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Ozone pollution and its bioindication

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1. Introduction

Triplet oxigen is a highly reactive molecule. Naturally it arises in the stratosphere, but it can as well develop through the chain reactions of photochemical smog in the troposphere. Photochemical smog occurs in highly polluted urban and industrial areas in the presence of high solar radiation. Ozone develops in the reaction of oxygen molecules with the singlet oxigen splitting off from nitrogen-oxides in the presence of UV-radiation. This reaction is quick and reversible, so the formation and degradation of ozone show steady-state balance (Crutzen et al., 1994). However, if there are hydrocarbons emitted in the atmosphere of a certain area, these will change the chemical reactions, interfering ozone to transform back to oxygen molecules. Thus, the quantity of ozone serves information about the quality and the components of photochemical smog. If nitrogen-oxides overweigh, after reacting with them, ozone dissolves again. Therefore in many cases the concentration of tropospheric ozone increases far away from the most polluted areas. Volatile organic compounds can also cause imbalance resulting ozone accumulation. Ozone and its precursors can float hundreds of kilometers from their sources and its formation often happens only during its moving with air masses. Since there are less chemical reagents by which its dissolution takes place far from the cities, the amount of ozone above cities is relatively small while passing away from urban areas this amount is gradually growing. Thus, ozone virtually originating from cities endangers natural vegetation and cultivated plants (Lorenzini and Saitanis, 2oo3).

Ozone effects cultivated plants in a short-term as well as in a long-term way. Visible symptoms and impairment of the photosynthetic efficiency can be named as short-term effects, while in a long term, in particular when high ozone concentrations frequently occur, it causes decrease in growth and yield, and leads to premature senescence. (Harmens et al., 2006).

The significance of ozone pollution and its effects has been clearly verified by several studies:

Ozone concentrations exceed the phytotoxic thresholds specified by the European Council all over Europe, and this amount grows by 5-20% per year (Sandermann et al., 1998).

Ozone reduces crop yield and biomass of sensitive species, and affects the crop quality (Hayes et al, 2007).

Based on the ozone levels of the year 2000, ozone induced yield losses for 23 crops in 47 European countries were estimated to be €6,7 billion per year (Holland et al., 2006).

Ozone reduces plant's Net Primary Production and the Net C Exchange thus increasing the C losses from different cropping systems; increases CO_2 emissions, crop nitrate loss and groundwater nitrate pollution. Several natural plant communities proved to be potentially ozone-sensitive (Mills et al., 2007). In natural oecosystems, in addition to the above mentioned effects, ozone can change the species composition causing similar changes in animal species composition as well (Fagnano and Maggio, 2008).

Thus, detection of phytotoxic levels of ozone and examination of its effects on sensitive plant species is highly important in economical as well as in environmental regards.

2. Ozone in the troposphere

2.1 Formation of ozone

The short wave radiation of solar spectrum is entirely absorbed by stratospheric ozone and molecular oxygen. The infrared part of the spectrum is mostly absorbed by water vapour and carbon dioxide and some other greenhouse gases. Photochemistry in the troposphere is therefore driven by radiation with wavelengths between 300 and 600 nm (Seinfeld and Pandis,1998).

Photooxidants are compounds formed by the oxidation processes of tropospheric gas phase chemistry. They include ozone and other compounds such as HNO_3, PAN and aldehydes.

Gas phase chemistry in the troposphere (as well as in the stratosphere) includes a variety of reactions that can be viewed as the reactions of a radical reaction chain which consists of the following type of reactions:

1. Initiation reactions: Photolysis of certain molecules (ozone, HCHO, HONO, NO_2), producing reactive radicals (O, OH, HO_2). HO_2 is also converted to OH, which is very reactive, oxidizing most gaseous (reactive) compounds. Thus, OH radicals determine the oxidation capacity of the troposphere, and they are called as the „cleansing agent" of the troposphere.

2. Propagation or radical chain: The very reactive radicals produced by the initiation reactions react with most molecules, causing sequences of radical reactions in which the same radicals are formed again, leading to a radical chain, e.g. one chlorine radical formed from one $CFCl_3$ depletes not only one O_3 but many O_3 molecules since Cl is reformed by the reaction of ClO with O.

3. Termination: If two radicals react with each other, less reactive non radical species can be formed. These reactions stop the radical chain.

(The molecules formed in the termination reactions can be activated again or different radical chains can interact with each other.)

There are two (connected) types of radical chains in tropospheric gas phase chemistry:

1. The NOx radical chain includes no initiation reaction. The nitrogen oxides (NOx: NO + NO_2) enter the system mainly by emissions from fuel combustion. NO_2 is the precursor of tropospheric ozone.

2. The members of the ROx/HOx radical chain reaction system are produced by photolysis.

These two radical chains are connected.

The radical yield of the reaction system is limited by the termination reaction which can include RO_2 and/or HO_2 radicals (forming peroxides), or OH and NO_2 (forming HNO_3). This latter termination reaction links the NOx and the ROx radical chains. This kind of termination is more important in strongly polluted air.

The oxygen atoms produced by the photolysis of NO_2 react very quickly with molecular oxygen, forming ozone. Ozone in turn reacts very quickly with NO to form NO_2 again. During sunlight these reactions form equilibrium called photostationary state, and this state is reached within minutes.

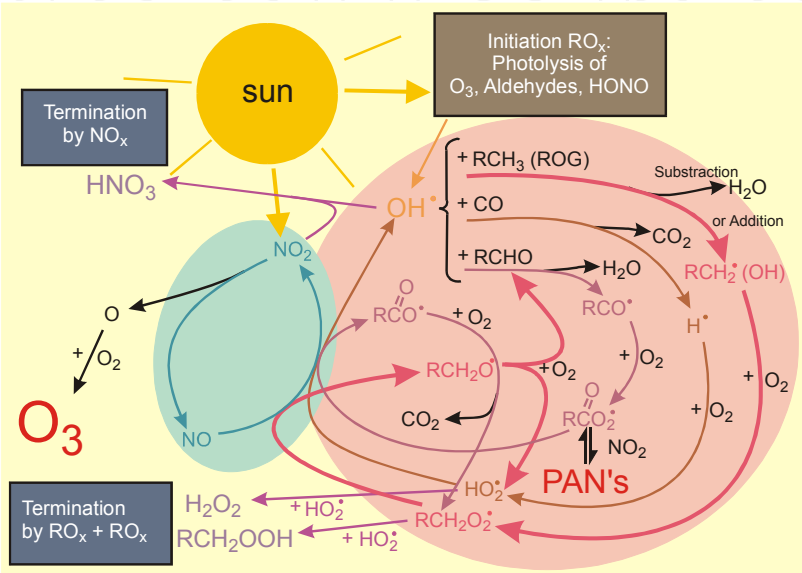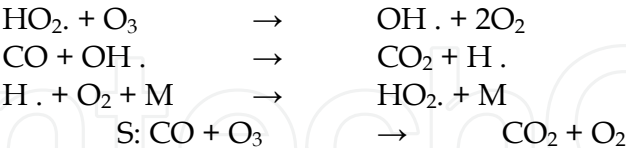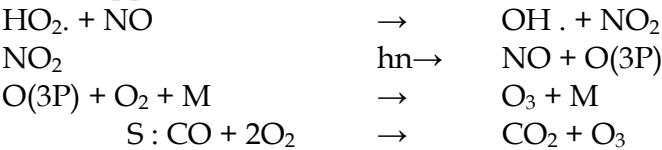There is no net O_3 production in the photostationary state.

Fig 1. Overview of photochemistry in the polluted planetary boundary layer (from Staehelin et al., 2000)

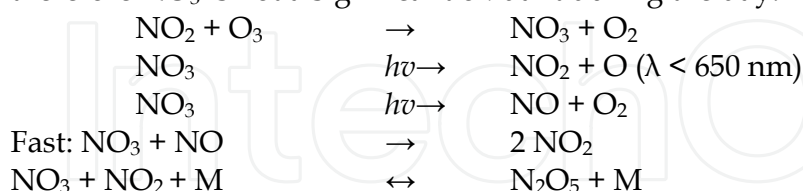In case of very low NOx concentrations ozone is chemically destroyed.
NO less than 10 ppt:

$$HO_2. + O_3 \rightarrow OH. + 2O_2$$
$$CO + OH. \rightarrow CO_2 + H.$$
$$H. + O_2 + M \rightarrow HO_2. + M$$
$$S: CO + O_3 \rightarrow CO_2 + O_2$$

Typically, NO concentrations need to be larger than around 10 ppt for the dominance of the reaction of HO_2 with NO leading to O_3.
NO more than 10ppt:

$$HO_2. + NO \rightarrow OH. + NO_2$$
$$NO_2 \xrightarrow{hn} NO + O(3P)$$
$$O(3P) + O_2 + M \rightarrow O_3 + M$$
$$S: CO + 2O_2 \rightarrow CO_2 + O_3$$

The dominance of the reaction channel of HO_2 depends on NO as well as on O_3 concentrations.
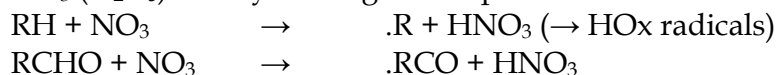
Organic chemistry in the troposphere is very complex (e.g. the reaction of alkenes with O_3 is an additional source of HOx). Precursors of ozone (NOx, Volatile Organic Compounds and CO) can be of anthropogenic or biogenic origin.

NO_3 is produced from reaction of NO_2 with O_3. This reaction also proceeds during day, but NO_3 is rapidly photolysed because of its strong absorption in the visible spectrum and therefore NO_3 is not a significant oxidant during the day.

$$NO_2 + O_3 \qquad \rightarrow \qquad NO_3 + O_2$$
$$NO_3 \qquad h\nu\rightarrow \qquad NO_2 + O \; (\lambda < 650 \text{ nm})$$
$$NO_3 \qquad h\nu\rightarrow \qquad NO + O_2$$
$$\text{Fast: } NO_3 + NO \qquad \rightarrow \qquad 2\,NO_2$$
$$NO_3 + NO_2 + M \qquad \leftrightarrow \qquad N_2O_5 + M$$

In the absence of sunlight, e.g. during night, no photolysis reactions take place. However, some gas phase oxidation still can proceed via the NO_3 radical.

NO_3 (N_2O_5) loss by heterogeneous processes:

$$RH + NO_3 \qquad \rightarrow \qquad .R + HNO_3 \; (\rightarrow \text{HOx radicals})$$
$$RCHO + NO_3 \qquad \rightarrow \qquad .RCO + HNO_3$$

During night, NO_3 is a strong oxidant reacting with some organic compounds in a similar way as OH radicals, but only with specific compounds. NO_3 quickly reacts with NO and NO_2 which limits NO_3 concentrations.

Thus, the main oxidant agent in the presence of solar radiation is OH (its concentration strongly depends on pollution level, but it is around 10^6 cm^{-3}). In absence of solar radiation, main oxidant is NO_3 (concentrations move around 5×10^8 cm^{-3}).

A few compounds (e.g. some reactive alkenes) can be oxidized by O_3 (with mean concentration approximately of 10^{12} cm^{-3}) both during day and night, but only under specific conditions.

Typical sequence of chemical regimes of an air parcel loaded by ozone precursors:

1. Photostationary state: decrease in ozone by reaction with NO.
2. VOC-limitation: O_3 production increases with increasing VOC concentrations. In urban environments NO_2 concentrations are usually that large that HNO_3 formation dominates the reactions of OH radicals, which implies that local O_3 production is small.
3. Transition regime: maximum ozone production. When NO_x concentration is decreasing steadily the mixture of organic vs. NO_x concentration passes through a state in which the ratio of ozone precursor concentration is such that local O_3 production maximizes.
4. NO_x-limitation: When NO_x concentration is decreasing further, local O_3 production rate becomes limited by the availability of NO_x. Such conditions usually occur in rural environments.
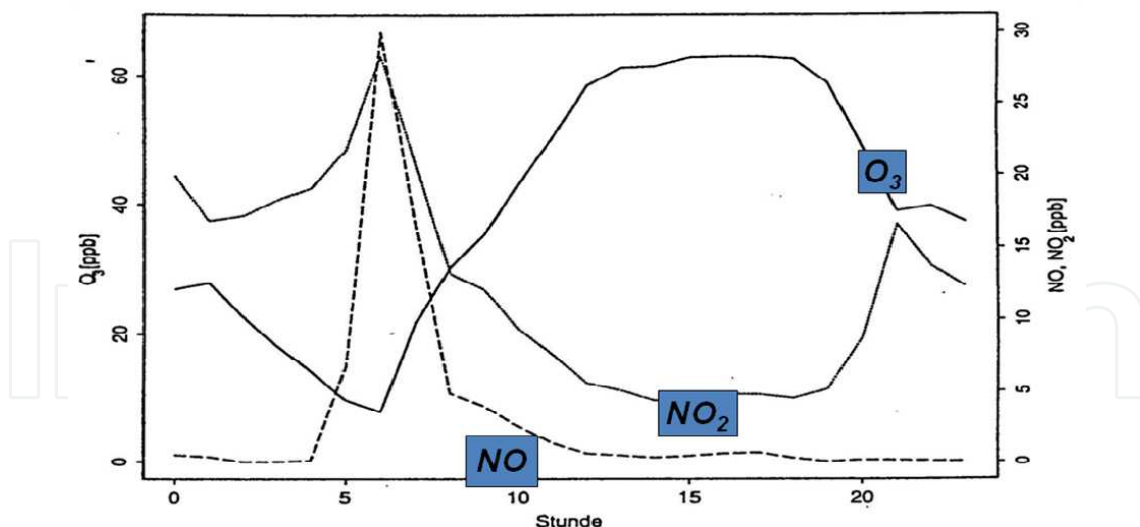5. Ozone destruction

Fig. 2. Diurnal variation of trace gas concentrations at an urban site close to traffic emissions (NABEL station Dübendorf, mean of hourly mean values 18.-12. July, 1996):

- During night an inversion layer inhibits vertical mixing, and the primary air pollutants are emitted from ground below this layer.
- Ozone concentrations decrease during night because of the reaction of NO and O_3 and dry deposition. At this measuring site NO is steadily released from a close traffic source.
- After midnight, the reaction of NO with O_3 yields an increase in NO_2 concentration (traffic dominantly emits NOx as NO).
- Early in the morning, the close traffic emissions lead to a NO_x maximum and NO increases as well (O_3 concentrations are very small this time).
- Later in the morning the inversion layer breaks, leading to the dilution of primary pollutants and the mixing down of O_3 from the layer lying above. Thus, NO_x decreases while O_3 increases (chemical transformations are not important compared to mixing in this phase).
- Around 20h the inversion layer forms again and the destruction of O_3 by NO begins.

The layer above the nocturnal inversion layer is called reservoir layer. The resrevoir layer (which constitutes a part of the planetary boundary layer) is decoupled from the inversion layer. In this layer, O_3 cannot be decomposed because NO emitted from surface is trapped below the inversion layer. Ozone (and other photooxidants) in the reservoir layer can be transported over large distances during night in summer smog episodes. Vertical mixing between the planetray boundary layer efficiently occurs during advective (smog) or convective (in summer) weather conditions.
Photocemistry of polluted air masses is exhaustively discussed by Steahelin et al., 2000.

2.2 Surface ozone concentrations, its measurements and trends

Ozone concentrations recorded in rural areas are higher than those in the city (Gregg et al., 2003). The main reasons of this phenomenon are the following:

- Since ozone is not a directly emitted pollutant, a considerable fraction of it is formed far away from its precursor sources.
- Nitrogen oxides leading to ozone depletion in the city's polluted atmosphere.
- In rural areas, biogenic VOCs (hydrocarbons and other organic trace gases) may contribute to ozone formation.

Daily maximum ozone values occur around midday, yearly peaks are at spring (during May) in the Northern Hemisphere while in the Mediterraneum, the highest concentrations occur from June to August (Paoletti, 2006).

Sources of background O_3:

- Transport from stratosphere
- Local ozone production through NOx reactions with methane above wetlands. NOx sources in this case are flashes of lightning, soil emissions and downward transport from stratosphere.
- Local ozone production through NOx reactions with biogenic VOCs.
- Long-range transport of polluted air masses.

Higher sites have atmosphere with higher ozone values, because lack of significant air mixing and higher transport of stratospheric ozone (Paoletti, 2007).

In the Northern Hemisphere, annual average ozone concentrations range between 20 and 45 ppb. By the year 2100, values are predicted to be between 42 and 84 ppb (Vingarzan, 2004).

Over the past three decades, background levels have been rising by 0.5-2% per year (Midgley et al, 2002). Although peak values are generally decreasing (Midgley et al, 2002) background values, that are increasing, have a larger impact on vegetation (Grennfelt, 2004).

Although already Schönbein, the discoverer of ozone (Schönbein 1844) developed a method in 1842 to show that O_3 is present in ambient air, this type of method is (quantitatively) not reliable. (At the time, mean values were about 10 ppb (Anfossi and Sandroni, 1994).) For the detection of ozone, Schönbein used impregnated papers which change color when exposed to ozone. This method was widely used in the 19th century.

From 1876 to 1911 ozone was measured by a chemical method using arsenite in the observatory of Montsouris. However, this method is susceptible to interference with sulfur dioxide and the representativeness of the measurements with respect to local influences is also questionable.

Around the end of World War II it was discovered that ozone could be produced in the troposphere by photochemical air pollution (Haagen-Smith, 1952).

In the 1930s, single measurements of O_3 close to Earth's surface were performed by (open path) spectroscopy. (Compared with this earlier measurements, ozone values measured at the same site in the period of 1989-1991 show more than a twofold increase.)

Chemical measurements have been widely used until the 1970s. Ozone measured by this method is also affected by interference with SO_2, and therefore only background measurements are sufficient for trend analysis (Staehelin et al. 1994). This method using electrochemical detection is applied for ozone profile measurements from light balloons (ozone sondes). A network of ozone sonde stations has been operating since the late 1960s providing a unique data set to document long-term tropospheric ozone changes (e.g., Logan et al. 1994). Different sensors have been developed over time (showing systematic

differences). The quality of the data gained from old ozone sonde measurements is not reliable.

O_3 measurements were made in the 1950s at the Alpine village Arosa and several places in the north of the Alps. Comparison of these results with the results of measurements made in the period of 1989-1991 confirms that ozone values doubled during these 40 years all over Europe. Similar changes have been demonstrated in ozone concentrations in the marine boundary layer in the West coast of North America and Mace Head (West coast of Ireland), and at Montsouris, which is close to Paris.

This increase in background ozone concentrations in this period is probably caused by a significant increase in ozone precursor emissions in the decades following World War II.

Measurements of the European ozone sonde stations show large increases in free tropospheric ozone from the early 1970s to the 1990s (5–25% per decade during 1970–1996 Logan et al. 1994).

Today it is well known that high ozone concentrations occur all over the world.

Reliable ozone measurements can be obtained by UV absorption using the Hg emission line at 253.7 nm. This method is nowadays commonly used in ozone monitoring (e.g., Klausen et al. 2003). Data from continuous ozone measurements are available from an increasing number of stations, but that data are not every time useful for long-term trend analysis from remote sites. The method is also used to measure ozone from air planes, as well as from ships. The extended datasets provided by the MOZAIC (Measurement of Ozone and Water Vapour by Airbus In-Service Aircraft) and the earlier GASP program (GlobalAtmospheric Sampling Program, 1975–1979) are valuable for trend analysis.

Ozone is a precursor of OH-radical which limits the tropospheric lifetimes of many important gaseous species such as methane. Ozone is also an important greenhouse gas: its increase has significantly contributed to changes in radiative forcing. Determining this anthropogenic radiative forcing by tropospheric ozone is difficult, since its complex formation reactions need to be described by complex numerical simulations of the tropospheric ozone cycle.

To understand tropospheric ozone trends, they need to be compared with changes in anthropogenic ozone precursor emissions. Emission models rely on the description of anthropogenic activities leading to emission factors that describe the type of technology. Emissions of society depend on economy, and due to economic growth, all emission models show large increases in the period following World War II. Due to the abatement legislation, anthropogenic emissions of developed countries stabilized and decreased after the 1980s, while the emissions of developing countries still increased during the 1990s (Staehelin and Poberaj, 2008). However, different emission models show considerable differences demonstrating uncertainties in data processing.

Since 1992, ozone concentrations measured at high mountain sites in the northern extratropics, have increased further (Brönnimann et al. 2002). Since anthropogenic ozone precursor emissions have decreased in Europe and North America since the early 1990s, these increases are difficult to explain. Within the MOZAIC project ozone has been continuously measured since 1994. These measurements show a considerable increase in upper tropospheric and lower stratospheric ozone which extends over much of the northern extratropics (Thouret et al. 2006).

A similar increase in ozone concentrations has been found at Mace Head, a station at the west coast of Ireland (Simmonds et al. 2005). All measurements support that ozone trends

are most pronounced in winter. Ozone sonde measurements in Europe do not accord with the data showing these increases, possibly because limitations in data quality (Ordóñez 2006).

As discussed in the literature (Staehelin and Poberaj, 2008), different causes for this remarkable increase can be:

- effects of more frequent biomass burning
- changes in transport of air masses over the Atlantic in association with changes of the North Atlantic Oscillation (and Arctic Oscillation)
- influence of the strongly increasing emissions from South East Asia
- changes in the transport of ozone from the stratosphere

Indeed, during the 1990s, ozone substantially increased in the lowermost stratosphere at northern midlatitudes. Strong correlations have been showed between the ozone anomalies in the lowermost stratosphere and ozone concentrations measured at three European high mountain stations in the 1990s (Ordóñez et al. 2007). There are several data from all over the world, with temporal trends which are difficult to explain by changes in anthropogenic ozone precursor emissions. This temporal change in upper tropospheric ozone was similar to the changes observed in the lowermost stratosphere (Staehelin and Poberaj, 2008).

These facts suggest that long-term tropospheric ozone trends are considerably influenced by changes in ozone in the lowermost stratosphere (Tarasick et al. 2005; Ordóñez et al. 2007). Probably, there is a major contribution of an increased flux of ozone from the stratosphere to the troposphere to the 1990's increase in Europe's background ozone concentrations.

However, present chemical transport models have problems to adequately describe the influence of stratosphere–troposphere exchange.

In the tropics, upward trends were reported from long-term measurements from ship cruises over the Atlantic for 1978–2004. In the measurements of the MOSAIC project (starting in 1994), twice as large increases have been found for the free tropical troposphere over the Atlantic. In both case, these large increases were attributed to increasing fossil-fuel emissions in the Atlantic regions.

Surface-ozone measurements from Hawaii (starting in 1974) and ozone sonde measurements from Hilo (starting in 1982) show moderate increases. Data analysis provided evidence that similarly to the northern extratopics, the most probably primary cause of this increase is the change in the origin of air (Oltmans et al. 2006).

In the southern extratoropics, ship measurements also show upward near-surface trends in the Southern midlatitude Atlantic region, although these trends are less pronounced than in the tropics. The only available sonde station in New Zealand shows a continued increase in the middle troposphere since 1986, which is qualitatively similar to the surface ozone increase reported from the long-term stations Cape Grim (Australia) and Cape Point (South Africa). Interestingly, the temporal evolution of surface ozone concentration at the South Pole shows a continuous decrease between the middle of the 1970s and the middle of the 1990s. This decrease is later followed by an increase (Staehelin and Poberaj, 2008).

However, according to recent studies, in the Arctic, there are special processes that evaluate ozone concentrations.

Because of the lack of available reliable long-term measurements, it seems premature to draw overall conclusions for the tropical regions as well as the southern midlatitudes (Staehelin and Poberaj, 2008).

Increases in ozone levels in the future are predicted to be larger in developing countries (Naja and Akimoto 2004; The Royal Society, 2008).

3. Phytotoxic effects of ozone

Current tropospheric O_3 concentrations are considered a toxic threat to vegetation (Ashmore, 2005).

Based on ozone emissions of the year 2000, ozone-induced crop yield loss for 23 crops was estimated to be around €6.7 billion per year (Harmens et al., 2006).

A database named OZOVEG (Ozone effects on vegetation) was established based on data collated from over 60 papers. On the grounds of this database, a model was developed that uses Ellenberg light and salinity values (Ellenberg et al., 1991) for predicting ozone sensitivity of particular species as well as of whole plant communities.

Using the European Nature Information System (EUNIS) Dry garsslands, Mesic grasslands, Seasonally-wet and wet grasslands, Woodland fringes, Alpine and subalpine grasslands and Temperate shrub heathlands were identified as potentially ozone sensitive.

Studies made to better understanding (Harmens and Mills, 2005)(Harmens et al., 2006) concluded that the response of vegetation to ozone and climate change is driven by complex interactions between several abiotic and biotic factors and making predictions is difficult (Harmens et al., 2006). There is a clear need for an approach that combines drivers when examining vegetation response to climate change. Long-term multifactorial field experiments and modelling that takes into account several climate change factors should be made.

The estimation of cause-effect relationships has to be more adequate when based on the amount of ozone entering the leaf tissues instead of being based on the amount of ozone present in ambient air (Ashmore et al., 2004).

Stomatal ozone uptake (flux-based approach) is modelled on the basis of maximum stomatal conductance values, taking into account the effects of several climatic and environmental parameters. Comparing with the concentration-based approach (Paoletti and Manning 2007), it is more precise since it includes environmental conditions that affect plant's ozone response. However, flux-based methods are species-specific, with the need of parametrisation for every particular investigated species (Paoletti et al, 2007). Considering estimations with the flux-based approach, risks are shown to be slightly lower (Baumgarten et al., 2009). Flux-based indices are considered to be more appropriate than exposure-based indices (Karlsson et al., 2009 Fredericksen et al., 1996; Karlsson et al., 2003; Matyssek et al., 2004; Pleijel et al.,2004).

The latest approach is the usage of dose-response models. This approach also needs parametrisation for certain species (Fernandez et al., 2010; Calvo et al.,2010).

The phytotoxic effect of ozone is commonly introduced through a description of stomatal behaviour based on plant's transpiration (Baldocchi et al., 1987; Meyers et al., 1998; Simpson et al.,2003). However, the conribution of non-stomatal sinks to the total ozone removal at the canopy scale can be on the order of 50% - 70%.

Also, at the shoot scale, several measurements revealed depositions exceeding the predictions based on the stomatal uptake (Rondón et al., 1993; Altimir et al., 2004) (van Hove et al., 1999). This non-stomatal deposition is a major unknown in present understanding of gas-exchange, which compiles heterogeneous chemical processes. These

processes can be reactions between ozone and Volatile Organic Compounds or nitrogen oxides emitted by the soil (Duyzer et al., 1983; Pilegaard, 2001)(Kurpius and Goldstein, 2003; Goldstein et al., 2004; Mikkelsen et al., 2000). Foliage surfaces can also sustain ozone removal through photochemical reactions or thermal decomposition of ozone on the leaf surface (Rondón et al. 1993; Coe et al. 1995; Fowler et al. 2001). Wetness of foliar surfaces and its relationship with deposition of gases has been discussed in many studies (Massman, 2004; Brewer and Smith, 1997). The foliage surface's ozone removal processes, such as scavenging reactions (in addition to stomatal uptake) are possibly controlled by several environmental factors, but it is difficult to determine the most important among these factors.

According to a study made on Scotch pine shoots and canopy in Finland (Altimir et al., 2005), ozone total deposition enhances when moist conditions occur. During moist conditions, only half of the measured ozone removal is attributable to the stomatal deposition at the shoot scale. This proportion is much higher in case of dry conditions. Among several analysed environmental factors, relative humidity was found to show the clearest correspondence with the estimated non-stomatal sink. However, this correspondence was only present when relative humidity was higher than 70%, a treshold at which surface moisture gathers at the foliage surface. This suggests that the non-stomatal sink is modulated by the foliage surface films. Moisture plays an enhancing role of ozone deposition. A part of the flux can only be explained by moisture film formation at the foliage surface. Total deposition, as well as the estimated non-stomatal deposition correspods with RH rather than with temperature, at least when RH is over 60-70%. Thus, the portion of ozone deposition that the stomatal uptake cannot account for is related to the ambient RH. Possible explanation of this phenomenon is that ozone reacts with the liquid films on the foliage surface.

There is a not negligible contribution of nocturnal ozone uptake, which is often assumed to be zero during estimates of ozone uptake. Stomatal closure can be incomplete at night, even if discussing C3 plants. In addition, the enhancing effect of RH is more prominent at night.

According to several studies, forestal ecosystems are at risk (Paoletti,2007 Baumgarten et al., 2009, Paoletti at al., 2007), being the thresholds of both flux-based and exposure-based O_3 indices are already exceeded and estimated to increase further in the future. Based on observed biomass losses and changes in ecosystem carbon-balance impairement carbon-sink strength of the forests of the Northern Hemisphere is found to be reduced by ambient ozone levels, and this reduction is predicted to be more serious in the future (Witting et al., 2009). Visible ozone injuries were observed in 55% of 67 forestal monitoring sites in an European ozone monitoring experiment (ICP Forests)(Lorenz et al., 2005). Direct ozone effects have been estimated to reduce forest productivity by 1-10% (Chappelka and Samuelson, 1998).

In a subalpine grassland ecosystem, respiration rates and gross primary production decreased under elevated O_3. The 8% O_3 effect on GPP indicated impairment of the photosynthetic system. However, this decrease did not alter seasonal C balance. The reason is that in this ecosystem most of the biomass is in belowground, providing stable resource of new photosynthetic canopy (Volk et al., 2010).

In a long-term experiment in Lithuania, strong positive correlation was found between AOT40 (accumulated doses over 40ppb) values and defoliation of *Fraxinus excelsior* as well as the proportion of healthy individuals of several investigated tree species. The experiment

showed the deciduous tree species to be more sensitive than conifers (Girgždienė et al., 2009). Species-specific responses to ozone as well as impairment of soil nutrient balance in polluted areas affect the competition of forest ecosystems and its biodiversity (Paoletti, 2007). In general, chances of poor competitors are weakened (McDonald et al., 2002).

The risk is also present regarding cultivated crops. Not only the quantity, but the quality of crops changes as an effect of ozone pollution. Chemical composition (lignin and phenolic concentrations, protein content) in rice straw was demonstrated to change as a result of elevated ozone concentration. This changes mean reduced digestibility and feed intake, on the whole, reduced quality of this kettle feed (Frei et al.,2010).

According to Karlsson et al. (2009), ambient ozone levels cause 2%-10% reduction in growth of trees and up to 15% reduction in crop's yield in Sweden. Visible injuries on bioindicator plants were observable. The relatively large ozone impacts in spite of relatively low ozone levels in the Northern hemisphere were explained by that the humid climate promoted high ozone uptake of leaves.

The effect of ozone is similar to several other stresses, triggering ethylene emission, stress-related gene transcription and major plant defence systems such as programmed cell death (Sandermann, 1996). Ozone injury mainly occurs in the mesophyll tissue. Stomata and epidermal cells resist until the plant's total necrosis (Hill et al., 1961).

The initial effect of ozone is the destruction of cell membranes (Heath, 1980). Beyond degradation of photosynthetic membranes, ozone-induced impairment of photosynthesis is attributed to decline in carboxilation efficiency, the electrontransport system, the synthesis and activity of Rubisco (Pell et al., 1991), and changes in carbon-dioxid supply because of changed stomatal function (although the exact processes of these changes are not clearly understood) (Paoletti and Grulke, 2005).

Effects of ozone and ozone injuries are highly similar whatever the species. In the field, injuries occur after sunny periods, particularly at the light exposed parts of light exposed plants. Broadleaved trees show intervenial bronzing and stippling, reddening, stippling and bleaching. Most severe injuries are shown on palisade parenchyma cells (Vollenweider et al., 2003), that are undregoing HR-like reaction (reaction similar to Hipersensitive Reaction). The surrounding tissues show ACS (accelerated cell senescence) and OS (oxdative stress) (Pellinen et al., 1999).

Cell walls form protrusions including pectin, polyphenolic or protein material (Günthardt-Goerg,1996; Günthardt-Goerg et al., 1996,). Such symptoms also appear in shaded and asymptomatic leaves if exposed to high ozone concentrations (Vollenweider et al., 2003). The cell wall generally thickens and its thickness becomes irregular (Vollenweider et al., 2003); the formation and allocation of starch declines and also becomes irregular in symptomatic tissues (Günthardt-Goerg et al., 1998).

Symptoms of conifers are mottling and bleaching (Günthardt-Goerg and Vollenweider, 2001) that are very similar to those in broadleaved species (Dalstein et al., 2002; Vollenweider et al.,2003). The injured cells have larger vacuolum, more nucleus condensations and less and smaller chloroplasts, discrete groups of dead cells with apoptotic-like bodies. Bronzing (caused by condensed tannins) (Vollenweider et al., 2003) cannot be observed in conifer species (Günthardt-Goerg* and Vollenweider, 2006).

Ozone most significantly affects the regulatory capacity of resource allocation, it alters source-sink balance decreasing below-ground carbon allocation (Andersen 2003). As a

defence reaction, plant's stomatal conductance is reduced when exposed to ozone. The direct reason of stomatal closure might be a reaction to an increased internal CO_2 concentration due to inhibited C assimilation (Paoletti and Grulke 2005). Ethylene emission and changed ion fluxes can also cause stomatal closure (Kangasjarvi et al., 2005), but it can be caused by direct O_3 effect on guard cells (Moldau et al., 1990).

However, above a certain concentration or after a certain time period ozone may impair stomatal control, causing sluggish stomatal response (Paoletti and Grulke 2005) and finally incomplete stomatal closure (Paoletti, 2005) which leads to lost control on transpiration. Increased nocturnal transpiration as a result of ozone exposure has been reported in several studies (Grulke et al., 2004, 2007). Ozone also inrcease sap-flow. Thus, in general, through its effect on stomata, ozone predisposes trees to drought stress (Paoletti, 2007).

As an ozone effect, stomatal density has been shown to increase (Paoletti and Grülke, 2005 Hetherington and Woodward, 2003) but with decreased stomatal or aperture size (Aasmaa et al., 2001; Paakkonen et al., 1997).

In trees, biomass production decreases rather through reduced leaf size and premature leaf loss than because of declined photosynthesis (Matyssek 2001).

In the Aspen-FACE experiment, where different tree species were exposed to elevated CO_2 contemporarily with elevated O_3 levels, 14%-18% decrease in growth of birch and a significant decrease of growth of maple trees were seen when exposed to both gases compared with plants grown only under elevated CO_2 (Karnosky et al., 2005).

Exposure to ozone affects flowering in several species (Black et al., 2000; Darbah et al., 2007).

As ozone decreases plant productivity, more CO_2 accumulates in the atmosphere, resulting indirect radiative forcing. This indirect effect may have larger contribution to global warming than the direct radiative forcing caused by increases in ground-level ozone concentrations (Stich et al., 2005; Paoletti, 2007).

4. Bioindication of ozone

Bioindicator plant species are species with high sensitivity to ozone. This sensitivity is manifested in changes in physiological parameters, biomass reduction and the appearance of specific visible symptoms when exposed to high levels of ozone. According to the extent of these injuries, conclusions can be drawn regarding the presence (and, for some extent, the amount) of ozone in the atmosphere of the site where the plants are exposed to ambient air. In addition, ozone bioindicator plants are widely used in researches aiming to clarify plant's response to the stressor, or, in general, to oxidative stress. Reduction in biomass of sensitive clones as an effect of ozone is also a widely investigated indicative feature of biomonitoring plants.

There are a range of plants that were proved to be sufficient for demonstrate ambient ozone levels. Most importants are *Nicotina Tabacum* var. Bel W 3 (applied together with the resistant Bel B clone); *Phaseolus vulgaris* var. *Pinto*; *Urtica urens*; *Spinacia oleracea* Var. *Monnopa* (Arndt et al. 1985); *Populus x euramericana* var. *Gelrica* (Arndt et al. 1992) as well as wheat, mallow and clover (Schafler, 1998).

Tobacco plants have been used for ozone bioindication in Europe since the early 1960's. This species is highly sensitive to ozone, chlorotic spots on its leaves appear even under O_3 concentrations of 40ppb. After being exposed to ozone for a relatively short time period,

large necrotic spatches are formed, finally whole leaves wither (Mülleder et al., 1992). Since its oversensitivity, *Nicotiana tabacum* is only usable if applied together with another bioindicator species. Symptomps on tobacco plants soon become so expansive that no differences can be seen between extents of injuries on different individuals (Keitel, A. 1989).

In spite of these disadvantages, tobacco has been used for ozone biomonitoring even in long-term experiments (Nali et al., 2006). It was demonstrated, that extent of ozone injuries on tobacco leaves is highly informative as regards the amount of ozone in ambient air (Ribas and Penuelas, 2002).

The white clover system was developed by Heagle et al. in 1995. Between 1996 and 2008 participants of the International Cooprative Programme on Effects of Air Pollution on Vegetation (ICP-Vegetation) have detected and evaluated effects of ozone on sensitive and resistant clones of *Trifolium repens* across Europe and in the USA. Initially, biomass ratio of the two clones was investigated, visible symptoms gained more attention only later (Harmens et al., 2006). Analysis of data of this long-term clover biomonitoring experiment is presented in Harmens et al. (2004) and Harmens et al. (2005).

Several individual studies were carried out using the clover system (e.g. Postiglione et al., 2000; Karlsson et al., 2002). Using the ICP-protocol, an investigation of the effect of ozone on the clover system was carried out during 1997 and 1998 at the Ruhr Valley (Köllner and Krause, 2002). Foliar injuries, protein content and biomass ratio were evaluated. This study found visible injuries on clover clones to be better bioindicator features than biomass ratio if ozone values at the experimental site are relatively low, or if the aim is to determine early ozone effects. Protein content of sensitive plants was reduced shortly after high level ozone periods.

Although visible ozone injuries are not eligible for exact quantitative estimations of ozone levels, sometimes very good relationship are shown between the extent of injuries on O_3 sensitive clones and ozone doses in ambient air (Mills et al., 1999b; Ribas and Penuelas, 2002).

Since its identification as relatively ozone-sensitive species (Buse et al., 2003a), *Centaurea jacea* has been used as bioindicator. In 2002, ozone biomonitoring experiments of the ICP-Vegetation have been conducted using seeds of sensitive and resistant clones of this species (Harmens et al., 2006).

Evaluation of ozone symptomps is easier on large leaves. Thus, since 2008, the ICP-Vegetation Programme uses sensitive and resistant clones of *Phaseolus vulgaris* as a new bioindicator system. Bean lines used in this system were first reported by Reinert and Eason (2000), and tested by Burkey et al. (2005).

Although there are several ozone biomonitoring systems operating with sensitive and resistant clone pairs of bioindicator plant species, there are uncertainties in understanding physiological background of ozone sensitivity. Crous et al. (2006) studied the physiological differences between sensitive and resistant clones of widely used bioindicator clover. The experiment has represented that with the exception of chlorophyll content (which is originally higher in resistant plants), physiological parameters of the two clones differ only after ozone exposure. Ozone resulted changes in physiological parameters of the sensitive plants. While resistant clone showed no response to cumulative uptake of high ambient ozone (CUO_3), sensitive clone reacted with decline of most investigated gas exchange parameters (e.g.: net photosynthesis and carboxilation capacity). Stomatal conductance of the two clones differed only after being exposed to ozone: after an initial increase during

lower ozone concentrations, stomatal conductance of the resistant clone significantly decreased. While maintaining higher photosynthesis, resistant clone showed higher non-photochemical quenching. This means that sensitive clone is more vulnerable to potentially generating reactive oxygen species that are harmful for cell membranes likely leading to visible symptoms. It has been concluded that the ozone resistance is based on stomatal function and the capacity of non-photochemical quenching. Physiological dysfunction may occur before visible symptoms develop (Pye, 1988; Fredericksen et al., 1996; Guidi et al., 2001).

5. Results of three year's Slovenian-Hungarian biomonitoring experiment

Experiments with two ozone bioindication plants (*Trifolium repens* r. cv. Regal and *Phaseolus vulgaris*) were conducted in a Slovenian and two Hungarian experimental sites.

Ljubljana (altitude: 320 m; average annual temperature: 11,4°C; yearly average precipitation: 1400 mm) is Slovenia's capital with significant public traffic.

Gödöllő (altitude: 249 m; mean annual temperature is between 9°C and 10°C; yearly average precipitation: 560 mm;) is a small town which is only 25 kilometers far from Budapest, so it must be affected by the pollutants of the capital city.

Szurdokpüspöki (altitude: 350 m; average annual temperature: 10,2°C; yearly average precipitation is 620 mm) is located in a rural environment in the Mátra mountains.

As it could be expected, Ljubljana had the lowest ozone concentrations among the three sites all over the three-year-long period between 2007 and 2009.

For planting and evaluating of ozone injuries we used the experimental protocol of the ICP-Vegetation (Hayes et al., 2006).
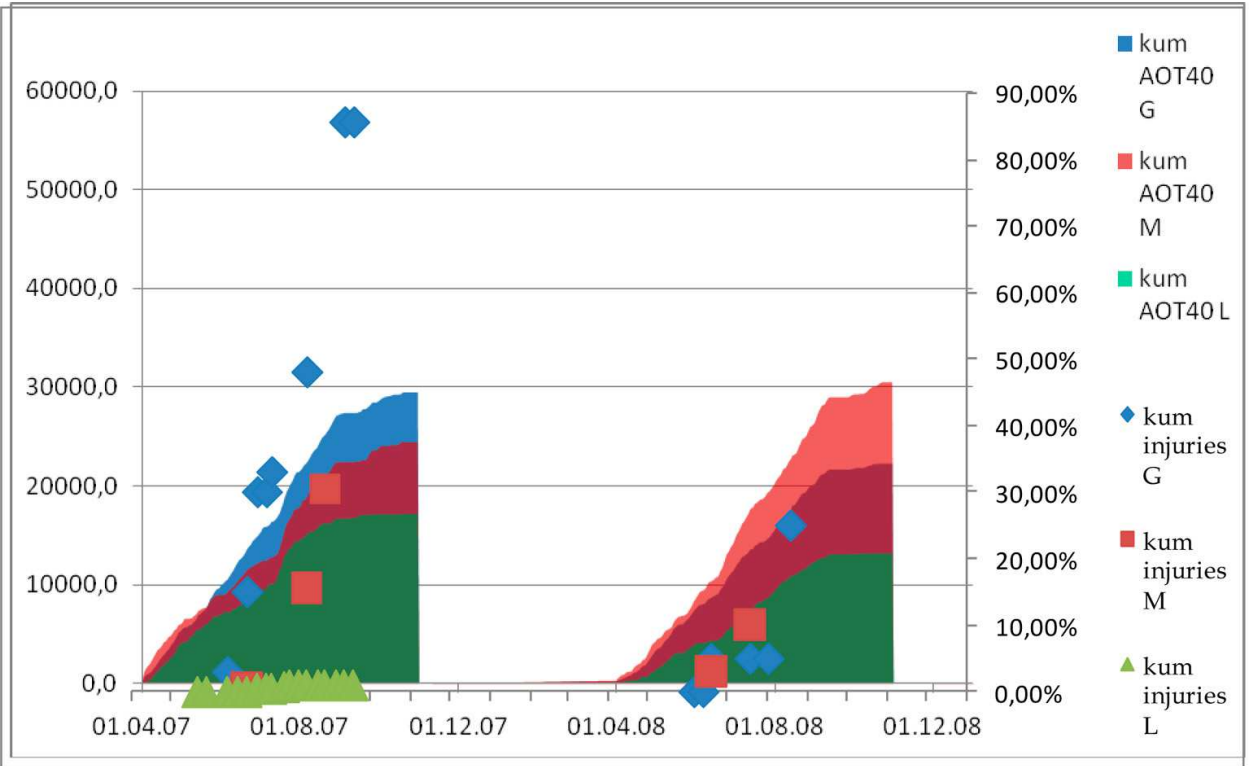

Fig 3. Two year's cumulative AOT40 values and results of ozone injury assessments on clover clones (Gödöllő-G; Mátra mountain-M; Ljubljana-L)

Ozone concentrations, ozone injuries, dry weight of clover plants and dry weight of bean's pods, number of pods were measured and evaluated.

On the base of three year's experiences in biomonitoring with the two species, we were trying to find out if bean plants were more suitable for this purpose than the clover clones.

Ozone symptoms on sensitive clover clones showed closer connection with AOT 40 values than on bean plants. Dry weight of the sensitive and resistant clones did not differ significantly; they seem to show connection with meteorological conditions rather than with ozone burden, as the dry weight of all experimental plants showed significant differences among the different sites, but these differences did not correspond with the differences in ozone values.

Neither the differences in ozone symptoms nor the dry weight of pods of ozone sensitive bean plants reflected the differences of ozone burden of the experimental sites.

Although the dry weight of pods on ozone sensitive bean strains usually remained under that on the resistant strains, this difference did not seem to have any connection with the AOT40 values. Supposedly, this is a genetic difference between the two strains in addition to but not in connection with their different reactions to ozone.

Regarding the usefulness in ozone bioindication, clover clones proved to be more valuable than bean strains. Not only had the injuries of clover clones closer connection with AOT40 values than that of the bean strains.
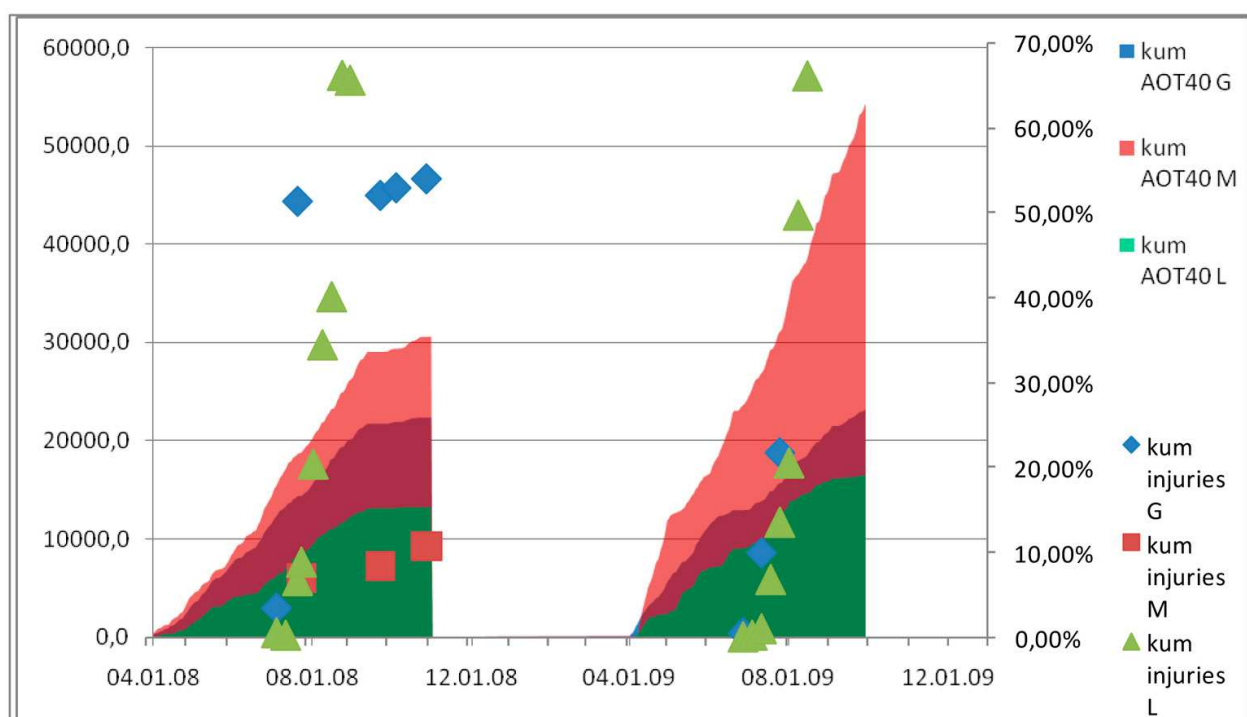

Fig 4. Two year's cumulative AOT40 values and results of ozone injury assessments on bean clones (Gödöllő-G; Mátra mountain-M; Ljubljana-L)

Comparing the bioindicator values of number of flowers on clover clones and number or dry weight of pods on bean strains, the clover clones again have appeared to be more useful. In addition, maintenance of clover clones is easier; bean plants are much more sensitive to other environmental stresses such as drought and high solar radiation which makes the experiments more complicated and their outcome more doubtful.

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Air Pollution

Edited by Vanda Villanyi

Although the climate of the Earth is continually changing from the very beginning, anthropogenic effects, the pollution of the air by combustion and industrial activities make it change so quickly that the adaptation is very difficult for all living organisms. Researcher's role is to make this adaptation easier, to prepare humankind to the new circumstances and challenges, to trace and predict the effects and, if possible, even decrease the harmfulness of these changes. In this book we provide an interdisciplinary collection of new studies and findings on the score of air pollution.

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