x.1 Ground level ozone concentrations and exposures

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Tropospheric ozone (O_3) concentrations from passive samplers have been monitored according to harmonized methodologies on ICP Forests intensive monitoring (Level II) sites, starting in the year 2000. The objective of measuring the concentrations of ozone is to contribute to a better understanding of the actual exposure of European forest ecosystems to air pollutants. In particular, we aim to (i) quantify ozone concentrations over the course of the vegetation period (April-September), (ii) estimate the related ozone exposures of forest ecosystems, and (iii) detect temporal and spatial trends across Europe.

Passive sampling is the standard method for ozone concentration measurements adopted by ICP Forests (Schaub et al., 2010) and was verified by means of specific tests carried out in comparison with conventional monitors. It has been proven to be a valuable method at remote sites (e.g. Sanz et al., 2007; Gottardini et al., 2010; Hůnová et al., 2011) where the availability of electric power is often limited. By means of passive sampling, the determination of ambient air concentrations can be achieved at relatively low costs and with sufficient accuracy at the very forest site. Here, we analyzed the temporal and spatial trends for i) ozone concentrations (reported as volume:volume, in parts per billions, ppb) and ii) ozone exposure (reported as ozone Accumulated Over a Threshold of 40 ppb, AOT40) for the 2000-2013 period on Level II sites across Europe.

The results presented here are based on 18’362 measurements from 214 sites and the following 20 countries: Austria (AUT), Belgium (BEL), Cyprus (CYP), Czech Republic (CZE), Estonia (EST), France (FRA), Germany (DEU), United Kingdom of Great Britain (GBR), Greece (GRC), Hungary (HUN), Ireland (IRL), Italy (ITA), Latvia (LVA), Luxembourg (LUX), Poland (POL), Romania (ROU), Slovakia (SVK), Slovenia (SVN), Spain (ESP) and Switzerland (CHE). In these countries, methods have been applied according to the ICP Forests Manual, Part XV on Monitoring Air Quality (Schaub et al., 2010). For quality assurance, only data measurements within the period from 1 April until 30 September that are higher than 5 ppb and lower than 140 ppb (plausibility check) have been considered. As the exposure time of passive samplers differed from time to time and among sites, mean calculations were weighted according to exposure time. For trend analyses, the Sen's slope method (Sen 1968) plus Xuebin Zhang's (Zhang 2000) and Yue-Pilon's (Yue 2002) pre whitening approaches to determining trends in climate data have been applied according to Bronaugh (2013).

April-September mean ozone concentrations ranged from 23 to 64 ppb. A decreasing south-north gradient across Europe is apparent with the highest concentrations being measured in Italy, southern Switzerland, Czech Republic, Slovakia and Greece (Figure 1). An overall trend analyses, including all data from 20 countries and 2000-2013 reveals a significant decrease of 0.5 ppb per year (n = 18’362;

p = 0.000) (Figure 2). When considering only sites with a data coverage of at least 6 years and 120 days (66%) from 1 April until 30 September, site-specific trend analyses did not reveal any uniform pattern across Europe.Ozone exposures in terms of AOT40 (EU Directive 2008/50 CE) have been assessed according to Ferretti et al. (2012).Mean AOT40 for 2000-2013 ranged from 2 to 67 ppm h. The AOT40 threshold of 5 ppm h set to protect forests from adverse ozone effects was exceeded on 75% of the plots from 80% of the participating countries.

Conclusions

ICP Forests ozone concentration data from in situ passive samplers reveal an overall decreasing trend of 0.5 ppb ozone per year over the period 2000 to 2013. This slight decrease matches the findings in EMEP (2014) where 6-months modeled maximum values decreased by 0.1 - 0.5 ppb/year for the April-September period in most of Europe during 2000 to 2012. A number of studies of tropospheric ozone trends have been published in the last years, as summarized in Tørseth et al. (2012) and Simpson et al. (2014). A fairly consistent picture has been found by Logan et al. (2012), Parrish et al. (2012) and Derwent et al. (2013), with a flattening or even reduction in the ozone levels, most pronounced in summer. EEA (2014) however, reports that measured ground-level ozone concentrations have reduced only marginally or have even increased due to long-range transport of pollutants from outside Europe. The differing outputs from various trend reports demonstrate the difficulty of modeling ozone concentration trends, which underlines the great value of long-term air pollution measurements at the very forest site, also in view of model validation. According to EEA (2013) up to 2009, approximately 250 sites and 10 countries had continuous ozone monitoring data for the past 11 years. The ICP Forests database for ozone concentration contains data from 214 forested sites and 20 countries. Data series from 81 sites, however, could not be considered for trend analyses as their data coverage was smaller than 6 years. It is therefore crucial to extend the data series of ozone concentrations on the already established sites.

Measurement of air pollutants in forests is important in order to evaluate the risk for vegetation and to document spatial patterns, temporal variability, and trends in areas not covered by conventional air quality monitoring networks. The presented results demonstrate that passive sampling represents a cost-effective and reliable method. Given the dense coverage of 214 forest monitoring sites from 20 countries where ozone measurement is carried out together with several other measurements on forest health, growth, nutrition, biodiversity and climate, the potential of the ICP Forests ozone data set is unique. Follow-up studies will focus on trend analyses based on more extended data series, and studies on the relationship between ozone, ozone-induced symptoms, tree health, and growth. Ozone data may be combined with extensive meteorological data series to be applied and tested for ozone flux modeling, in comparison with the respective EMEP outputs.

Literature

Bronaugh D (2013) Zhang + Yue-Pilon trends package, package 'zyp', http://cran.r-project.org/web/packages/zyp/zyp.pdf

Derwent RG, Manning AJ, Simmonds PG, Spain TG, O'Doherty S (2013) Analysis and interpretation of 25 years of ozone observations at the Mace Head Atmospheric Research Station on the Atlantic Ocean coast of Ireland from 1987 to 2012, *Atmospheric Environment* 80:361–368.

EMEP (2014) Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. EMEP Status Report 1/2014.

EEA (2014) Progress on resource efficiency and decoupling in the EU-27, EEA Technical report No 7/2014, European Environment Agency, Copenhagen, Denmark.

EU Directive 2008/50 CE of the European Parliament and Council of 21 May 2008 on ambient air quality and cleaner air for Europe. Official Journal of the European Union. 11 June 2008. L152/1–L152/44.

Ferretti M, Cristofolini F, Cristofori A, Gerosa G, Gottardini E (2012) A simple linear model for estimating ozone AOT40 at forest sites from raw passive sampling data. *J. Environ. Monit.* 14(194):2238-2244.

Gottardini E, Cristofori A, Cristofolini F, Ferretti M (2010) Variability of ozone concentration in a montane environment, northern Italy. Atmospheric Environment 44:147-152.

Hůnová I, Matoušková L, Srnenský R, Koželková K (2011) Ozone influence on native vegetation in the Jizerske hory Mts. of the Czech Republic: results based on ozone exposure and ozone-induced visible symptoms. Environmental Monitoring Assessment 183:501-515.

Logan JA (1999) An Analysis of Ozonesonde Data for the Troposphere: Recommendations for Testing 3-D Models, and Development of a Gridded Climatology for Tropospheric Ozone, *J. Geophys. Res.* 104:16115-16149.

Sanz MJ, Calatayud V, Sanchez-Peña G (2007) Measures of ozone concentrations using passive sampling in forests of South-Western Europe. *Environmental Pollution* 145(3):620-628.

Parrish DD, Law KS, Staehelin J, Derwent R, Cooper OR, Tanimoto H, Volz-Thomas A, Gilge S, Scheel HE, Steinbacher M, Chan E (2012) Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes. *Atmospheric Chemistry and Physics* 12(11):485-11 504.

Schaub M, Calatayud V, Ferretti M, Brunialti G, Lövblad G, Krause G, Sanz MJ (2010) Monitoring of Air Quality. 13 pp. Part XV. In: Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. UNECE, ICP Forests Programme Co-ordinating Centre, Hamburg. ISBN: 978-3-926301-03-1. [http://www.icpforests.org/Manual.htm]

Sen PK (1968) Estimates of the Regression Coefficient Based on Kendall's Tau. *Journal of the American Statistical Association* 63(324):1379-1389.

Yue S, Pilon P, Phinney B, Cavadias G (2002) The influence of autocorrelation on the ability to detect trend in hydrological series. *Hydrological Processes* 16:1807-1829.

Zhang X, Vincent LA, Hogg WD, Niitsoo A (2000) Temperature and Precipitation Trends in Canada during the 20th Century. *Atmosphere-Ocean* 38(3):395-429.

Figures

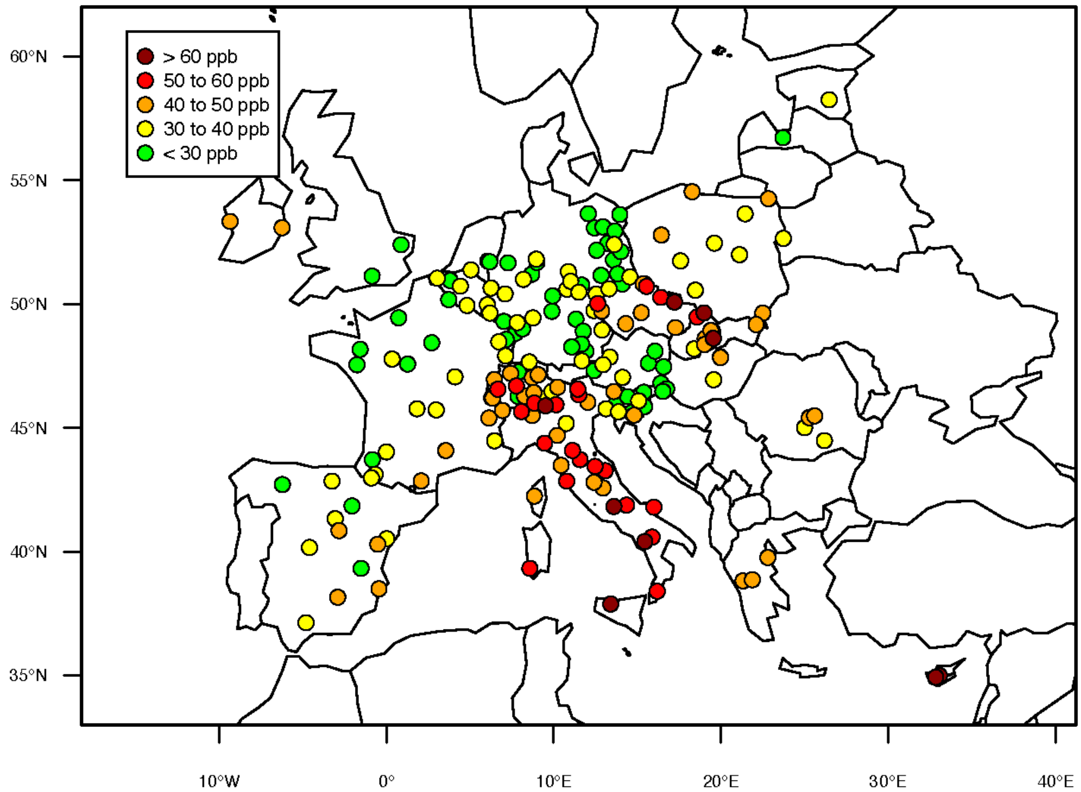

Figure 1. Mean ozone concentration classes from passive samplers on 214 plots during 2000-2013.

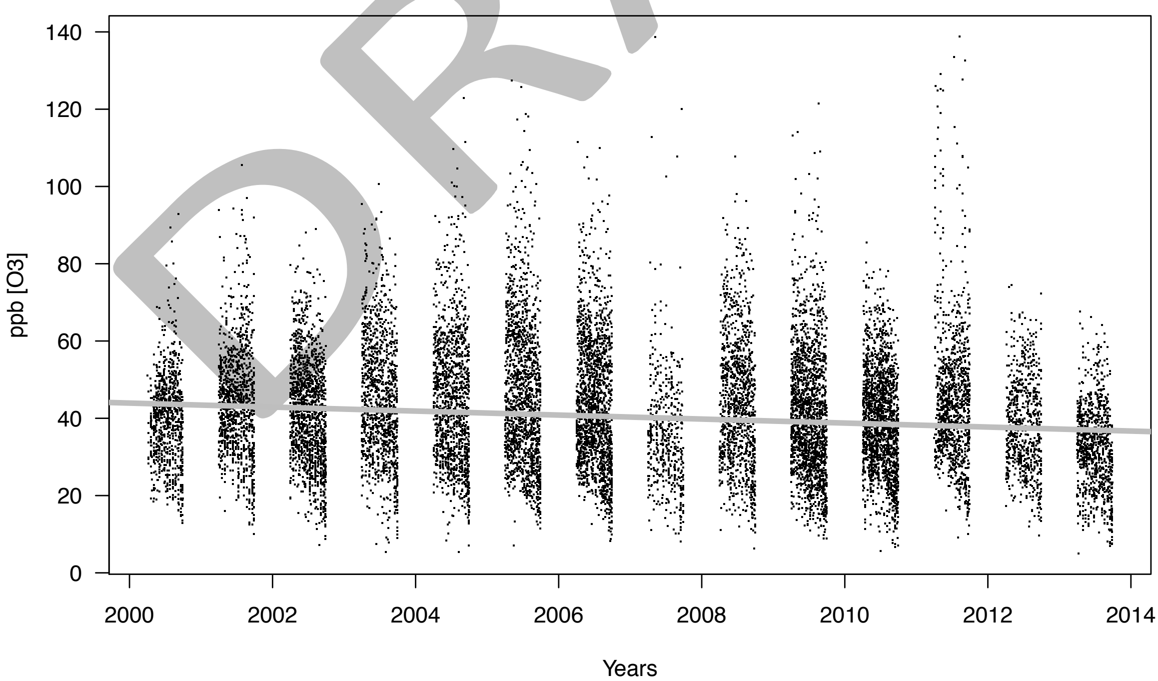

Figure 2. Scatter plot for ozone concentration from passive samplers exposed in 20 countries from 2000 until 2013 with a significant decrease of 0.5 ppb/year (n=18'362; p=0.000).