6.5	4.5	6.5	5.5	6.5	5.5
2004	26.5	31.5	27.5	31.5	1.6	13.5	7.6	30.5	28.5
2005	12.5	-	8.5	16.5	5.5	3.5	16.5	17.5	9.5
2006	18.4	6.5	8.5	12.5	7.5	5.5	10.5	10.5	8.5
2007	14.5	14.5	19.5	5.5	13.5	5.5	11.5	13.5	10.5
2008	17.5	13.5	3.6	21.5	14.5	16.5	25.5	30.5	22.5
Average	8.5	13.5	14.5	14.5	11.5	13.5	16.5	16.5	13.5

Krkonose-Rychory sites (38 ppm·h in 1994), and Bily Kriz (37.7 ppm·h in 1995) in the North. Apart from these mountain sites, fairly high AOT40 was recorded also in lower altitude at the Mikulov site (34 ppm·h in 2003).

The annual trend of AOT40 differed depending on the meteorological conditions. The critical level of 5 ppm·h was usually reached in the beginning of the growing season (Tab. 4), with few exceptions. As an example, we present the accumulation of AOT40 over the growing seasons 2003-2008 at two sites: a mountain site (3. Krkonose-Rychory) and a rural site situated at a medium altitude (15. Kostelni Myslova - Fig. 6). Rapid AOT40 rise was recorded in 2003, when the critical level of 5 ppm·h at the Krkonose-Rychory site was reached as early as before the end of April and at the Kostelni Myslova site in the beginning of May. Ne-

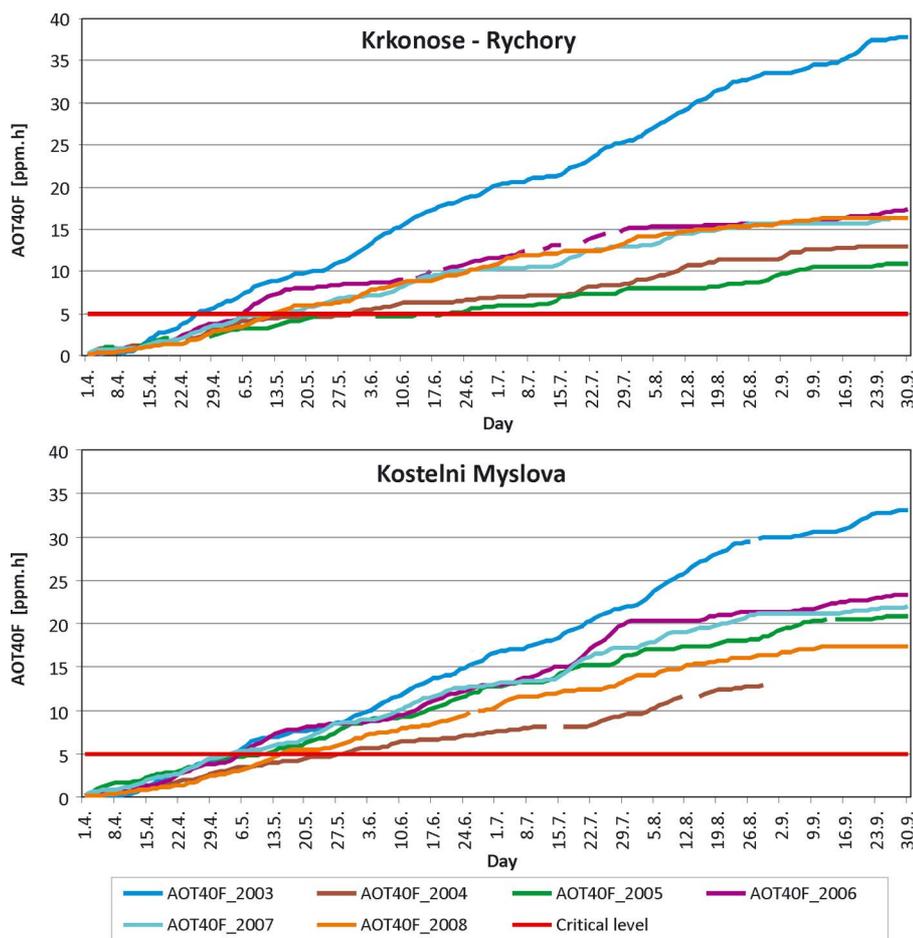


Fig. 6 - Annual trend of AOT40 at Krkonoše-Rýchory (1001 m a.s.l.) and Kostelní Myslova (569 m a.s.l.), 2003-2008 growing seasons.

vertheless, even in the years with meteorological situations not conducive to O_3 formation, the critical level of 5 ppm·h was usually reached during May.

Fig. 7 shows the spatial distribution of AOT40 in 2003 when the exceedances of 5 ppm·h were the highest ever recorded. The critical level was exceeded more than 6 times over one third of the Czech forested area. The highest values were recorded over the border mountains - the Krkonoše, the western part of the Krušné hory Mts., the Český les, the Sumava, and also inland over the Czech-Moravian Uplands (Českomoravská Vysocina) and the Brdy. Fig. 8 shows the spatial distribution of AOT40 in 2006 which belonged to the years abundant in O_3 (though lower as compared to the extreme year of 2003) as a consequence of a very warm and dry summer in Central Europe. In contrast to 2003, the relative share of forested area with AOT40 above 30 ppm·h was < 3%. The highest values were recorded in the South, in the Sumava and Novohradské hory Mts. Fig. 9 shows the year 2007 with even lower O_3 levels. Still, 78 % of the

Czech forested area experienced an exceedance of the critical level by a factor of 3-4.

Discussion

The crucial factors for ambient O_3 concentrations are emission of precursors and prevailing meteorological conditions. Solar intensity is of particular importance. Hot sunny calm weather leads to high O_3 concentrations. High temperature, high solar intensity, low wind speed, low atmospheric humidity and absence of precipitation are factors generally considered as favorable for photochemical O_3 formation (Seinfeldt & Pandis 1998). While anthropogenic O_3 precursor emissions in Europe have decreased (EEA 2007), the air temperature tends to increase. Observational evidence from all continents shows that many natural systems are being affected by regional climate changes, particularly temperature increases (IPCC 2007). For CR, Tolasz et al. (2007) reported a statistically significant temperature increase for the period 1961-2000: annual average temperature increases by $0.028 \text{ }^\circ\text{C year}^{-1}$ ($R^2 = 0.195$) and growing season average tempe-

rate increases by $0.025 \text{ }^\circ\text{C year}^{-1}$ ($R^2 = 0.151$). A similar trend is still observable and we can summarize that the average temperature in the CR increases by $0.3 \text{ }^\circ\text{C}$ per decade in the last 50 years (<http://www.chmi.cz>).

Ambient O_3 is a regional phenomenon and for its formation the emissions from broader regions are of importance. According to European Environmental Agency (EEA), emissions of the main ambient O_3 precursor pollutants have decreased significantly across the EEA region between 1990 and 2009 as follows: NO_x by 44 %, non-methane VOCs by 55 %, CO by 62 % and CH_4 by 27 % (EEA 2010). These estimates correspond with the trend in the CR, though the O_3 precursor emission decrease in the CR was even more pronounced as compared to the EEA region. Though the uncertainties associated with estimated emissions are relatively high, accounting for about 50 % for VOCs and CH_4 and 30 % for NO_x (De Leeuw 2002), the progress in reducing emissions is obvious. We have to keep in mind, however, that O_3 formation changes under differing NO_x and VOC regimes (Seinfeldt & Pandis 1998), and tropospheric ozone-forming potential differs for individual precursor gases (De Leeuw 2002).

There is a discrepancy between the substantial cuts in O_3 precursor emissions and observed non-decreasing annual average O_3 concentrations in Europe. Reasons include increasing inter-continental transport of O_3 and its precursors in the northern hemisphere, climate change, biogenic non-methane VOC emission, which are difficult to quantify, and natural fires (EEA 2010).

An inherent property of AOT40 as a cumulative index is that it is very sensitive to the quality of input data. For calculating AOT40Forest, O_3 concentrations were measured in real time, thoroughly checked and considered as highly variable; the calculated index, however, is not robust (Sofiev & Tuovinen 2001) and is likely to be burdened by high uncertainty. Consideration of the spatial scale is a crucial issue for air pollution mapping, as stressed by Diem (2003). A spatial resolution of $1 \times 1 \text{ km}$, as used in our mapping, is detailed enough, provides consistent results, and is considered appropriate for a country-scale mapping (Gottardini et al. 2010). The relative uncertainty of the AOT40Forest maps analyzed by cross-validation and expressed by the root mean square error (RMSE) was about 20 % as shown earlier by Hůnová et al. (2012) in a comparison of 11 different interpolation approaches for ambient O_3 mapping. The relative uncertainty of AOT40Forest maps is worse when compared to maps of seasonal mean O_3 concentrations, but it is still acceptable.

A similar approach for O_3 phytotoxic potential assessment based on O_3 concentra-

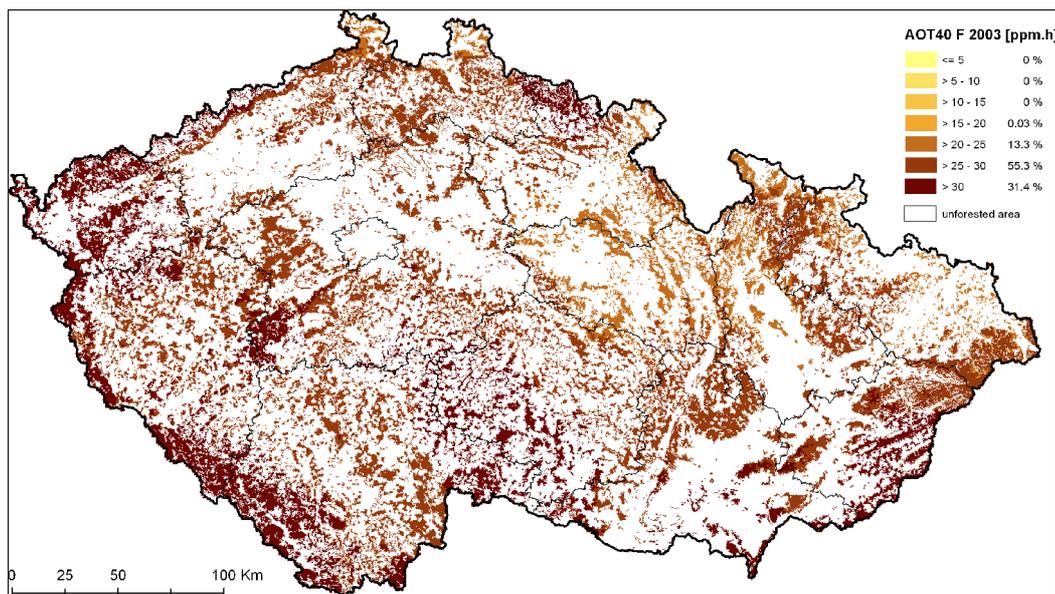


Fig. 7 - Spatial pattern of the AOT40 for forests, 2003.

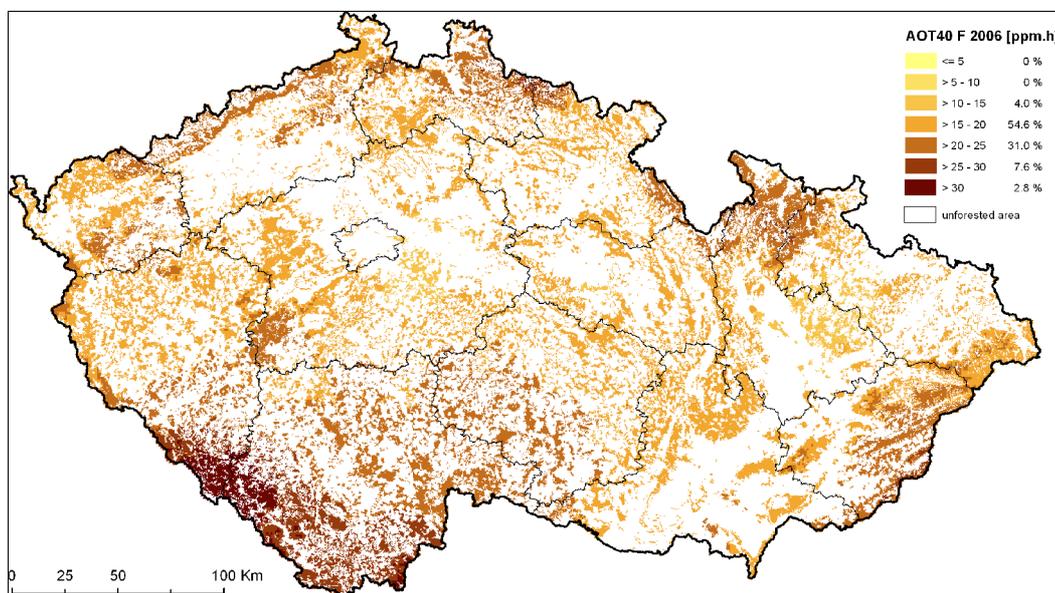


Fig. 8 - Spatial pattern of the AOT40 for forests, 2006.

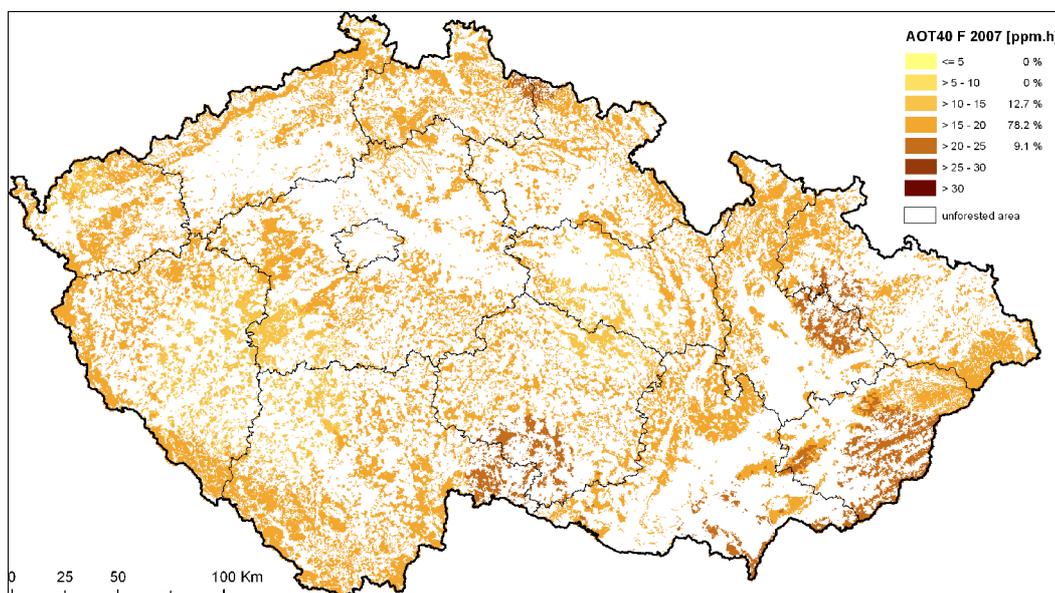


Fig. 9 - Spatial pattern of the AOT40 for forests, 2007.

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