THESES OF DOCTORAL DISSERTATION

MEASURING AND EXAMINING SURFACE OZONE IN HUNGARY

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Introduction

Besides natural components there are several other substances in the air that can be categorized as air pollutants. Although surface ozone can naturally be found near the surface, we normally categorize it as an air pollutant above a certain level of natural concentration due to the fact that ozone develops from primal air pollutants (NOx, NMVOC, CO) in a photochemical way, as it has unwanted effects.

The aim of my dissertation is to provide a short historic and general overview of the results and effects of the researches of the natural and anthropogenic production of ozone; to give a general outline on the European legislative and measuring environment; to give an overview of the Hungarian circumstances of measuring ozone by evaluating the Hungarian situation of the transgression of general and warning thresholds and finally to reveal the difficulties and to evaluate them.

In the second part of my dissertation I introduce the history and results of the historical ozone measurements of the 19th-century in Szeged together with the introduction of the latest results of ozone measurement in the 20-21st centuries; I describe the challenges of ozone measurement, followed by the evaluation of data between 1997-2003 in a sequence based on occurrence and the values of higher ozone concentration. Based on the above I would like to

outline status of air pollution of the “City of Sunshine“ on the banks of the river Tisza.

Based on a passive sampler method, my thesis tries to find an answer to how relevant the data provided by an ozone monitor operating in Szeged may be for the whole city, following this I describe the future challenges and opportunities of surface ozone research which will set the direction for my future work.

My doctoral thesis is connected to the research on city-ecology conducted by the Department of Physical Geography and Geo-infomatics in Szeged and—based on the results achieved—aims at improving the ecological standards of the city.

Methods applied

By providing data of certain monitoring stations I demonstrate the extent how much air pollution depends on different criteria e.g.: the typical daily and annual patterns, weather conditions, primal air pollutants (their level and composition), transport processes, environmental decomposition and many other factors. First I evaluate the long trends and fluctuations of the data from Hungarian measuring stations (1997-2003) based on the monthly average and on the excess of the threshold limit value for human health in the light of their volume and value. I also present some data discrepancies of some measuring stations.

I compared and evaluated the long-term trends and fluctuations of the data from Hungarian measuring stations (1997-2003) based on the monthly average and the transgression of threshold limit value for human health in the light of their occurrence and value.

By transforming the ozone occurrence values measured in Szeged from 1853 into the values used nowadays, by using potassium-starch reagent slips as described at the beginning of paragraph 8—which was possible by using the Pavelin correction diagram developed in the 20th century and showing the correlation between air humidity and the change in colour of the paper slip—I managed to compare the past and present figures for Szeged. Of course, the data received originate only from qualitative and/or semi-quantitative measurements. Despite this fact they are extremely valuable, as this is the only method that can by relied on for ozone values before the age of industrialisation.

Finally I introduce the measurements made in par with ozone monitoring between May and July 2000 at 30 different points of Szeged by using so called "indigo" passive monitors, or SAM (Surface Active Monitoring) procedure.

I defined the quantity of the yellow isatine - deriving from the decomposition of the blue indigo as a result of the oxidizing effect of ozone, collected in the samples every 5 days for examination, after dissolving it in alcohol - by a photometric method. For this examination it was necessary to have a constant measuring device

in addition to the passive sampler, as the data collected in the photometric way are only so-called concentration-graded extinction values. By "authorizing" these parallel values I was able to calculate real values of $\mu g/m^3$ comparable with the extinction figures of the monitors of the other measuring points.

Results and conclusions

The first surface ozone observations were made in Hungary in the middle of the 19th century applying the Schönbein-method. After this similar research activities were launched in the country in the mid-1980's.The first monitoring station was put into operation in 1990, and after the deployment of equipment within the framework of the PHARE and JICA programmes, new OMSZ and KÖFE measuring stations were established as an extension to the monitoring network.

In total surface ozone measuring in Hungary was carried out - after completing the development in 2003 - in 50 places. The data originating from two of these stations - one regional background station and one transport station (urban background station in European registration) - are forwarded to the European Office of Environmental Protection.

During measuring activities there are a number of problems connected with calibration, validation and information technology, which have an impact on the quality of the data.

Summarizing my evaluations it can be stated that in Hungary periods with extremely high values generated by the photo-oxidants occur once or twice a year in clearly visible episodes ranging from a couple of days to a couple of weeks between May and September depending on the weather.

Based on the research data we can conclude that the really high values (above 200 µg/m³) can be detected only very rarely and for a short period of time in Hungary. Values above this threshold were measured more frequently only in ozone-rich years (1997, 1998, 2003). 30-minute periods of extremely high concentration over 240 µg/m³ are detected very rarely. Out of the 14 years examined this phenomenon is detected only in 5 years, and even in these years the annual average amounts only to a period of 1-5 hours. This means that--based on the data of the measuring networks--ozone smog has not built up in Hungary so far.

Based on the evaluation of these data we can expect a rather high ground-level with exceeding peaks occurring only rarely. In Hungary, the highest ever air pollution by ozone was measured at 292 µg/m³ in 1998 in Oszlár.

In every few years when the weather is extremely hot for a longer period of time over Western Europe combined with the right macrosynoptic situation there are ozone episodes, smog situations

measured in many locations at different levels. During these periods the ozone level measured in Hungary is also higher than the usual values. The high values of ozone measured in Western und Southern Europe (300-400 µg/m³) have not been captured in Hungary yet; possibly as a result of the different air pollution levels.

The new EU directives (2002/3/EG) to be introduced in Hungary by mid-2004 as part of the harmonisation of legislation to EU standards will dictate a lower smog threshold. With a view to this and to the fact that the measuring stations were upgraded and extended in 2003 we have to face the possibility of smog alerts depending on the weather conditions.

In the 19th century ozone, and in this connection "the forest air thick with ozone" had positive connotations, and were regarded to have a positive influence on the general state of human health. However, for some time we have been aware of the fact that this gas—when near to the surface and depending on its concentration—does not exclusively have positive effects. According to the observed figures in the old Szeged in the 19th century the level of ozone was balanced, there were no such enormous differences between the summer and winter concentrations as we can witness today. The monthly averages used to be in the interval between 10-14 ppb. While the monthly average figures at the beginning and at the end of the year were

similar even after 150 years, by the late 20th century and early 21st century the ozone quantity of the summer months has risen by nearly 200 % of the original value.

The Szeged-measuring station established in 1997 can be characterised as a traffic station, but based on the monthly average of the data it provides, it is mainly described as an urban background station. Its annual averages and the averages of the six months of the none heating season are lower than the concentration captured on urban background and rural background stations, however, it follows their trends. This trend in Szeged can also be described by a weak but increasing pattern.
Based on the data of the 7 years of research we can conclude that the most frequently occurring data exceeding the previous threshold limit for human health are between 110-140 µg/m³. These are prevalent in relatively many hours (total 1162 hours) of the day, and nearly in every hour, though to varying extent.

Occurrences above these categories are less frequent and cover shorter periods. During these 7 years values between 140-160 µg/m³ were captured 190 times and values between 160-180 µg/m³ 50 times. Values above 180 µg/m³ were captured only 3 times for hourly average values. The really high concentration periods are between 3-6 pm.

However, days with concentration between 110-160 µg/m³ occur quite frequently. If we compare this frequency to the data captured in other measuring stations in Hungary we can see that during the May-August period there are simultaneous occurrences in Laborc street in Budapest, K-Puszta and Szeged.

It can also be observed that-- for some reason--other simultaneous occurrences of threshold transgressions or ozone episodes in other European countries or in several parts of Hungary cannot be detected in Szeged, or if so, only with very low values.

Most of the days exceeding the threshold (i.e. when the most 30-minute periods occurred with concentration-values higher than the previous threshold limits for human health) occurred in 1998, with 63 days, and the least occurrence was 22 days in 2000. 1998 is a record setting year in terms of the number of exceeding hours and 30-minute periods too, with 351 hours (680x 30-min periods). All these data are only for information.

The highest surface ozone value to the hour measured in Szeged was 188,5 µg/m³ in September 2003. The highest 8-hour average – the new threshold value for human health – was captured on 9th August 2003 at 168,9µg/m³. However, we should not forget that due to the gaps in data availability these ozone concentration values might not have been the absolute records in Szeged.

When evaluating the ozone data by the direction of the wind it is clearly visible that values exceeding 160µg/m³ do not occur from an east-south-east and south-west direction, and they occur in a minimum amount from the two neighbouring sectors, too. This means that if the wind blows from the direction of Kossuth L. avenue at the monitoring station, high concentration values will not occur, which demonstrates how heavily traffic can influence monitoring stations.

Based on the above example—among others—the question has arisen whether we can doubt the relevance of the data provided by some stations, given that they are registered at EEA as urban background stations. In reality, these stations are based next to roads with heavy traffic and their data cannot be relevant to the whole of the city. The average air pollution by ozone and the captured exceeding of threshold at these stations and at other parts of the city might be very different.

Based on my research with passive measuring, 12 monitoring points out of 31 in Szeged were characterized by loading values higher than the ones measured by the monitor, i.e. 38.7 % of the stations. Here the multiplier of 1,1-1,7 was valid, meaning that the loading of these places with ozone is higher by 10-17 % on average compared with the values of the monitor. (see Figure 1, last page) I found 4 stations with extinction averages (resulting from the total period) similar to the monitor figures. Lower than

the monitor figures were recorded at 48,4 % of the stations, i.e. at 15 stations, where the figures showed 60-90 % of the monitored values.

Based on the research results I arrived at the following conclusions. Firstly: the monitor would not have been better situated in the Széchenyi square - where the measuring container was originally planned to be placed in 1997 - this can be charaterized by the multiplier 0,8 shown in the experiement. Secondly: on drawing up the reconstruction plan and the smog alert scheme - to be made under consideration of the urban loading - it must be considered that the values recorded by the monitor can be regarded only as mid-values. With this modification the monitor data used by the Authority of Environmental Protection can be usefully applied, however, it must be drawn under consideration that - based on the above - the highest values of ozone in the city may considerably surpass the values known so far.

In the final part of my thesis I enumerate the future tasks relating to surface ozone and point out the necessary fields and related directions of activities.
Additionally I publish the results of my ozone-related survey made also in Szeged in 2000 among the inhabitants of the city and reflecting the necessity of awareness-building activities with a view to greater sensibility of the topic and showing some evidence of the lack of the above.

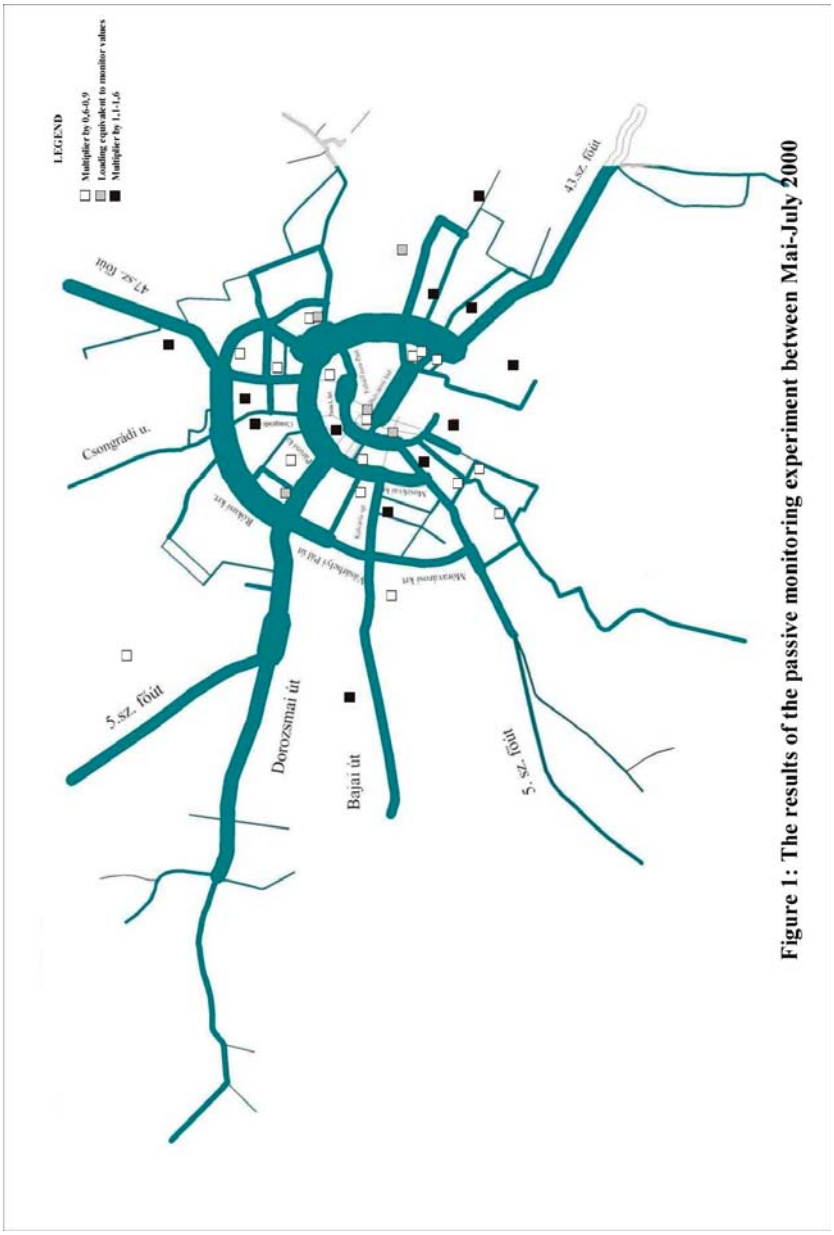

Figure 1: The results of the passive monitoring experiment between Mai-July 2000

List of articles published and being published on this topic

Divéky, E. (1999.): Bodennahe Ozonmessungen in Ungarn – Probleme und erste Ergebnisse Poszter Berner Ökotag (Berni Ökológiai Napok) - 1999. május

Divéky, E. (1999.): Bodennahes Ozon – Probleme und Aufgaben der Messungen, der gesetzlichen Regelungen und Bewertung in Europa, Deutschland und Ungarn - Reihe Bausteine No. 5. pp 43 Selbstverlag des Institutes für Didaktik der Geographie, Frankfurt am Main 1999.

Divéky, E. (1999.): Felszínközeli ózon Magyarországon – Geográfus Doktoranduszok IV. Országos Konferenciája Szeged, 1999. Október 22-23. - A természet- és társadalomföldrajzi szekcióban elhangzott előadások JATE TTK Földrajzi Tanszékcsoport, Szeged

Divéky, E. (2000.): Surface Ozone in Hungary – ACTA Geographica Szegediensis Tomus XXXVII. 109-116.

Divéky, E. (2003.).: Ózonmérés Szegeden a XIX. században - Légkör XLVIII. évf. 2003/4. 30-35.

Divéky, E. (2004.).: Bioindikátorok alkalmazása a felszínközeli ózon kimutatásában - Földrajzi Közlemények - elfogadva

Divéky, E. (2004.).: A felszínközeli ózon vizsgálata Szegeden – Városökológiai tanulmányok Szeged példáján – megjelenés alatt