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Study of links between biogenic VOC emissions and concentration of tropospheric ozone

by

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In Prague, 29.4.2010 Kateřina Zemánková

ABSTRACT

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Presented work focuses on influence of volatile organic compounds from biogenic sources on concentration of tropospheric ozone. Volatile organic compounds (VOC) play an important role in the tropospheric chemical system. Together with oxides of nitrogen they form two major components of reactions leading to low-level ozone formation. Volatile organic compounds are emitted into the atmosphere from anthropogenic as well as from biogenic sources. In global, VOCs from natural sources are approximately ten times higher in magnitude than those of anthropogenic origin. Biogenic VOCs are emitted from various sources among which the forest ecosystems predominate. Group of VOCs of natural origin comprises wide range of chemical compounds. Those emitted in highest concentrations are isoprene and group of monoterpenes.

Emissions of biogenic VOCs from the area of the Czech Republic have been estimated based on the high resolution land cover data giving detailed information of sigle tree species distribution. Emission potentials for five tree species common in the Czech Republic were obtained from emission flux measurements performed with tree samples grown in the Czech Republic in IBAF laboratory in Rome, Italy. Presented is annual profile of BVOC emissions, spatial distribution of annual BVOC estimates together with differences between BVOC emissions in summer and in winter. Amounts of estimated BVOC emissions were compared to data from national inventory of anthropogenic VOC emissions.

Ozone concentrations during episode of Spring, 2007 were simulated applying chemical transport model CAMx on three nested domains covering whole area of Europe with the smallest domain being focused on the region of the Czech Republic. Two datasets of biogenic VOC emission estimates were tested in the CAMx model and their impact on ozone formation compared to model run with anthropogenic emissions only was investigated. Modeled concentrations of tropospheric ozone were compared to measurements from selected stations from european and czech measuring network.

ABSTRAKT

Název disertační práce: Studium vazeb mezi biogenními emisemi VOC a koncentracemi přízemního ozonu

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Prezentovaná práce se zabývá studiem vlivu těkavých organických látek emitovaných z biogenních zdrojů na koncentraci přízemního ozonu. Těkavé organické látky (VOC) hrají důležitou roli v chemickém systému troposféry. Společně s oxidy dusíku tvoří dvě hlavní složky chemických reakcí, které vedou ke vzniku přízemního ozonu. Těkavé organické látky jsou do atmosféry vypouštěny jak z antropogenních, tak z přírodních zdrojů. V globálním měřítku je podíl VOC z biogenních zdrojů na celkovém množství těchto látek v ovzduší až desetkrát vyšší než podíl VOC antropogenního původu. Biogenní VOC jsou vypouštěny z různých zdrojů, přičemž nejvýznamnějšími z nich jsou lesní ekosystémy. Do skupiny biogenních VOC patří široká škála chemických látek mezi nimiž co do emitovaného množství dominují isopren a monoterpeny.

Emise biogenních VOC v oblasti České republiky byly odhadnuty na základě detailních map rostlinného porostu s vysokým prostorovým rozlišením. Emisní faktory pěti druhů stromů nejčastěji se vyskytujících na území ČR byly naměřeny v laboratořích IBAF-CNR v Římě, kde byly pozorovány emisní toky isoprenu a monoterpenů na rostlinách vypěstovaných v ČR. V předkládané práci je uveden roční chod odhadu celkových emisí biogenních VOC v ČR, stejně jako postorové rozložení ročních emisních sum a prezentovány jsou také rozdíly emisí biogenních VOC v letním a zimním období. Odhadnuté množství VOC biogenního původu bylo srovnáno s daty z národního inventáře antropogenních emisí VOC.

Aplikováním chemického transportního modelu CAMx byly simulovány koncentrace přízemního ozonu během epizody na jaře roku 2007 na třech vnořených modelových doménách, s největší z nich pokrývající oblast Evropy a s nejmenší doménou zaměřenou na oblast České republiky. V bezích modelu CAMx byly testovány dva inventáře biogenních emisí VOC. Vliv biogenních emisí VOC na tvorbu přízemního ozonu byl studován srovnáním s během modelu CAMx, ve kterém byly uvažovány pouze antropogenní emise VOC. Modelové koncentrace ozonu byly porovnány s měřením z vybraných stanic evropské a české měřící sítě.

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Contents

Chapter 1

Introduction

Tropospheric ozone is recognized as one of the main elements of air pollution having negative effect on all living organisms (e.g. [1], [2]). It is a gaseous compound which is not directly emitted into the atmosphere from the Earth's surface. Tropospheric ozone is a secondary pollutant formed in the atmosphere as a result of photochemical reactions [3]. Since solar radiation plays a crucial role in the tropospheric ozone forming process, highest ozone concentrations are being observed during hot, sunny periods, typically occuring during summer. Appearance of high ozone levels is therefore often entitled as *summer photochemical smog*.

Concentration of ozone in the troposphere is a result of complex system of reactions involving various chemical species. Compounds of major importance in tropospheric ozone formation are nitrogen monoxide, nitrogen dioxide and group of volatile organic compounds (VOC) [4]. Ozone is produced in reaction of oxygen molecule with oxygen atom. In lower parts of the atmosphere the only source of atomic oxygen is photolysis of nitrogen dioxide. Ozone then acts as an oxidizing agent being consumed mainly by nitrogen monoxide. If VOCs are present in the air, they produce radicals which replace ozone in oxidative reactions and hence support ozone accumulation in the troposphere.

While human activity is nowadays assigned to be the main source of oxides of nitrogen (NOx) [5], significant amounts of VOCs are emitted from anthropogenic sources as well as from natural ecosystems. On global scale, emissions of VOCs from biogenic sources are estimated to be ten times higher than the global magnitude of anthropogenic VOCs [6].

Volatile organic compounds of natural origin are released from marine water, wetlands, soils, but the prevailing source of biogenic VOCs is vegetation, especially forest ecosystems [7]. The main contributor to global totals of biogenic VOCs is tropical forest [8]. Myriad of species have been so far recognized to be emitted from vegetation [9]. The predominant compounds emitted in highest concentrations are isoprene and group of monoterpenes [10].

The purpose, processes of formation as well as quantification of BVOC emissions have been subject of investigation since the effect of these compounds on tropospheric chemistry had been discovered. Series of studies have uncovered the ecophysiological functions of various BVOC species although many uncertainties remain. BVOCs have been proven to be present in flower scents to attract pollinators [11], they are being emitted in order to defend plant against parasites and herbivory [12], or play role in plant protection against stressing environmental conditions (such as high temperature [13] or oxidative stress [14]).

Findings concerning VOC formation in plants and dependence of VOC production and emission on environmental factors served as a base for methods for spatially and temporally resolved estimates of VOC emissions. There are two general approaches of VOC modelling. The first approach concentrates on description and simulation of biosynthetical processes of VOC formation inside the plant (e.g. [15], [16]). Second approach focuses on investigation of plants potentials to emit particular chemical compound and its dependence on environmental conditions [8]. Major factors influencing BVOC emissions are temperature and solar radiation. Sigfnificant effect have also humidity, chemical composition of the ambient air, developmental stage of the plant and the actual plant condition.

Biogenic emissions of VOC can have significant consequences in the chemistry of the troposphere. Compounds belonging into this group are higly reactive which can be demonstrated on their atmospheric chemical lifetime typically ranging from few hours to few minutes [12]. Effect of biogenic VOCs on tropospheric ozone formation has already been mentioned. These compounds are especially important in forested areas where emissions are expected to reach high values. If the location is also rich in NOx concentration, supply of additional VOCs from natural sources can result in significant rise of ozone levels (e.g. [17], [18], [19]).

Furthermore, biogenic VOCs and their oxidative products are effective sources of secondary organic aerosols. These gas-phase compounds either condense on existing particles in the atmosphere or form new particles via nucleation [20]. BVOCs are part of the complex system of atmospheric chemistry significantly impacting on its oxidative capacity [10].

Presented thesis aims to summarize methods for BVOC emission estimation and to apply these approaches in order to quantify annual emissions of BVOCs from ecosystems in the Czech Republic utilizing high resolution land cover data together with laboratory measurements of tree species grown in the Czech Republic. Second goal of the thesis is to investigate the impact of BVOC emissions on concentration of tropospheric ozone by application of chemical transport model.

Introduction into chemistry of tropospheric ozone is given in the first part of the thesis together with brief description of theoretical backround of the problematics of volatile organic compounds in the atmosphere. Special attention is aimed to VOCs originating from natural sources, focusing on composition of this group of compounds, nature of their formation and emission, and finally on methods of biogenic VOC emission modelling.

Estimate of biogenic VOC emissions in the area of the Czech Republic has been performed and is presented in the second half of the thesis. Obtained results were compared to national inventory of anthropogenic VOC emissions.

Influence of BVOC emissions on ozone concentration has been studied applying chemical transport model on European as well as on regional level. Results of the comparison between model runs when biogenic VOC emissions were omitted and model runs when biogenic VOCs were included into model input data together with the comparison of modeled data to measurements.

The final chapter is dedicated to summary and conclusion of the results.

Chapter 2

Tropospheric Ozone Chemistry

The lowest part of the Earth's atmosphere - troposphere is a chemical system relatively separated from the upper parts of the atmosphere. The transport of species between troposphere and stratosphere is much smaller then the mixing within troposphere itself. Troposphere is a place where the atmosphere interacts with the Earth's surface and it is a medium through which they exchange mass and energy. Thousands of species are emitted at the Earth's surface and those with chemical lifetime less then or about one year or so are destroyed in the troposphere [3].

According to variety of species of compounds mixed in the troposphere there are innumerable many types of interactions among them depending on the intensities of their sources, efficiency of sinks, environmental conditions and of course the chemical characteristics of each compound. In terms of this work the main focus in this section will be concentrated on gas-phase photochemistry with special interest on reactions involving ozone.

Likewise in the stratosphere, ozone forming and destructing reactions are central for the troposphere as well. While ozone layer in the stratosphere protects the Earth's surface against ultraviolet radiation, tropospheric ozone acts like an oxidizing agent and when present in high concentrations causes damage to biota and to human health. The low-level ozone is thought to be one of the major elements of the tropospheric air pollution.

In general, tropospheric chemistry may be compared to low-temperature combustion system [21]. However, it is not a thermal process but a radical mediated process initiated and propagated by solar energy. Although most of the short-wavelength solar radiation is trapped in the stratosphere, radiation reaching troposphere is still sufficiently energetic to drive photochemical reactions in the troposphere. These reactions in the gas-phase involve mainly oxidation of organic compounds in the presence of oxides of nitrogen. In the backround tropospheric chemistry the main organic constituent of these chemical reactions is methane, the most prevailing hydrocarbon in the troposphere. Over urban and continental regions many other hydrocarbons and organic compounds are emitted from both anthropogenic and biogenic sources and take part in the oxidative processes. There are several other factors that play a key role in tropospheric chemistry like a relatively high concentration of water vapour or presence of NO_x compounds (i.e. NO_2 and NO). Even though their concentration in non-polluted areas is several ppb, they are crucial for the photochemistry.

In the following sections basic photochemical cycle of ozone and oxides of nitrogen is outlined as well as the role of hydroxyl radical, nitrogen radicals, the interactions of ozone with carbon containing species and the consequences of different ratios between volatile organic compounds and nitrogen oxides.

2.1 Ozone in the Atmosphere

Ozone is a molecule of three oxygen atoms, O_3. Ozone was first recognized by Christian Friedrich Schönbein in 1840 who suggested a presence of a gas with peculiar smell which was an accompaniment of electrical sparks in laboratory or lightning storms in nature. Because of its characterictic odour, Schönbein named this gas after a Greek word *ozien* - "to smell". The molecular formula was suggested by Jacques-Luis Soret and confirmed by Schönbein in late 1860's [22].

The spectroscopic studies at the end of the 19^{th} century have shown that ozone is present at higher mixing ratios in the stratosphere, approximately between 25 and 35 km above ground. Owing to ozone's ability to absorb short-wavelength radiation stratospheric ozone layer is essential in protection of the Earth's surface against harmful ultraviolet solar radiation. Beside the stratospheric layer, ozone is present in lower parts of the atmosphere, in troposphere, as well. However, tropospheric ozone is regarded as an air pollutant because when present in high concentrations it can cause serious effects on human respiratory system (e.g. [1], [23]) and on vegetation (e.g. [2], [24], [25]).

Ozone is not released into the troposphere directly, it is a secondary pollutant which is formed in the air as a product of photochemical reactions of its precursors - nitrogen oxides and hydrocarbons. In polluted areas under photochemically favourable conditions of high amounts of sunlight and high temperature the low-level ozone concentration tends to increase. This phenomenon of so called *photochemical smog* has first been recognized in Los Angeles in the mid-1940's. Nowadays, it is observed in cities and polluted areas worldwide during bright sunlight periods, especially in summer. Ozone is a stong oxidizing agent playing an important role in the troposheric chemistry.

2.2 Ozone formation in the troposphere

The only way how ozone is formed in the atmosphere is an addition of single atom of oxygen to molecule of O_2 with presence of another independent molecule M which stabilizes the molecule of ozone by absobing redundant energy, this stabilizator is usually N_2 or O_2. The difference between ozone formation in troposphere and stratosphere is in the origin of atomic oxygen. While in the stratosphere the atom of oxygen is a product of photodissociation of O_2 by short-wavelenth radiation, this is not possible in the troposphere because the wavelength of radiation reaching the troposphere is more then 290 nm and the molecule of O_2 is not able to absorb it. The source of atomic oxygen in the troposphere is nitrogen dioxide NO_2 which photolyzes under the radiation of wavelengths less then 400 nm.

$$NO_2 + h\nu(\lambda < 400nm) \rightarrow NO + O \tag{2.1}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2.2}$$

The ozone then reacts back with NO to regenerate nitrogen dioxide NO_2

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2.3}$$

When assuming a system of only these reactions in a medium of constant volume and temperature and irradiated, then a pseudostacionary state of NO_2, NO and O_3 would be established and the rate of ozone formation would equal to ozone destruction rate. This balance may be described by the following equation

$$k_1[NO_2] = k_2[NO][O_3] \tag{2.4}$$

where coefficients k_1 and k_2 are the photodissociation rate of NO_2 and oxidizing rate of NO, respectively. The square brackets represent the concentration of the compound. The ozone concentration in a system of only NO and NO_2 would then be

$$[O_3] = \frac{k_1[NO_2]}{k_2[NO]} \tag{2.5}$$

This expression has been named the *photostationary state relation* [3]. The steady-state ozone concentration is proportional to $[NO_2]/[NO]$ ratio. For example in a system of initial concentrations $[O_3]_0 = [NO]_0 = 0$ and $[NO_2]_0 = 100$ppb, the steady-state ozone concentration would stabilize at 27 ppb. However, this is much lower then ozone concentrations observed in the atmosphere, even with lower NO_2 amounts [4]. This fact leads us to a conclusion that there are other processes of NO oxidation by compounds other than ozone causing the ozone storage in the atmosphere. But before the alternative oxidizing reactions will be described another important constituent of tropospheric chemistry has to be introduced - the hydroxyl radical.

2.3 The hydroxyl radical

The hydroxyl radical OH is the most significant oxidizing agent in the troposhere. There are several ways how the OH radical is produced. Primarily, it is through the photodissociation of ozone in the presence of water vapour, mainly in the lower troposphere where the mixing ratio of water vapour is high. At wavelenghts less then 350 nm [10] ozone photolysis to produce either electronically excited oxygen atom $O(^1D)$ or atom of oxygen in ground state $O(^3P)$

$$O_3 + h\nu(\lambda < 350nm) \rightarrow O(^1D) + O_2 \tag{2.6}$$

$$\rightarrow O(^3P) + O_2 \tag{2.7}$$

The ground state atom practically immidiately recombines back with O_2 to form molecule of ozone. The excited atom $O(^1D)$ is either degraded to atom in ground state by collision with other molecule (N_2 or O_2) or reacts with water vapour to produce hydroxyl radical OH

$$O(^1D) + H_2O \rightarrow 2OH\cdot \tag{2.8}$$

At relative humidity of 50% and temperature of 258K about 0.2 OH is formed per each $O(^1D)$ atom of oxygen [26].

Other possibilities of OH formation in the troposphere is photodecomposition of nitrous acid, HONO

$$HONO + h\nu \rightarrow NO + OH\cdot \tag{2.9}$$

This compound is present mainly in urban areas and reaches maximum concentrations over nighttime because during the day the HONO photodissociation is relatively quick (about 10 min). If HONO accumulates over night, it may be a significant source of OH in the morning before other sources become dominant [27].

Hydroxyl radical is also a side product in oxidizing reaction of NO and peroxyradical HO_2. This interaction is decribed in more detail in section 2.4.

The OH concentration in the atmosphere is very difficult to measure due to its high reactivity and variability in space and time owing to variation in water vapour concentration, changes in actinic flux values and the distribution of many chemical species. It is possible to estimate the OH concentration by simulating chemical mechanisms in tropospheric chemical models. Such studies suggest the seasonally, diurnally and globally averaged OH concentrations in range of 2.10^5 to 10^6 molecules cm^{-3} [3]. The OH concentration is predected to reach the highest values in the tropics where the conditions of high humidity and sufficient sunlight favour the photolysis of O_3 and further reaction with H_2O [28].

Direct and indirect measurement techniques have been used to confirm modeled OH levels. An indirect method is based on monitoring a budget of species which are known to be consumed only by OH. One of such species is methyl chloroform, CH_3CCl_3, which is emitted strictly from anthropogenic sources and its atmospheric level is known to reasonable accuracy. A global average tropospheric concentration of OH equal to approximately 10^6 molecules cm^{-3} has been derived from the mean residence time of methyl chloroform in the atmosphere [29]. Several direct measurements of OH have been performed in the last few years. For example measuring campaign in September 1993 in Los Angeles using spectroscopy technique showed peak day-time OH concentration in polluted environment around 5.10^6 molecules cm^{-3} and proved the strong OH concentration daily profile which more or less follows the profile of solar radiation - maximum values around noon and minimum during night [30].

2.4 Influence of carbon containing species on ozone formation

2.4.1 Tropospheric chemistry of carbon monoxide and formaldehyde

As it has been noted earlier, the pure system of NO_x and O_3 would not be able to explain the amount of ozone present in the troposphere and therefore other processes have to come into account as well. The clue of elevated ozone concentration is presence of carbon containig species which are emitted into the atmosphere from both anthropogenic and biogenic sources. The influence of carbon containing species on ozone formation in the troposphere will be demonstrated on a simple example of carbon monoxide, CO, and formaldehyde, HCHO.

In the case of carbon monoxide, the reaction with hydroxyl radical $OH\cdot$ leads to formation of hydrogen radical $H\cdot$ which immediately combines with O_2 to produce hydroperoxyl radical $HO_2\cdot$

$$CO + OH\cdot \rightarrow CO_2 + H\cdot \tag{2.10}$$

$$H \cdot + O_2 + M \rightarrow HO_2 \cdot + M \tag{2.11}$$

The addition of H atom to molecule of O_2 weakens the O-O bond so that the resulting radical $HO_2\cdot$ reacts more freely then O_2 itself [3]. If NO is present in the air it is oxidized by $HO_2\cdot$ to produce NO_2

$$NO + HO_2\cdot \rightarrow NO_2 + OH\cdot \tag{2.12}$$

Beside the NO oxidation, $HO_2\cdot$ radical combines with other $HO_2\cdot$ radical and forms hydroperoxid H_2O_2

$$H_2 \cdot + H_2\cdot \rightarrow H_2O_2 + O_2 \tag{2.13}$$

The comparison of reactions (2.3) and (2.12) leads us to the fact that $HO_2\cdot$ radical substitutes ozone in the oxidation of NO, therefore ozone is not consumed and accumulates in the troposphere. The hydroperoxyl radical in this process is converted to $OH\cdot$ radical which is then available to react with another CO molecule. Despite its simplicity, the example of reaction mechanism between CO and NO_x demonstrates the key features of the involvment of more complex organic compounds in NO oxidation. In particular, the role of $OH\cdot$ radical as the oxidizing agent and the NO to NO_2 conversion by $HO_2\cdot$ are central to every interaction of organic compounds with NO_x. The reaction mechanism of formaldehyde, in somewhat more complicated molecule than CO, is not an exception.

Formaldehyde, HCHO, is mainly a product of hydrocarbon oxidation in the atmosphere but in small amounts is also emitted from the Earth's surface (e.g. foliage decompositon, leakage in the industry). Formaldehyde undergoes two main reactions in the troposphere - photolysis and reaction with $OH\cdot$ radical

$$HCHO + h\nu \rightarrow H \cdot + CO_2 \tag{2.14}$$

$$\rightarrow H_2 + CO \tag{2.15}$$

$$HCHO + OH\cdot \rightarrow HCO + H_2O \tag{2.16}$$

For the overhead sun the photolysis proceeds from 45% in the way of reaction (2.14) and from 55% of reaction (2.15) [3]. As it has been shown in reaction (2.11), the hydrogen atom combines with O_2 to form hydroperoxyl radical. The formyl radical, $HCO\cdot$, also reacts very quickly with O_2 and produces again $HO_2\cdot$ and carbon monoxide

$$HCO \cdot + O_2 \rightarrow HO_2 \cdot + CO \tag{2.17}$$

The consequences of $HO_2\cdot$ radical on tropospheric chemistry have been described already in the preceding paragraph. Depending on the path of the HCHO photolysis, either none or two $HO_2\cdot$ radicals are formed. Since these paths are roughly comparable in rate, we can approximately say that each HCHO molecule leads to one $HO_2\cdot$ production. Thus the influence of HCHO on NO oxidation and ozone formation depends on the amount od HCHO in the atmosphere.

2.4.2 Backround tropospheric chemistry of CH_4

When describing the chemical involvement of hydrocarbons in the troposphere, the chemistry of methane CH_4 can not be omitted. Methane is the simpliest alkane species emitted into the atmosphere from anthropogenic as well as natural sources. The globally averaged atmospheric surface methane concentration according to year 1998 is about 1750 ppb and its most significant emitters are wetlands, rice fields, landfills and livesock agriculture [31]. Methane has relatively long residence time in the atmosphere of approximately 10 years [32]. Due to its high concentration even in non-polluted areas, the chemistry of methane may be seen as a chemistry of the backround troposphere.

Similarly to reactions of CO and HCHO, methane reacts with hydroxyl radical to form methyl radical $CH_3\cdot$ which is then oxidized by O_2 and produces methyl peroxy radical $CH_3O_2\cdot$

$$CH_4 + OH\cdot \rightarrow CH_3 \cdot + H_2O \tag{2.18}$$
$$CH_3 \cdot + O_2 + M \rightarrow CH_3O_2 \cdot + M \tag{2.19}$$

There are three possibilities of further evolvement of $CH_3O_2\cdot$ radical in the troposphere - reaction with NO, NO_2 or with organic peroxy radicals (general formula $RO_2\cdot$) such as $HO_2\cdot$, while the reactions with NO and $HO_2\cdot$ are the most important [3].

The reaction of methyl peroxy radical with NO_2 leads to formation of methyl peroxynitrate CH_3OONO_2

$$CH_3O_2 \cdot + NO_2 + M \leftrightarrow CH_3OONO_2 + M \tag{2.20}$$

Methyl peroxynitrate thermaly dissociates back to the reactants with a lifetime dependent on the ambient temperature. At room temperature and air pressure the thermal decomposition is in range of seconds and increases to range of days for the temperature and pressure of the upper troposphere [33]. Methyl peroxynitrate can act like a temporary reservoir of $CH_3O_2\cdot$ and NO_2 in the upper troposphere.

When $CH_3O_2\cdot$ reacts with hydroperoxy radical $HO_2\cdot$ the methyl hydroperoxide CH_3OOH is produced

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{2.21}$$

The methyl hydroperoxide formation is followed either by photolysis producing methoxy radical $CH_3O\cdot$ or by reaction with $OH\cdot$ radical

$$CH_3OOH + h\nu \rightarrow CH_3O \cdot + OH\cdot \tag{2.22}$$

$$CH_3OOH + OH\cdot \rightarrow H_2O + CH_3O_2\cdot \tag{2.23}$$

$$\rightarrow H_2O + CH_2OOH\cdot \tag{2.24}$$

Under conditions of ambient temperature 278K the two thirds of reactions between methyl hydroperoxide and OH form methyl peroxy radical, reaction (2.23), and the rest proceeds the reaction (2.24) [3]. Radical $CH_2OOH\cdot$ produced in the last reaction very fastly dissociates to formaldehyde HCHO and $OH\cdot$ radical.

As it has been mentioned above, methyl peroxy radical $CH_3O_2\cdot$ interacts also with NO and produces methoxy radical CH_3O

$$CH_3O_2 \cdot + NO \rightarrow CH_3O \cdot + NO_2 \tag{2.25}$$

The only important reaction of methoxy radical $CH_3O\cdot$ under troposphric conditions is again production of formaldehyde and $HO_2\cdot$ radical

$$CH_3O \cdot + O_2 \rightarrow HCHO + HO_2\cdot \tag{2.26}$$

Formaldehyde further undergoes chemical reactions described in section (2.4.1). Formaldehyde is the first product of tropospheric methane oxidation with lifetime longer then few seconds. The overall formaldehyde troposheric lifetime for overhead sun conditions is approximately 3 hours [3].

2.4.3 General mechanism of hydrocarbon oxidation in troposphere

The mentioned three examples of carbon containing species together with the chemistry mechanisms they take part in and with further consequences of their chemical products on ozone concentration can be generalized into a set of reactions that are typical for all reactive organic hydrocarbons in troposphere, in polluted as well as in rural environment.

Volatile organic compounds (VOC), which are to more detail discribed in Chapter 3, dominate within the group of reactive organic hydrocarbons and therefore the following consideration of reactive hydrocarbons will be focused on VOCs only.

The process of tropospheric VOC oxidation can be devided into five steps while the complexity of the mechanisms increases with the complexity of the initial hydrocarbon compound [4].

- Organic radical formation by photolysis, by H atom abstraction from C-H bond by hydroxyl radical $OH\cdot$ and NO_3, or by addition to C=C bond by $OH\cdot$ radicals, NO_3 radicals and O_3 [10]. The reaction rates of organic radical $R\cdot$ production vary with the VOC species, while the most reactive species are alkens and aromatics (excluding benzene) [4].

$$VOC + OH; h\nu; NO_3; O_3 \rightarrow R \cdot + ... \tag{2.27}$$

- Addition of O_2 to organic radical leading to formation of peroxy radical $RO_2\cdot$

$$R \cdot + O_2 + M \rightarrow RO_2 \cdot + M \tag{2.28}$$

- Reduction of $RO_2\cdot$ radical mostly in reaction with NO to produce NO_2. In this step, organic peroxy radical replaces ozone in the oxidizing reaction of NO and therefore supports accumulation of ozone in troposphere. Furthermore, $RO_2\cdot$ radical reacts with $HO_2\cdot$ or with other $RO_2\cdot$ radicals (e.g. reaction (2.13))

$$RO_2 \cdot + NO \rightarrow RO \cdot + NO_2 \tag{2.29}$$

- Radical $RO\cdot$ formed in previous step reacts with oxygen molecule O_2 and produces carbonyl compounds and $HO_2\cdot$ radical. Beside that it can also isomerize or dissociate back to $R\cdot$ radical which quicly recombines with O_2 and regenerates peroxy radical $RO_2\cdot$.

$$RO \cdot + O_2 + M \rightarrow RCHO + HO_2 \cdot \tag{2.30}$$

- The main terminating mechanism in this system is consumption of $OH\cdot$ radical and NO_2 in reaction leading to nitric acid HNO_3 production which is then removed from the atmosphere by wet and dry deposition.

$$NO_2 + OH \cdot + M \rightarrow HNO_3 + M \tag{2.31}$$

2.5 Nitrogen oxides and nitrate radical

The previous sections have shown the importance of NO_x photochemistry in ozone formation. However, other reactions involving nitrogen oxides play significant role in tropospheric chemistry as well. Most importantly it is a production of NO_3 radical together with the NO_x function in nighttime chemistry and in termination mechanisms of hydrocarbon oxidation.

Relatively slow oxidation of NO_2 by O_3 leads to the formation od nitrate radical NO_3

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{2.32}$$

Nitrate radical NO_3 is a strong oxidizing agent reacting with a number of other atmospheric species. In lower troposphere it is in equilibrium with dinitrogen pentoxide N_20_5

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \tag{2.33}$$

The daytime concentration of N_2O_5 is relatively low due to photolysis of NO_3 but during nighttime its concentration rises and by forming a nitric acid in reaction with water vapour it is an important intermediator of nitrogen removal from the atmosphere during night.

Nitrogen radical NO_3 strongly absorbs in the visible range of solar radiation [21] and it photolysis to either NO (10% of reactions) or to NO_2 (90% of reactions) and so the day-light NO_3 levels are low [4]

$$NO_3 + h\nu \rightarrow NO + O_2 \tag{2.34}$$

$$\rightarrow NO_2 + O(^3P) \tag{2.35}$$

Further, NO_3 reacts rapidly with NO

$$NO_3 + NO \rightarrow NO_2 + NO_2 \tag{2.36}$$

which can have significant daytime concentrations in contrast to the nighttime, where away from strong source regions NO concentrations should be zero.

The removal of NO_x from the atmosphere is realized through wet and dry deposition of nitric acid HNO_3. By acting as a sink of atmospheric nitrogen it is a possible terminating mechanism of many oxidizing reaction chains. There are two reactions leading to HNO_3 production. Reaction of NO_2 with $OH\cdot$ radical during the day and reaction of N_2O_5 with water during night

$$OH \cdot + NO_2 + M \rightarrow HNO_3 + M \tag{2.37}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{2.38}$$

It is worth noting that in urban areas at nighttime the reaction of $OH\cdot$ radical and NO produces nitrous acid, HONO, another sink of atmospheric nitrogen. Both, HNO_3 and HONO are then removed from the atmosphere by wet and dry deposition.

2.6 The importance of VOC/NO_x ratio in ozone formation

The hydroxyl radical is the key reactive species in the chemistry of ozone formation. There is a competition for $OH\cdot$ radical between VOCs and NO_x. The reaction of $OH\cdot$ radical with VOCs (e.g. general reaction (2.27)) leads to ozone concentration increase due to formation of free radicals which alter ozone in oxidizing reactions of NO. On the other hand reaction of $OH\cdot$ with NO_x causes removal of nitrogen compounds from the air by wet and dry deposition of nitric and nitrous acids. That

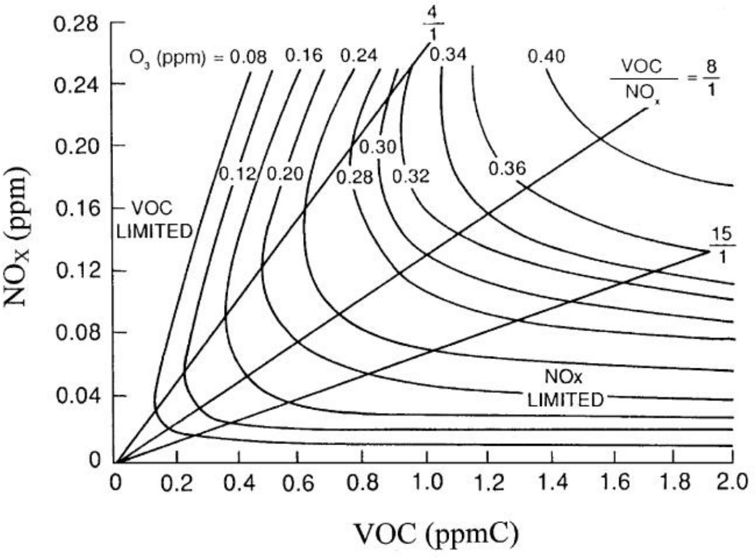


Figure 2.1: Example of an isopleth diagram illustrating calculated peak O_3 concentrations generated from various initial concentrations of NO_x and a specfed VOC mixture using the US EPA empirical kinetic modelling approach (adapted from [35])

means lower level of NO_2, the source of tropospheric ozone. The ozone concentration therefore depends on ratio between VOC and NO_x. If the VOC to NO_x ratio is high, the $OH\cdot$ reacts mainly with VOCs, if the ratio is low, reactions of $OH\cdot$ with NO_x predominate.

At a certain value of VOC to NO_x ratio the reaction rates of $OH\cdot$ with VOC and NO_x will be equal. This value depends on a particular VOC. When considering a usual urban composition of VOCs the value of VOC to NO_x ratio for balanced reactions with OH is 5.5. That means that NO_x tends to be removed from the atmosphere 5.5 times faster than VOCs. Under these conditions, a decrease in NO_x concentration favours O_3 formation as the VOC/NO_x ratio rises. At a sufficiently low NO_x concentration, or sufficiently high VOC/NO_x ratio, peroxy radical - peroxy radical reactions begin to be important and the free radicals removal retards O_3 formation [34].

In general, the increase of VOCs leads to higher ozone concentration, while the increase of NO_x can lead to more or less ozone, depending on the actual VOC/NO_x ratio and the rate of ozone production is not simply proportional to NO_x concentration. At a given level of VOCs, there exist an optimum VOC/NO_x ratio, i.e. a NO_x concentration at which a maximum amount of ozone is produced.

The dependence of O_3 production on initial VOC and NO_x concentrations can be graphically represented as an *ozone isopleth diagram.* Such a digram is a contour plot depicting maximum ozone concentrations as a function of VOC and NO_x initial levels. An example of *ozone isopleth diagram* is shown in Figure 2.1.

The isopleth ridge line identifies the maximum O_3 concentration at certain VOC level, allowing NO_x levels to vary. If the NO_x concentration will increase or decrease when compared to that at the ridge line keeping the VOC level constant, the ozone concentration will always decrease. The region in the *ozone isopleth diagram* below the ridge line is often called NO_x-limited, region above the ridge line VOC-limited [3]. The ridge line defines the VOC/NO_x ratio when all the NO_x is converted to nitrogen-containing products and there is no more left for NO-NO_2 reactions nor for NO_2 photolysis.

Chapter 3

Volatile Organic Compounds in the Atmosphere

Group of volatile organic compounds (VOC) embraces myriad of organic carbon-containing species present in the ambient air in mixing ratios of several ppb down to several ppt. However, the most abundant organic compound - methane, is excluded from this group because, from the tropospheric chemistry point of view, methane is less reactive than the other VOCs, its atmospheric lifetime ranges in the order of years. Therefore, the remaining subset of VOCs are often referred to as non-methane hydrocarbons or non-methane volatile organic compounds (NMVOC). To preserve brevity, further use of the term *VOC group* in this work will be ment to refer to NMVOC, if not otherwise stated.

Compounds belonging to VOCs are not only pure hydrocarbons but also oxygenated hydrocarbons or organic compounds containing also other heteroatoms, such as nitrogen, sulphur or halogen atoms. There have been subsequent attempts to give an exact deffinition of VOCs. The one given by US EPA describes VOCs as organic compounds having a vapour pressure greater then 10 Pa at 25°C, a boiling point of up to 260°C at atmospheric pressure, and 15 or less carbon atoms [36]. The remaining compounds are designated as semivolatile organic compounds (SVOCs). Simply, VOCs can be described as organic chemical compounds which, under normal conditions, have the vapour pressure high enough to vaporize into the atmosphere.

VOCs are emitted into the atmosphere from various kinds of sources and one can meet them in daily life. They are found in significant amounts in remote oceans, rural areas as well as in urban environments. On global scale the highest amounts of VOCs originate from natural sources, although in urban areas anthropogenic sources dominate. Among human activities which are connected with VOC production mainly belong a production and combustion of fossil fuels, application of solvents and solvent-containing species and biological processes in agriculture. The prevailing natural source of VOCs is vegetation and a certain amounts are emitted also from wetlands, soils and oceans. One of the major sources of VOCs which hasn't been mentioned yet is biomass burning. It is arguable whether it should be assigned to biogenic or anthropogenic sources since it could be regarded as natural process but significantly enhanced by human practices. It is considered that biogenic sources are about ten

Compound	**Average Lifetime**	**Compound**	**Average Lifetime**
Alkanes	Months - Days	*Aromatic compounds*	Weeks - Hours
• Ethane	2.5 Month	• Benzene	2 Weeks
• Propane	2.5 Weeks	• Toluene	2 Days
• n-Pentane	4 Days	• 1,3,5-Trimethylbenzene	7.5 h
Alkenes	Days - Hours	*Biogenic Compounds*	Hours - Minutes
• Ethene	1.5 Days	• Isoprene	3 h
• Propene	11 h	• α-pinene	4 h
• 1-Butene	10 h	• Limonene	30 min
Cyclic Compounds	Days - Hours		
• Cyclopentane	4 Days		
• Methylcyclohexane	2 Days		
• Cyclohexane	3 h		

Table 3.1: Overview of average tropospheric lifetimes of VOC compound groups and examples of some selected VOC species. Lifetimes are given for an average concentration of OH radical equal to 6.10^5 per cm^3 and an average ozone concentration of 7.10^{11} per cm^3.[36]

times larger than the sum of anthropogenic emissions including fossil fuel emissions [6].

The most important sink of atmospheric VOCs are oxidative processes usually initiated by OH radical and to a lesser extent by O_3 and NO_3. These chemical processes lead to production of CO_2 and H_2O and to a side formation of various intermediates whose amount and complexity depend on the specific VOC species undergoing the oxidation. Furthermore, VOCs are efficiently physically removed from the atmosphere through dry deposition on the surfaces such as vegetation or aerosol and through wet depostion in rain. Some VOC species which are able to absorb solar light can photolyse to smaller fragments. At certain circumstances biological uptake of VOCs can be also an effective removal of these compounds from the air. Especially under high ambient concentrations it has been seen that some plants switch from VOC emission to VOC uptake, crossing the so called *compensation point* [37].

Due to their relatively high reactivity, the lifetime of VOC species in troposhere ranges from minutes to several days. The average tropospheric lifetimes of VOC compound groups are listed in Table 3.1 together with lifetimes of several examples of species representing each group.

As it has been discussed in Chapter 2. volatile organic compounds are an essential "fuel" for oxidative photochemical processes in the troposphere controlling the concentration of ozone and the most important oxidizing agent - OH radical. In addition to influence on photochemistry on local as well as on global scale, several VOC species can also have an impact on climate. Either due to their properties as greenhouse gases or due to their ability to form aerosol particles.

Despite the importance of VOCs in the troposphere it is relatively difficult to estimate their amount in the air. There are two general approaches of VOC abundance estimation. Using the so called "bottom-up" approach the emission inventory is build based on identification of the sources of a particular VOC species. The emission rates assigned to each source together with the spatial and temporal variability are then aggregated into an emission database. Other possibility of VOC estimation is direct measurement of concentrations in the ambient air ("bottom-down" approach). The difficulty of both methods lies in the high diversity of VOC species. There are various potential sources of VOCs, their determination and description is rather complicated and therefore the emission inventories carry high uncertainties. Similarily, the detection of VOCs in the ambient air requires variety of sensitive and specific sensors with respect to particular VOC species, its chemical and physical properties. Nevertheless, a lot of progress has been done in this field. The up-to-date methods have been employed to produce the global and regional estimates of anthropogenic and biogenic VOC emissions with highest possible accuracy.

Since the aim of this work is to investigate the abundance of biogenic VOCs in the atmosphere and to study the influence of BVOCs on tropospheric chemistry, Chapter 4. is dedicated to describe this group of compounds thoroughly, describing the BVOC group composition, the main BVOC sources, the mechanisms of formation and release and finaly the methods of BVOC measurements and modelling. However, volatile organic compounds with anthropogenic emissions can not be omitted and therefore are briefly discussed in the following section.

3.1 VOCs from anthropogenic sources

Emissions of volatile organic compounds with anthropogenic origin are caused mostly by combustion processes, production of fossil fuels, solvent use and industrial processes. Among the main combustion processes belong the internal engine vehicle combustion, combustion in plants and furnaces. The solvent species can be found for example in paints, varnishes, metal degreasig agents and adhesives. The biological processes are dominantly linked with methane production and include especially digestive processes of ruminants, handling of animal manure and disposal of organic wastes. Although the distinction between biogenic and anthropogenic VOCs in the atmosphere is far from the straightforward, it is considered that the prevailing anthropogenic VOCs are alkanes and aromatics emitted as a result of incomplete combustion of fossil fuels and from its vaporization [38].

An effort has been made to estimate the global VOC emissions from anthropogenic sources and point out the most important contributors. According to [39] the total global emissions for year 1990 were estimated to be as high as 142 $Tg.yr^{-1}$. The rates for individual source types are shown in Table 3.2. The EDGAR inventory which is a world-wide approach providing estimates of anthropogenic emissions of greenhouse gases and air pollutants offers the estimate of global anthropogenic VOCs for year 2000 equaling to 186 $Tg.yr^{-1}$ [40].

Higher VOC concetrations are observed in the winter time in urban areas due to much shallower boundary layer and reduced solar flux, reducing the production of hydroxyl radical which is responsible for VOC removal. VOC concentrations exhibit a tendency to be elevated at night, when vertical dispersion is least effective, decreasing to minimum during mid-afternoon as the planetary boundary layer rises and wind speeds increase, and then rising to the nighttime maximum [41].

Individual anthropogenic VOC sources are to more detail described in the following sections. The sources are classified into three groups according to processes related to VOC production, i.e. combustion, solvent production and application, and other industrial and biological processes.

3.1.1 Emissions from combustion processes

Process of a complete combustion can be described by the following equation

$$C_nH_m + (n + m/4)O_2 \rightarrow nCO_2 + m/2H_2O \qquad (3.1)$$

where C_nH_m represents a fossil fuel or other organic material with a certain amount of carbon and hydrogen, and $(n + m/4)O_2$ indicates the stoichiometric amount of oxygen that is theoretically needed for a complete combustion. Products of such complete combustion are carbon dioxide and water. However, technical combustion processes are more or less incomplete. One possible reason for it is that for combustion of real materials more than the stoichiometric amount of oxygen is needed due to inhomogenities of the fuel - oxygen mixture. Other reasons for incomplete combustion may be the low combustion temperature or the residence time of the fuel in the burner zone being too short [38].

Incomplete combustion of fosil fuels leads to emissions of CO, an intermediate product of carbon oxidation to CO_2, and to production of VOCs of various kinds. Combustion emissions include unoxidized forms of hydrocarbons, such as alkanes and aromatics, partially oxidized hydrocarbons (e.g. aldehydes) and newly formed VOCs as a result of reactions with radicals as well. Generally, the more incomplete a combustion is, the more VOC species are produced.

From this point of view the least effective and therefore the major source of VOCs from combustion are motor vehicles. This fact is also demonstrated in Table 3.2 which summarizes estimates of anthropogenic VOC emissions on global scale. Emissions resulting from road transport may be divided into emissions from exhaust and fugitive emissions by evaporation [42]. According to [38] highest VOC emitters are two-stroke gas enigines whose exhaust contains not only noncombusted or partially combusted gasoline but also a noncombusted or partially combusted motor oils. Motor engine emissions decrease with the increasing engine combustion effectivness through four-stroke gas engines, heavy and light-duty diesel engines to diesel engines of passenger cars which have the lowest emission factors. Within the past decades the emissions from transport have declined as a result of increased use of catalytic converters and the switch from gasoline to diesel cars [41].

Regarding the emissions from stationary sources such as furnaces and stationary plants, factors contolling the emission rates are fuel type and combustion techniques determining the completness of combustion. In general, the combustion of gaseous and liquid fuels leads to less VOC emissions than the use of coal, wood or other solid fuels. The only exception are coal dust combustion installations which produce even less VOCs than heavy fuel oil power plants [38]. Although the fuel comsuption of large

Activity	**Emission** ($Tg.yr^{-1}$)
Fuel Production / Distribution	
Petroleum	8
Natural gas	2
Oil refining	5
Gasline ditribution	2.5
Fuel Consumtion	
Coal	3.5
Wood	25
Crop residues (including waste)	14.5
Charcoal	2.5
Dung cakes	3
Road transport	36
Chemical industry	2
Solvent use	20
Uncontrolled waste burniing	8
Other	10
Total	142

Table 3.2: Estimated global emissions of VOCs from anthropogenic sources for year 1990.[39]

industrial installations is vast, in the overall sum more important stationary sources are small furnaces in households. Usually large combustion plants are equipped with complex and costly technologies ensuring the more or less complete combustion of specially prepared fuel while the construction of household furnaces is relatively simple and the combustion here is not that optimal.

3.1.2 Solvent-use emissions

In industrialized countries, the application of solvents and solvent-containing products is one of the major sources of VOCs. Large amounts of solvents are used in the chemical industry. However, this category is not usually important emitter because the reactions are carried out in self-contained installations where the emissions are much lower compared to the input amounts. On the other hand, significant evaporation of solvents is observed at processes related to application of paint, printing inks, adhesives, cleansing agents, etc. In these cases, the evaporation losses are enhanced by the use of organic solvents with high vapour pressures and treatment or drying of materials at increased temperature. If no extraction process has been implemented, the solvents used are released into the atmosphere almost completely.

The solvent-containing products are being used in various branches of industry. When considering, for example, application of paints, it occures in the industrial production as well as in commercial and private sector. Large amounts of paints and thinners are applied for instance in shipbuilding, manufacturing of automobiles, mechanical engineering, car repair and building trades (painting and lacquering). Not negligible is the contribution of cleaning agents in commercial dry cleaning, application of printing inks and auxiliary chemicals in printing industry [38].

3.1.3 Emissions from industrial and agricultural processes

An important processes of industrial VOC release which have not been mentioned yet are mining, treatment, storage and distribution of solid, liquid and gaseous fuels. The so-called firedamps can be found in the deep coal fields and are filled mainly with methane and in lesser amounts with ethane and propane. During the coal mining, the firedamps often result in emission release into the atmosphere since it is not economical to use it as a fuel. Compared to further emissions of methane from coal storage and treatment the firedamp emissions dominate.

Another source of VOC emissions is crude oil production as well as its following treatment, the petroleum refining industry. The undesired VOC release is often caused by gas venting and flaring, leakage in maintanance devices such as seals and valves. Potentinal source of emissions is also a storage of gasoline which represents a product with a very high volatility. The distribution chain of gasoline starting at the petroleum rafinery and ending at the undergroung storage tanks of gasoline service stations offers many opportunities for considerable liquid evaporation and release of vapour-loaded air above the liquid surface in tanks.

There is a long list of industrial branches which are to smaller or bigger extent related to VOC production. Beside those already described we can further mention pharmaceutic production, food and bevarage industry, production of synthetic materials, etc.

Human driven biological processes, e.g. in agriculture, belong to main sources of anthropogenic VOCs. Especially methane, but also other compounds are released in large amounts from flooded rice fields, livestock husbandry and as a product of municipal and domestic waste disposal. The decomposition of organic materials occures partially under aerobic and partially under anaerobic conditions. The latter process results mainly in methane and carbon dioxide production. Anaerobic decomposition may be controlled by frequently removing the waste. However, methane has been recently utilized as a biofuel and therefore some facilities build a gas sampling systems to collect methane production for its future use as an energy source.

Chapter 4

VOCs from natural sources

The interaction between biosphere and atmosphere is essential for all living systems and organisms. Biosphere and atmosphere form a coupled system within which they influence each other by exchanging mass and energy. When considering the exchange of gaseous compounds, fluxes that predominate involve three gases - carbon dioxide, oxygen a nitrogen. Carbon dioxide is being produced by respiring organisms and uptaken during photosynthesis. On the contrary, oxygen (O_2) is a product of photosynthetic organisms and is consumed by aerobic respiration. Nitrogen (N_2) is a result of denitrifying bacteria production and is taken up by nitrogen-fixing bacteria. These fluxes have determined the composition of current atmosphere. Significant is the high proportion of oxygen in the atmosphere due to rise of photosynthetic organisms. Oxygen-rich atmosphere resulted, beside other consequences, in ozone and OH radical formation, reactive species having an important impact on chemistry of the atmosphere.

In addition to mentioned gas fluxes, most living systems directly or indirectly emit and uptake volatile organic compounds. There are hundreds of VOC species being released from biogenic sources. The first biogenic volatile organic compound (BVOC) specifically identified to be important for atmospheric composition was isoprene [43]. Subsequently, [44] has suggested that the "blue haze" being observed in the summertime in forested areas, such as the Blue Mountains (Australia) or Smoky Mountains (United States), might be a result of photochemical reactions of volatile organic substances emitted by vegetation. These findings led to an idea that emissions of biogenic VOCs might contribute to tropospheric ozone formation and initiated following research activities focused on BVOC role in tropospheric and stratospheric chemistry, modelling BVOC emissions and investigation of BVOC formation and biological function.

The main BVOC emitter is vegetation but certain amounts are released also from oceans and soils. The early estimates of the type of compounds emitted from vegetation resulted in a list of 300 different compounds which was later extended with compounds detected in emissions from cut branches [45] and floral scents [46] resulting in aproximately 1000 compounds known to be entering the atmosphere [9]. The biogenic VOCs include isoprenoids (isoprene and terpenes), alkanes, alkenes, carbonyls, alcohols, esters, ethers and acids, while the predominant species are isoprene and monoterpenes [12].

Biogenic VOC species are often categorized into isoprene, monoterpenes and generalized groups of Other Reactive VOCs (ORVOC) and Other VOCs (OVOC). The latter two groups distinguish compounds with atmospheric lifetimes less than 1 day (ORVOC) and greater than 1 day (OVOC) [47]. Lately, two more categories were added reflecting the findings of recent studies - group of oxygenated VOCs (oxVOC) and Very Reactive VOCs (VR-VOC) [20]. Examples of biogenic VOCs are listed on Figure 4.1 showing compounds' chemical formulas and structures.

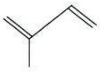
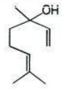
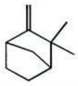
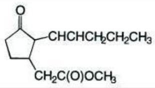
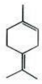
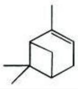
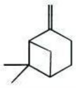
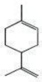
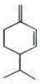
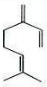
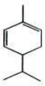
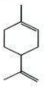
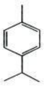
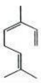
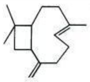
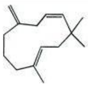
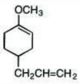
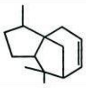
Compound name	**Chemical formula**	**Chemical structure**	**Compound name**	**Chemical formula**	**Chemical structure**
Isoprene	C_5H_8		Linalool	$C_{10}H_{18}O$	
Camphene	$C_{10}H_{16}$		Methyl jasmonate		
3-Carene	$C_{10}H_{16}$		Terpinolene	$C_{10}H_{16}$	
α-Pinene	$C_{10}H_{16}$		*γ*-Terpinene	$C_{10}H_{16}$	
β-Pinene	$C_{10}H_{16}$		*α*-Terpinene	$C_{10}H_{16}$	
Limonene	$C_{10}H_{16}$		*β*-Phellandrene	$C_{10}H_{16}$	
Myrcene	$C_{10}H_{16}$		*α*-Phellandrene	$C_{10}H_{16}$	
Terpinolene	$C_{10}H_{16}$		p-Cymene		
Sabinene	$C_{10}H_{16}$		c-*β*-Ocimene		
β-Caryophyllene	$C_{15}H_{24}$		t-*β*-Ocimene		
α-Humulene	$C_{15}H_{24}$		*α*-Copaene		
Methyl chavicol			*α*-Cedrene		

Figure 4.1: Examples of non-methane volatile organic compounds emitted by vegetation (adapted from [48])

Isoprene and monoterpenes belong to the biochemical group of isoprenoids (or terpenoids). These compounds' carbon skeletons are composed of characteristic C_5 units. According to number of C_5 units, they are subdivided into hemiterpenes (C_5, e.g. isoprene), monoterpenes (C_{10}, e.g. α-pinene, menthol, camphor), sesquiterpenes (C_{15}, e.g. β-cariophyllene) and the larger C_{20}, C_{25} and C_{30} molecules [12]. Usually these compounds are strong smelling, hardly water-soluble and found in plants as well as in animals and microorganisms.

Oxygenated VOCs are defined as carbon-based compounds containing an oxygen atom. Dominantly observed species from this category are methanol, ethanol, methylbutenol (MBO), formaldehyde, acetaldehyde and acetone. Biogenic emissions are the prevailing source of these compounds in the atmosphere, having a significant impact on atmospheric chemistry [20].

Analysis from recent field measurements have suggested existence of terpenoid compounds which react so quicly within the forest canopy that they are not being detected by the above canopy flux measurements. For example, [49] have measured branch emissions from various citrus plants in orange orchard in Spain. The detected terpene species were upscaled to canopy level to determine canopy emission rates, these were then compared with values obtained from measurements above the canopy. Substantial removal of these very reactive terpenes was detected during transport from the canopy to the atmospheric boudary layer. Another experiment conducted by [50] in Pendrosa pine forest in California revealed large quantites of oxidation products of short-lived biogenic precursors. Comparison of observed amounts of oxidation products within and above the forest canopy has proven high emissions of biogenic precursors which are being oxidized before escaping the canopy. These terpene compounds were termed VR-VOCs.

Although vegetation is the main BVOC source, soil and marine water contributes to this compound group as well. Even though methane is not usually included in the group of BVOCs, it is worthy to note that significant amounts of methane are emitted due to bacteria production in soils, sediments and other anaerobic environments. Over the oceans and in marine environments, an organosulfur compound dimethylsulfide (DMS) is emitted into the atmosphere as the result of processes associated with phytoplankton. Except for methane and DMS, these sources are, however, much weaker emitters then terrestrial plants. The lack of other significant emissions resides in part from their large capacity for microbiological oxidation of hydrocarbons and other organic species, which largely prevents release of VOCs to the atmosphere. For example, only 10% of methane produced in soils and sediments escapes the microbiological oxidation [9].

Nonmethane BVOCs play an important role in shaping tropospheric chemistry by affecting global as well as regional photochemical oxidant formation, balancing the carbon cycle and producing organic acids which contribute to acidic deposition in rural areas. Atmospheric concentrations of BVOCs range from few ppt to several ppb [12]. The reactivity of these compounds is high as reflected by their chemical lifetimes which range from minutes to hours (Table 4.1). Many species of biogenic VOCs are rapidly oxidized by ozone, OH radical or NO_3 radical. Such reactions lead to production of secondary chemical species which can enhance concentrations of low-level ozone and other oxidants in areas rich in nitrogen oxides [10]. On the other

Name	**Chemical lifetime** *Day*	 *Night*	**Example**	**Atmospheric concentrations**
Isoprene	3 hrs	1.5 hrs	isoprene	ppt to several ppb
Monoterpenes	2-3 hrs	5-30 min	α-pinene, β-pinene, sabinene	ppt to several ppb
	40-80 min	5-20 min	limonene, t-β-ocimene, myrcene	
	15-20 min	<1 min	terpinolene, α-phellandrene	
	<5 min	<2 min	α-terpinene	
Sesquiterpenes	<4 min	<2 min	β-caryophyllene	not detectable due to high reactivity
ORVOC	<1 day		2-methyl-3-buten-2-ol	1-3 ppb
OVOC	>1 day		methanol, acetone	2-30 ppb

Table 4.1: Comparison of nonmethane volatile organic compounds (NMVOC) categories. [12]
Lifetimes are estimated in relation to $[NO_3]$ = 10 ppt, $[O_3]$ = 20 ppb for night; and [OH] = 10^6 molecules/cm^3, $[O_3]$ = 20 ppb for daylight conditions.

hand, the oxidation of BVOCs under low concentrations of NO_x lead to formation of peroxides and acids [51]. Acids as well as some other BVOC oxidation products may undergo gas-to-particle conversion leading to the growth of secondary organic aerosols (SOA) [52]. Furthermore, consumption of OH radical in oxidizing reactions of BVOC may cause an increase of atmospheric methane concentration since reaction with OH radical is the major sink of tropospheric methane [53]. Fomation of aerosols, which control the Earth's energy balance, and accumulation of methane, one of the major greenhouse gases, are two examples of how biogenic VOCs directly influence the Earth's climate. The relation of biogenic VOCs to tropospheric chemistry is to more detail discussed in Section 4.4.

Because of the BVOC importance in the composition and chemical processes in the atmosphere with impact on air quality and climate, the aim is to build up a model to estimate BVOC emissions and include them in the chemical modelling of the atmopsphere. Althoug biogenic VOCs are still connected with many uncertainties, a lot of progress has been done in this field over the last two decades. In the following sections, the overview of current knowledge about BVOC formation, release and function is given together with the description of roles of external factors influencing BVOC emissions. The methods of BVOC measurement techniques and approaches of BVOC modelling are outlined as well. The main focus is on isoprene and monoterpenes, as these are the prevailing compounds of biogenic VOC emissions.

4.1 BVOC formation and mechanisms of release

The ability to build a sophisticated model to estimate the biogenic VOC emissions starts with the observation and understanding of the biological mechanisms involved in the BVOC formation.

4.1.1 Isoprene

Isoprene is one of the most studied biogenic hydrocarbons, very reactive species with relatively high global annual emissions estimated to roughly equal emissions of methane from all sources [54]. Isoprene, which has a chemical structure 2-methyl-

1,3-butadiene, is emitted mainly from woody plants, but also from some firns, vines and other herbaceous species [9]. However, there is no clear phylogenetic basis for isoprene emissions in plants, the pattern of decision whether the plant is isoprene emitter is not known. Even in plant families that contain isoprene emitting species, a non-emitters are found.

Isoprene is produced via de novo synthesis which means that it is emitted immediately after the formation and is directly linked to photosynthesis [55]. Isoprene biosynthetic pathway starts with fixation of photosynthetic carbon which then undergoes a set of biochemical reactions to form isopentyl pyrophospate (IPP) which then isomerizes to dimethylallyl pyrophosphate (DMAPP). This compound, DMAPP, is enzymatically catalyzed in chloroplasts to form isoprene. The enzyme responsible for isoprene production is called *isoprene synthase.* It appears to be a light activated enzyme which catalyzes the elimination of pyrophosphate in DMAPP [56]. Isoprene emission is dependent on leaf developmental stage. In the study of [57] it has been proven that isoprene synthase is active only in mature leaves.

After its formation, isoprene is not stored in the plant, but is immeadiately lost by volatilization [12]. Isoprene is emitted through leaf stomata, however, it is not effected by stomatal conductance. When stomata are closed and isoprene production is still active, the decrease of stomatal conductance is compensated by the increase of intercellular isoprene concentration. The enhanced gradient between intercellular and atmospheric isoprene mixing ratio enables isoprene release despite the diffusive limitations of closed stomata [58].

4.1.2 Monoterpenes

Monoterpene compounds are emitted especially by conifers such as pine, spruce, fir, by mint or citrus families [48] and are known to constitute the main fraction of terpenic or essential oils produced in plant secretory organs [12]. Monoterpene emissions are mostly dependent on ambient temperature, although few species (e.g. oaks) show ligh-dependence of emissions suggesting link between monoterpene formation and photosynthetic processes.

The biosynthesis of monoterpenes is similar to that of isoprene. By adding another IPP unit to DMAPP, the monoterpene geranyl pyrophosphate (GPP) is produced by merging two five-carbon branched chains. GPP is the starting unit for monoterpene compounds as well as the origin for further addition of IPP units to produce sesqui- and diterpene species. Different types of monoterpene species are synthetized based on the activities of different monoterpene cyclases [12].

There are two pathways of monoterpene formation that relate to the nature of emissions. Temperature dependent monoterpenes are usually synthetized in leucoplasts or cytosol and then are stored in secretory organs in the plant. These storage structures can be either internal to the leaf (e.g. resin ducts in a pine tree) or external (e.g. glandular trichrome on the surface of mint leaves) [20]. The second pathway relates to light and temperature dependent monoterpene emissions. The biosythesis of these compounds is similar to that of isoprene and is linked to photosynthetic cycle. These types of monoterpenes are produced in chloroplasts and are immediately emitted without storage [59]. Monoterpene production is highest in the specialized storage tissues of young leaves and declines with the leaf development. Reason for monoterpene enrichment in expanding leaves lies in plant protecting function of monoterpenes against insects and herbivories [9]. The ecophysiological roles of monoterpenes as well as other BVOCs are further discussed in the Section 4.2.

Monoterpene release into the air again depends on the formation pathway. Either it is volatilization from the storage pools controlled by temperature, or direct emission through the stomata as in the case of isoprene. Additional mechanism of monoterpene release is a respond to mechanical wounding of monoterpene storage organs, which can occure after the herbivory or insect attack on the plant, or is caused by anthropogenic interference such as pasture cutting or forest thinning. Monoterpene emissions can last long after the physical damage. [60]

4.1.3 Other VOCs

Many other volatile organic compounds are emitted from biogenic sources. Several examples of compounds other then isoprene and monoterpenes are given in this section.

Considerable plant emissions of methanol were first observed by [61] and further work of [62] showed that methanol is emitted mainly during the leaf expansion and the emissions decline with increasing leaf age. They also showed that methanol is released by leaf stomata and the emission is dependent on stomatal conductance as measurements proved reduction in methanol emissions after the stomata closed. Emissions of methanol can also occure due to plant wounding or from decomposition of leaf and soil litter [20].

Emissions from poplar trees were examined by [63] who indicated increased leaf emission of acetaldehyde and ethanol while flooding of the roots. They suggested that flooded root system causes an activation of alcoholic fermentation which leads to significantly increased ethanol concentration in the xylem. Ethanol is then transported by the transpiration stream to the leaves, where can be oxidized to acetaldehyde and both compounds are released to the ambient air. Furthermore, bursts of acetaldehyde from various plants were observed during light-dark transitions [64].

Similar to isoprene formation mechanism is production of methylbutenol (MBO). It is formed via the same biosynthetic pathway with DMAPP as a precusor, but MBO is emitted from different type of vegetation than isoprene. Another compound emitted in large quantities from the vegetation is acetone. It can be emitted during leaf wounding or from light-dependent as well as light-independent responses in the leaf [20].

The list of volatile organic compounds emitted from various biogenic sources could be long and except for compounds already mentioned could include compound groups such as alkanes and alkenes (e.g. ethane, propane, butane), organic acids (e.g. formic and acetic acids), other carbonyl compounds (e.g. formaldehyde) and many others. The analysis and identification of chemical species emitted and understanding of their formation processes are the continuous subject of recent reserch. However, it is an uneasy task as each group of species requires special techniques and approaches.

More detailed review of species emitted from natural sources can be found in the literature, e.g. [12], [65].

4.2 Ecophysiological functions of BVOCs

The purpose of isoprene emission is still subject of speculation. Usually 0.5 - 2% of carbon fixed by photosynthesis is converted into isoprene [66]. The biochemical energy needed to convert CO_2 to isoprene is relatively high. Since nature acts very economically, there has to be a good reason for plants to make such effort to produce isoprene, but the reason is still not very clear.

The experiments of [67] suggested the influence of isoprene on plant flowering. They showed that presence of isoprene significantly accelerated the onset of flowering. This observation led to an idea that by emitting isoprene, plants may control the timing of flowering in order to get an advantage over the other plants in attracting the pollinators.

Other possible role of isoprene emissions is in plant tolerance of ozone and other reactive oxygen species. In the work of [14] it has been presented that plants emitting isoprene were less sensitive to exposure to high ozone concentrations than isoprene non-emitters. Isoprene protected plants against the damaging impact of ozone on photosynthesis and on stomatal conductance. The protective effect was more evident when plant was exposed to relatively low ozone levels for a long time than when the exposure was short but under high ozone levels. On the other hand, when plants emit isoprene into the air with high nitrogen oxide concentration, the emissions may enhance the ozone formation and therefore rise the likelihood of oxdative stress on the plant. In such environment, isoprene emitting plants will tend to be better protected against such damage than plants which do not produce isoprene. This fact may lead to change in the ecosystem composition, where isoprene emitters will be favoured because of their greater resistance to ozone damage [68].

The most discussed possible function of isoprene is protection of plants against heat stress. Thermotolerance was first suggested by [13] who indicated that isoprene emission had some relationship to temperature effects. In the experiments of [69] the isoprene emitting plants were kept in conditions suppresing the internal isoprene synthesis in order to test the effects of isoprene by controlled isoprene fumigation on the leaves. Measurements have shown that isoprene fumigation increased the temperature at which the thermal damage occured in isoprene emitting species and the thermotolerance ability was even enhanced by increased light conditions. Contrastingly, thermotolerance was not observed in leaves of isoprene non-emitter. In support of this model is the finding that leaves of plants grown in relatively low temperatures emit no or little isoprene, and then rapidly induce isoprene synthesis when exposed to high temperatures [9].

Furthermore, hypothesis published by [70] suggested that isoprene formation inside chloroplasts could serve to prevent light damage by dissipating the excessive energy.

Despite many experimental findings which demonstrated the role of isoprene, the reason why some plants invest relatively high amount of energy into isoprene production and some don't is still not fully understood.

On the other hand, some ecophysiological functions of certain monoterpene compounds have been well described. Monoterpene species, such as linalool, have been found in the flowering fragrances playing an important role of attracting the pollinators [11]. However, plants usually emit a whole mixture of VOCs. The reason for it is the fact that mixture has higher importance than only a single species. For example, alfalfa flower has a relatively simple mixture of honeybee attractants consisting of only five major VOCs. When testing the effects of individual VOC species, most of them caused neutral or even repellent reaction and none of them provided the effectivness of the whole mixture [9].

Special organs on plant leaf tissues for monoterpene storage indicate importance of these compounds in the plant protection against invading parasites and pathogens. After wounding, storage organs are damaged and monoterpenes volatilize into the ambient air and deter parasite, herbivore and other intruders. Furthermore, additional production of monoterpenes is induced after the attack (e.g. [71], [12]). For instance, some monoterpenes possess a deterrent odour or taste that stops herbivorous mammals from feeding, or protects plants against colonization or oviposition by insects [12].

Interesting is a monoterpene function in the plant signaling. For instance, tobacco plants, when infected by tobacco mosaic virus, release methyl salicylate acting as an atmospheric signal to warn other tobacco plants against infection [72]. The study of [73] described an extraordinarily cooperative system of protection of corn seedlings induced by monoterpene emission. Under normal growing conditions, corn seedlings are monoterpene non-emitters. However, when under attack by a certain catterpillar, they release monoterpene species reacting specifically to the animal's saliva. This emission signal attracts a wasp, caterpillar's natural enemy, which deposits its eggs into the caterpillar. Thus, corn seedlings defend themselves against the overpopulation of their predators. Furthermore, some monoterpenes released from plants have been proven to provide an allelopathic function, i.e. a negative effect on other plant species growth and development caused by emited biochemicals. For example, monoterpene oils produced by several types of thyme caused a limitted seed germination and growth of other plants in the neighbourhood [74].

The role of light induced monoterpene production and emissions is not yet clear, but a thermal protective role like that of isoprene has been suggested by [59].

4.3 Influence of environmental factors on BVOC emission

As it has been mentioned in the preceding sections, emissions of VOCs from biogenic sources are subject to great variability. Beside the genetically predetermined biodiversity of the vegetation emissions, the release of VOCs by a given plant species exhibits significant variation in time and space. The VOC emission variability is a result of complex interactions between the organism and its environment that are only partially understood [75]. Emissions vary from plant to plant dending on its developmental stage, possible damage or plant injury, geographical location and of course with respect to the local ambient conditions. There are many local environemntal factors which influence VOC emissions, in short-term as well as in long-term scale. The immediate emissions vary most importantly in relation to temperature, light and the chemical compostion of the ambient air. All these factors are to more detail discussed in the following sections.

4.3.1 Temperature control

Temperature can influence emissions of all biogenic VOC categories. Especially, it is a dominant controlling factor for monoterpenes stored in the reservoir organs as the vapour pressure of these compounds increases with rising temperature [48]. For compounds such as isoprene and monoterpenes which are not released from preexisting pools, temperature response of emissions is caused by the impact of temperature on the underlying metabolism [76].

Experiments conducted by [77] on eucalyptus trees, and later by [8], had an ambition to develop a leaf emission model of isoprene and monoterpenes with a foundation in the physiological processes of a leaf, especially in temperature and light. Under constant light conditions, they have observed an exponential increase in monoterpene emission with increasing temperature. In case of isoprene, emission increased exponentially with temperature up to 35 to 45°C and then decreased as temperature continued to rise. Initially, it was thought that the decline in isoprene emission was due to denaturation of isoprene synthase enzyme [78]. Recent studies suggest that decrease in isoprene emissions is a result of temperature regulation and that the regulation is a reversible process [79]. Monoterpenes dependent on temperature as well as on light respond to temperature in the similar manner as isoprene. Dependencies of isoprene and monoterpene on leaf temperature are depicted on Figure 4.2.

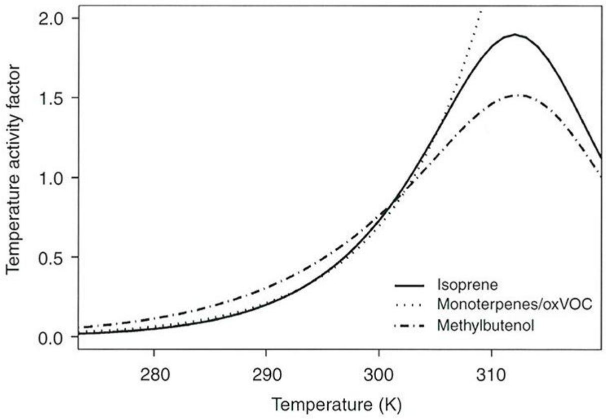


Figure 4.2: Dependence of BVOCs on temperature under constant light conditons (adapted from [20])

Although isoprene and monoterpenes are the most investigated compounds, several studies focused on other VOCs as well. For instance, [80] observed that MBO (2-methyl-3-buten-2-ol) emitted from pine species behaved similarily to isoprene. The MBO emission increased with temperature up to approximately 35°C and above 42°C emissions decreased rapidly. However, most of oxygenated volatile organic compounds are exponentially dependent on temeperature similarly as monoterpenes as it arises from measurements above the pendrosa pine plantations published by [81].

4.3.2 Light control

The dependence of isoprene on light has been observed already at the time of its discovery in late 1960's. Successively, some monoterpene species and some OVOC exhibited emission dependence on light, more accurately on photosynthetically active radiation (PAR). PAR is a portion of photons with wavelength in range 400 - 700 nm which activate photosynthesis, it is usually expressed in $\mu mol.m^{-2}.s^{-1}$. The response of isoprene to PAR is hyperbolic, emissions increase with PAR until they reach a saturation point. This relation has been measured and empirically decribed by [77] and [8] (Figure 4.3). Isoprene emissions decline to zero during night.

As it has been already mentioned earlier, recent studies have shown that some plants (e.g. Mediterranean oak) emit monoterpene species as a function of temperature as well as PAR [82], [20]. Furthermore, leaf-level emissions of MBO have been proven to respond to light in similar way as isoprene [80].

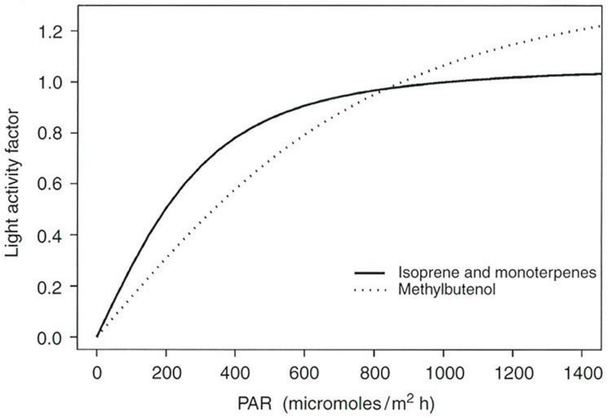


Figure 4.3: Dependence of BVOCs on photosynthetically active radiation (PAR) under constant temperature conditons (adapted from [20])

4.3.3 Influence of ambient air chemical composition

Several studies based on laboratory measurements have investigated inflUcence of chemical composition of the ambient air on BVOC emissions. The behaviour of plants in atmosphere rich for carbon dioxide is of special interest in the context of future climate as it is predicted that the concentration of CO_2 will rise within the next century.

Elevated levels of CO_2 indirectly effect the BVOC emissions. If the carbon dioxide levels are about to rise, the Net Primary Production will respond with a significant growth [83]. Furthermore, since it has been proven that BVOC emissions are positively correlated with temperature [77], the potential increase in surface temperature would lead to higher biogenic VOC emissions.

Direct effects of high and low CO_2 concentrations on plants has been investigated as well. The review in [84] indicate that the short-term exposure to increasig CO_2 concentration can lead to inhibition of isoprene emissions while the decreasing CO_2 concentration has the opposite effect, unless the CO_2 level is zero. Although not all experiments mentioned in the review prove this relation. For example, the effect of high CO_2 levels on isoprene emissions was studied on oak and aspen plants. Oak leaves grown under elevated CO_2 (CO_2 partial pressure of 65 Pa) emitted twice the amount of isoprene when compared to leaves grown under low levels of CO_2 (40 Pa). However, aspen leaves behaved oppositely. Aspen leaves grown under high CO_2 concentrations decreased their emissions to 40 - 60 % of the value emitted under low CO_2 [85].

The evaluation of overall effect of CO_2 concentration levels is not yet totally understood and probably strongly depends on the vegetation type. Neverthless, the direct and indirect CO_2 effects clearly have to be treated simultaneously while modelling isoprene emissions, since a number of effects may counterbalance each other [84].

As it has been discussed earlier, the emissions of BVOC play an important role in the formation of tropospheric ozone. Interestingly, leaf gas exchange measurements indicate that ozone itself can influence physiology of plants and thus have an important repercussion on isoprenoid biosynthesis and emission. Studies investigating reaction of plants on high ozone stress usually conclude that plants affected by high ozone concentrations emit isoprenoides as a kind of self-protection. Released BVOCs play a role of plant antioxidants (see Section 4.2).

Direct effects of high O_3 levels were observed in many studies by fumigating plant leaves, branches and whole plants. Experiment with monoterpene emitter, Holly oak (*Quercus ilex* (L.)), when whole plant as well as single leaves only were fumigated by growing ozone concentrations, resulted in a stimulation of monoterpene emissions [86]. Other experiments on oak species [87] and on poplar [88] showed increase in isoprene emission when treating plants enclosed to special cuvettes and fumigated by high ozone levels. The study of [88] also showed that new leaves developped inside the cuvette better resisted the ozone stress. Furthermore, new leaves grown outside the cuvette, i.e. under ambient O_3 concentrations, also enhanced isoprene emission indicating that the signal stimulating isoprene biosynthesis is transported inside the plant. Studies of ozone influence on plants suggest that plants permanently affected by elevated ozone build resistance against this pollutant.

4.4 BVOC impact on tropospeheric chemistry

The hydrocarbon chemistry in the troposphere has important impact on tropospheric chemical composition. Biogenic hydrocarbons step into oxidizing reactions producing high amounts of secondary compounds with significant influence on low-level ozone production, formation of secondary organic aerosols and on tropospheric oxidation capacity which further affects reactions of other chemical species.

As BVOCs are released into the troposphere they are either photolyzed, removed from the atmosphere by wet and dry deposition or they enter the reaction with hydroxyl radical (OH), nitrate radical (NO_3) or ozone (O_3). Possible is also reaction with chlorine (Cl), which can be important in costal areas. For most of the BVOCs, wet and dry deposition is of minor importance though it can be a significant sink of chemically long-lived species, such as methanol. Mostly, BVOCs undergo oxidizing reactions. The atmospheric concentrations of ozone, OH and NO_3 radicals have pronounced diurnal profile. Hence, lifetimes of BVOCs depend on the time of day, season, latitude, cloud cover, and on chemical composition of the air mass containing BVOCs. VOCs emitted from biogenic sources are more reactive then VOCs with anthropogenic origin. [10]

The following sections are dedicated to the influence of biogenic VOCs on ozone and secondary organic aerosols, but several other consequences of natural VOC in the atmosphere are worth of mentioning.

For instance, relation of BVOCs to chemical bugdet of OH radical. Oxidation of non-methane hydrocarbons can lead to 20 - 60% reduction in OH radical concentration in areas over NMHC sources and on the contrary can increase OH radical rate by 10 - 20 % in remote oceanic boundary layer due to the enhancements in NO_x and O_3 concentrations. Reduction of OH radical can further cause an increase in methane concentrations, as OH radical is the major sink of CH_4 in the atmosphere [53]. By effecting atmospheric methane concentration, VOC chemistry influences the Earth's climite as methane is one of the most abundant greenhouse gases.

Furthermore, it has been shown that isoprene oxidative products can lead to formation of peroxyacetyl nitrate (PAN) and add to tropospheric production of this compound from NO_2. PAN is a secondary air pollutant which can be regarded as a storage of NO_x with a potential to be trasported over vast distances and therefore act as a source of NO_x far away from the primary sources, especially in non-polluted areas [89].

4.4.1 Ozone formation

The chemical processes of VOCs in the troposphere resulting in ozone production have already been described in Chapter 2. Results of experiments and modelling studies which investigated the influence of natural VOC sources on ozone formation are presented in this section.

The role of biogenic hydrocarbons in polluted urban areas has been studied by monitoring the influence of oak tree emissions in the suburb of Atlanta on urban ozone concentrations during summer ozone episode [17]. The study has indicated that

BVOC emissions can significantly affect the urban ozone levels and therefore can not be neglected in the consideration of ozone abatement strategies.

Various model studies outlined the importance of natural hydrocarbons for the chemistry of the atmposphere under a wide range of ambient NO_x concentrations and illustrated the varying role that they can play in the budget of ozone and other oxidants.

In the study of [90] a simple canopy model was used to predict profiles of temterature and light intensity within the forest combined with the land use data and emission algorithm to give estimates of BVOCs in the northeastern United States. The BVOC estimate appeared to be of the same order of magnitude as the anthropogenic VOCs. The sensitivity of regional ozone concentration to biogenic VOC emissions was studied using an Eulerian photochemical model. Results of model runs accounting for biogenic and then for anthropogenic emissions only were compared and have shown the ozone maxima varied in space in relation to the source location.

A revised emission inventory of biogenic VOC emissions produced by second generation of the BEIS model system (see Section 4.6.2) has been used for the analysis of VOC emissions influence on elevated ozone modelling in the eastern part of the North America [18]. A sensitivity analysis was performed by RADM model (Regional Acid Deposition model). Increased isoprene emissions were found to produce a shift in elevated ozone concentrations from VOC sensitivity to NO_x sensitivity over many areas of the domain. The model results were verified with measured concentrations.

In Europe, several studies focused on the Mediterranean region which, owing to climate conditions and vegetation composition, is one of the most isoprene producing regions in Europe. A modelling study performed by [91] concentrated on the east coast of Spain, site where the measurement field campaign of the BEMA (Biogenic Emissions in the Mediterranean area) project took place in June 1997. The impact of biogenic emissions on ozone concentration was investigated in simulations of the chemical mechanism RACM (Regional Atmospheric Chemical Mechanism) with and without inclusion of BVOCs while keeping the anthropogenic sources constant. A factor separation technique was applied to isolate the influence of biogenic VOCs on ozone formation. Suprisingly, the results indicated that the influence of VOC of natural origin on ozone levels represented less then 10%. In this study, the ozone levels were most sensitive to NO_x and anthropogenic VOC concentrations.

Another study from Mediterranean region investigated the impact of BVOCs on anthropogenic plumes [19]. The modelling experiment was set up in the surroundings of two anthropogenic sources - urban area of Marseille and industrial area of Martigues, and was performed using meso-scale non-hydrostatic chemical model Meso-NH-C. The model simulations have shown that the emissions from forest can enhance the maximum ozone formation by 30% when the forest is situated in the sub-urban region within 30-90 km distance from the city.

A comprehensive study of biogenic VOC emission impact on ozone concentration on European domain was presented by [92]. By applying chemical transport model CHIMERE, surface ozone levels were modeled for period from April to September for four years (1997, 2000, 2001, 2003). It has been shown that biogenic VOC enhaneced average summer ozone maxima by 5% over the domain. The highest impact was recognized in Portugal and in Mediterranean region, while the influence of BVOC on ozone was smallest in the northern part of Europe. Most profound results were obtined for extraordingly hot and phtochemically active summer of 2003.

4.4.2 Formation of Secondary Organic Aerosols

Atmospheric aerosol is a liquid or solid particle suspended in the air. Aerosols can diffuse and absorb incoming solar radiation and therefore affect the energetic balance of the Earth's surface. Further, aerosols act as a site where many heterogenous reactions take place and as a condensation nuclei for cloud droplets.

Biogenic secondary organic aerosols (SOA) can be formed via two possible ways. The first way of SOA production is condensation of gas-phase oxidation products on existing particles in the atmosphere. While trying to establish the equilibrium between gas and particle phases, these oxidation products condense due to their low volatility. The second mechanism of SOA formation is via nucleation, or the formation of new particles, although there is no solid evidence at this time that nucleation is a significant source of aerosol to the atmosphere [20]. The ability of biogenic VOCs to form SOA depends on their atmospheric abundance, chemical reactivity and the volatility of their products [3].

Smog chamber studies have shown that isoprene does not contribute to SOA formation because of its small size and high volatility of its products. On the other hand, monoterpene photooxidation can be a significant source of secondary aerosol in rural environments and in urban areas with extended natural vegetation [93]. Monoterpenes and sesquiterpenes were assigned to be the primary contributors to the formation of secondary organic aerosols [52]. However, recent studies have indicated that even isoprene can be a source of SOA due to coversion via heterogeneous reactions in the presence of an acid catalyst such as sulphuric acid [94]. Another possible pathway of SOA formation from isoprene and its gas-phase oxidantion products is through oxidation by hydrogen peroxide under acidic conditions [95].

Reactions of VOCs with ozone and, for selected hydrocarbons, with NO_3 were found to represent efficient routes to the formation of condensable products. For initial hydrocarbon mixing ratios of about 100 ppb, the fractional aerosol yields from daylight runs have been estimated to range from 5% for open-chain hydrocarbons, such as ocimene and linalool, 5-25 % for monounsaturated cyclic monoterpenes, such as α-pinene, d-3-carene, or terpinene-4-ol, and 40% for a cyclic monoterpene with two double bonds like d-limonene. For the only sesquiterpene investigated, trans-caryophyllene, a fractional aerosol yield of close to 100% was observed. The majority of the compounds studied showed an even higher aerosol yield during dark experiments in the presence of ozone. [96]

Assuming a range of yields between 5 and 40%, [97] obtained an estimate of 30 to 270 $Tg.year^{-1}$ for the production of secondary organic aerosols from biogenic VOCs. Subsequent study of [98] presented an estimate of SOA from biogenic precursors equaling to 18.5 Tg. Method used for this estimate combined results from smog chamber, temporally and spatially resolved, compounds-specific estimates of BVOCs together with OH and O_3 concentration fields. Implemating global transport model,

[99] obtained global SOA production of 11.2 $Tg.year^{-1}$, with 91% due to O_3 and OH oxidation.

4.5 Measurements of BVOC

Invetories of biogenic VOCs are necessary for evaluation of BVOC impact on tropospheric chemistry and are an essential part of BVOC modelling. Several measurement techniques are used to identify emitted compounds and to obtain BVOC emission rates from vegetation. Depending on the scale of measurements they range from enclosure measurements which allow controled environmental conditions and observation of individual foliage elements, branches or even whole plants, to micrometeorological techniques deriving emission fluxes at the plant ecosystem level. Brief summary of BVOC measurement methods is given below.

4.5.1 Mixing ratio measurement techniques

Measurements of BVOC mixing ratio are realized by using variety of sampling methods including sampling air into the canisters, collecting air samples on solid adsorbents and using automated in-situ instrumentation. Samples collected in the canisters are then analyzed in the laboratory following cryocondensation and injection into a gas chromatgraph equipped with one of several types of detectors, for instance flame ionisation detector (FID), photoionisation detector (PID) or quadrupole mass spectrometer. Because some reactive BVOCs are not able to recover from canisters, especially oxygenated VOC and terpeniods, samples are being stored on carbon-based solid adsorbent catridges which are then thermally desorbed for injection into gas chromatograph [20]. In order to obtain more temporally representative observation of VOCs many field in-situ measurement system have been developed and are being couppled with the flux measurements (e.g. [100]).

Newly introduced spectormetric methods are being used in laboratory as well as in field measurements of VOCs, as for example, isotope ratio mass spectrometry (IRMS) measuring relative abundance of isotopes in a given sample or proton trasfer reaction mass spectrometry. Proton transfer reaction mass spectometer (PTR-MS), is a fast-response, high-sensitivity measuring tool which enables real-time detection of volatile organic compounds with detection limit of several ppt. The princip of PTR-MS is in proton detection. The VOC trace gases with proton affinity higher than that of water undergo proton transfer from H_3O^+ ions and proceed to the mass analyzer where the VOC concentration is calculated based on the detected mass [101].

4.5.2 Flux measurement techniques

Enclosure measurements

Enclosure measurements of biogenic VOCs are base technique for determination of emission factors of particular plants for modelling purposes. Whole plants or branches are enclosed in teflon or tedlar bag (e.g. [102], [103]), or when measuring on a leaf level, leaves are placed inside a cuvette (e.g [104]). The ambient air is then pumped through the bag or cuvette and the inlet (c_{in}) and outlet (C_{out}) VOC flux is monitored. When the area of enclosed leaves or branches (A) is known and the passing air has a flow rate f, the resulting VOC emission rate E eaquals

$$E = \frac{f}{A} \left(c_{out} - c_{in} \right) \tag{4.1}$$

BVOC emission factors are determined either per area or per dry leaf mass and are measured under or recalculated to standart environmental conditions of $30°C$ and PAR equal to 1000 $\mu mol.m^{-2}.s^{-1}$ (so called *basal emissions*). In the study of [105] it has been presented that leaf level emission factors tend to be higher than branch level ones, due to the light effects caused by shading within the canopy.

Relaxed Eddy Accumulation technique

Relaxed eddy accumulation (REA) is micrometeorological technique for determination of emission fluxes on canopy or landscape level. This method is used to determine the flux (F) exchanged between the biosphere and atmosphere by separatelly collecting and analysing mixing ratios of the species in updrafts (c_{up}) and downdrafts (c_{down}) of air:

$$F = \beta \sigma_w \left(c_{up} - c_{down} \right) \tag{4.2}$$

where β is an empirical coefficient dependent on the atmospheric stability, and σ_w is the standard deviation of the vertical wind speed. Measurements are usually placed on the flux measurement towers in the level reaching the top of ecosystem canopy. This method is particulary effective for measuring ecosystem-scale fluxes of compounds that are not amenable to current fast-response measurements [20], [106].

Eddy Covariance technique

Eddy covariance (EC), similarily as REA, is a micrometeorological method suitable for measuring fluxes between biosphere and atmosphere on the ecosystem scale. However, it is considered to be more rigorous method than REA and has been widely applied in measurements of carbon dioxide, water and heat fluxes to or from the forest [48]. Fluxes F are determined from the covariance of BVOC mixing ratio and the vertical wind speeds using the following equation:

$$F = \rho_a \overline{w'c'} \tag{4.3}$$

where ρ_a is mean air density, w' is deviation from the mean vertical wind speed and c' is deviation from the mixing ratio of biogenic VOC. This method requires fast responding measurement instruments because the mixing ration of BVOC has to be measured as the eddies carry the flux past the sensor.

More detailed review of hydrocarbon measurement techniques can be found in [107].

4.6 Modelling of BVOC emissions

Hydrocarbon emission models are necessary component of the chemistry transport models which are a powerful tool for investigation and analysis of the atmospheric composition. As it has been shown in the literature (e.g. [47], [108]) and also in Chapter 6 of this work, VOC emissions from biogenic sources are comparable to those of anthropogenic origin. Both biogenic and anthropogenic emissions are important for global atmospheric chemistry, however, the total annual emission rate of VOCs to the global atmoshpere is dominated by biogenic sources [109]. Given the importance of BVOCs in atmospheric processes, its proper estimate of magnitude and dynamics is one of the crucial tasks of tropospheric chemical modelling.

The BVOC modelling approaches usually rely on the experimental findings from observations of single tree species or portions of the ecosystems which are then extrapolated to regional or even global scales. This bottom-up method is mostly the only possibility for BVOC estimation since no global observations exist. With only one exception, i.e. remote sensing. Recently, satelite measurements have offered a way for bottom-down isoprene estimation by measuring short-term variations of high-yield isoprene oxidation product - formaldehyde (HCHO) [110].

At present, there are two main methods for BVOC estimation. The first approach is based on the empirically discovered dependencies of emission rates on evironmental factors. The emission rates are obtained from measurements of various types of vegetation under standardized conditions. Second group of so called process-based models utilizes the knowledge of biochemical processes inside the plant which lead to VOC production and release.

4.6.1 Modelling methods

Approach of *Guenther et al.*

Model most widely used for BVOC emission estimation was developped by [77] and [8] and was further modified by [7] and [111]. The model is based on species or ecosystem specific *emission rate* which is determined under standardized environmental conditions. Emission rate is sometimes also called *basal emission* or *emission factor*. The standardized conditions consist of $30°C$ temperature and flux of photosynthetically active radiation equaling to 1000 $\mu mol.m^{-2}.s^{-1}$. Laboratory measurements of eucalyptus tree [77] and later additionally with sweetgum, aspen and velvet bean [8] proved non-linear dependence of isoprene and monoterpene emission rates on temperature and light (see Figures 4.3 and 4.2). Experiments led to derivation of empirical factors discribing response of emission rates to light and temperature.

The actual emission E ($\mu g.m^{-2}.h^{-1}$) of hydrocarbon compound is then calculated as

$$E = D.\epsilon.\gamma.\lambda_A \tag{4.4}$$

where D is foliar density (g(dry leaf weight)$.m^{-2}$), ϵ is emission rate expressed in $\mu g.g$(leaf dry weight)$^{-1}.h^{-1}$, γ is non-dimensional environmental adjustment factor for light and temperature and λ_A is leaf age correction factor.

Foliar density D

The evaluation of BVOC emissions requires determination of land cover which provides information about the vegetation type and the biomass density. Nowadays, land cover inventories based on the satellite data are freely available giving the coarse-resolution information of land cover category (forest, agricultrual field, urban area etc.) or even going to more detailed description of vegetation composition to the level of single tree species.

There are several ways how the value and temporal variation of foliar density can be defined. In the work of [8], the peak foliar density (i.e. the maximum monthly average) was estimated based on the Net Primary Production (NPP) and seasonal variation was calculated using the satelite-derived vegetation index.

When a detailed forestry dataset is available, foliar mass, determined by destructive sampling or leaf fall collection, can be allocated to the horizontal canopy coverage (e.g. [112]).

Further, sophisticated dynamic global vegetation models for simulation of vegetation distribution, physiological activity and phenology are being incorporated into BVOC estimation models (reviewed in [113]).

Emission rates

Emission rate ϵ of a particular vegetation type can be determined from the enclosure measurements (leaf or branch) of a single tree species which are then aggregated to produce emission factor of an ecosystem category used in the model. Basal emissions of various plants are being measured in the field and laboratory studies all over the world and are integrated into the basal emission databases (e.g. [114], [115]). However, the range of vegetation species for which emission rates have been measured represent only a small fraction of the potential emitters. Furthermore, great portion of data relates to plants grown in (sub)tropical and temperate environments and so its applicability in boreal and (sub)arctic regions is arguable [84]. Emission rates of a specific plant can vary over spatial and temporal scales and therefore are great source of uncertaity in this type of model.

Another possible way to determine emission factor of a vegetation type is direct micrometeorological measurement above the vegetation canopy. Examples of such measurement techniques are desribed in Section 4.5.

Environmental factors

The original model suggested two approaches to evaluate VOC variation due to environmental factors. First approach assuming dependence on both light and temeperature, and second to be temperature dependent only. The light and tempreature model well fits to the emissions of isoprene and monoterpenes which are released from the plant immediately after the formation (as discussed in Section 4.3). The model of temperature dependence fairly well desribes emissions of monoterpenes volatilizing from the plant storage organs and emissions of other VOCs.

The environmental factor γ for **light and temperature dependence** is then calculated as a product of two coefficients - C_T for temperature and C_L for light adjustment.

$$\gamma = C_T . C_L \tag{4.5}$$

Coefficient accounting for temeprature influence equals

$$C_T = \frac{\exp\left(\frac{C_{T1}(T-T_S)}{RT_S T}\right)}{C_{T3} + \exp\left(\frac{C_{T2}(T-T_M)}{RT_S T}\right)} \tag{4.6}$$

where T is leaf temperature (K), T_S is leaf temperature under standard conditions (i.e 303 K), R is ideal gas constant (= 8314 $J.K^{-1}.mol^{-1}$) and T_M (= 314 K), C_{T1} (= 95000 $J.mol^{-1}$), C_{T2} (= 230000 $J.mol^{-1}$) and C_{T3} are empirical coefficients. The original formula accounted with the C_{T3} coefficient being equal to 1, but its value was later changed to 0.961 so that the factor γ normalizes to 1 under standard temperature and light conditions [7].

Coefficient discribing the dependence on light (more precisely on PAR) is defined as

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{1 + \alpha^2 L^2}} \tag{4.7}$$

where L is the flux of PAR ($\mu mol.m^{-2}.s^{-1}$) and α (= 0.0027) and C_{L1} (= 1.066) are empirical coefficients.

The γ factor for emissions proving **temperature dependence** only equals

$$\gamma = exp[\beta(T - T_S)] \tag{4.8}$$

where T and T_S are leaf and standard temperature, respectively. As reviewed in [8], coefficient β establishes the temperature dependence and varies from 0.057 to 0.144 K^{-1} according to different plant species. The differences in estimates of β can be attributed to leaf-to-leaf and seasonal emission rate variations, different vapour pressures and solubilities for different monoterpenes, different storage and emission pathways in different plants (particulary between conifers and non-conifers) and experimental error. Nevertheless, [8] recommend β to equal 0.09 K^{-1}.

The forest canopy is often simplified to be represented as a compact layer with unifrom meteorological conditions from the bottom to the top. Of course the reality is much more complicated than that. The profile of temperature, humidity, wind speed and light significantly changes through the canopy. To account for these effects, various types of canopy transfer models were developped. An example of canopy radiative transfer model accounting for effects of canopy shading is given in [47], [116]. An evaluation of forest canopy models for isoprene emission estimation is presented in [117] where the measured emissions scaled-up to canopy level were compared to different canopy models determining the leaf microclimate as input to isoprene emission algorithms.

Leaf age correction factor

In reaction to observations that young and old leaves emit isoprene at substantially lower rates [7] the leaf age correction factor λ_A has been added into the emission model. The leaf age emission activity is estimated as a function of the amount of foliage present during the current and previous months. For more detail see [111].

Approach of *Niinemets et al.*

Physiological model of isoprene emission has been developed by [15] based on electron requirement for isoprene synthesis in *Liquidambar* and *Quercus* species. Later, similar approach has been used for monoterpene process-based emission model construction [118] using evergreen *Quercus* species. Emission rates are related to the activity of the particular synthase enzyme to predict the capacity of the synthesis pathway and to foliar photosynthetic metabolism via the photosynthetic electron transport rate.

In the model of **isoprene**, the production is primarily controlled by the supply of DMAPP for isoprene synthesis. The biosynthetical processes of isoprene formation in plants are more described in Section 4.1. Isoprene emission rate E per leaf area ($\mu mol.m^{-2}.s^{-1}$) is calculated as a product of leaf dry mass M_A ($g.m^{-2}$) altering the content of enzymes per unit leaf area, the fraction of total electron flow ϵ used for isoprene synthesis ($mol.mol^{-1}$), the rate of photosynthetic electron transport J ($\mu mol.g^{-1}.s^{-1}$) which supplies compounds for carbon reduction from CO_2 to isoprene and parameter α reflecting J dependence on tempearture, light and CO_2

$$E = M_A \epsilon J \alpha \tag{4.9}$$

Parameter α accounting for influence of temperature and CO_2 concentration translates the electron flux into isoprene equivalents and is defined as

$$\alpha = \frac{(C_i - \Gamma^*)}{6(4.67C_i + 9.33\Gamma^*)} \tag{4.10}$$

where C_i is the intercellular CO_2 concentration ($\mu mol.mol^{-1}$) and Γ^* is the CO_2 compensation point in the absence of mitochondrial respiration continuing in the light ($\mu mol.mol^{-1}$).

Assuming that total activity of **monoterpene** synthases controls the pathway flux, similar model as the one for isoprene has been developed for monoterpenes. The α parameter for monoterpenes is calculated as

$$\alpha = \frac{C_i - \Gamma^*}{12(4C_i + 8\Gamma^*) + 2(C_i - \Gamma^*)(\vartheta - 24)} \tag{4.11}$$

with C_i and Γ^* being same parameters as in formula for isoprene. Parameter ϑ is the amount of NADPH (nicotinamide adenine dinucleotide phosphate) needed for reduction of CO_2 to monoterpene ($mol.mol^{-1}$).

Approach of *Martin et al.*

A mechanistic process-based model was constructed by [16] utilizing the knowledge of the biochemical pathway of isoprene synthesis. As the isoprene production rate is governed by the slowest reaction of its biochemical pathway, the emission can be calculated in accordance to the limiting process under given environmental conditions. The model takes into account three processes potencially limiting isoprene synthesis

- supply of carbon to isoprene synthesis by pyruvate
- supply of adenosin triphosphate (ATP) for phosphorylation to DMAPP
- rate of isoprene synthesis from DMAPP which depends on the temperature controlled enzyme isoprene synthase

Using mechanistic methods wherever possible, model simulations predict the relative effects of changing photon flux density, carbon dioxide concentrations and temperature on leaf isoprene emission rates.

Beside the three mentioned approaches of biogenic VOC modelling, several other methods have been introduced, mainly employing process-based methods. More information can be found in the review of [84].

Methods of Guenther et al., Niinemets et al. and Martin et al., were applied in the study of [119] to model isoprenoid emission inventory for European forest. Differences between modelling methods were investigated and model results were compared to tower flux measurements at mid-latitude forest sites. The comparison showed that models are quite similarly able to reproduce the short-term variations in isoprene emissions, accurately capturing the diurnal profile of emissions driven by light and temperature.

The *Guenther et al. model*, since accounting only for temperature and light conditions, could not capture mid-day decline in drought conditions which led to general overestimation of total emissions. Neverthless, despite its simplicity, results of this model were comparable to the other two, more complex models. The *Niinemets et al. model* was shown to be slightly less responsive to temperature than the other two models. The *Martin et al. model* better reproduced the diurnal time-series, it was able to capture both the day-to-day variability and the average diurnal time-course. All models could not properly capture the long-term emissions. There are still many unanswered questions about the emission drivers and controls.

4.6.2 Global and Regional BVOC models

A lot of effort have been made to compile the up-to-date knowledge about natural VOC formation, processes of emission and modelling methods into a sophisticated software system joining together procedures of input data preparation, model evaluation and arrangement of the resulting emission inventory in the desired form. Various modelling systems have been developed for use in regional as well as in global scale. In the following section examples of currently applied models are given.

The **BEIS** model (Biogenic Emission Inventory System) is a system of model routines for estimation of VOC emissions from natural sources and nitric oxide and carbon monoxide emissions resulting from microbilogical activity from certain soils. The first version of the model was developed in late 1980's as a product of collaboration between U.S. EPA (Environmental Protection Agency) and NCAR (National Center for Atmospheric Research). Latest version of the BEIS model is incorporrated as a stand alone module into the SMOKE model (Sparse Matrix Operational Kernel Emissions). SMOKE is a system for generating gridded, temporally resolved emissions (athropogenic and biogenic) in a format consistent for air quality modelling. BEIS model is based on the modelling approach of *Guenther et al.* (see Section 4.6.1). BEIS model defaulty works with land cover information from BELD (Biogenic Emissions Landcover Database) which comprises of more than 200 land cover categories and for the area of the North America is available in 1 km resolution. Unfortunately, BELD data are not compiled for remaining areas of the world. Nevertheless, BEIS model is applicable worldwide as long as the user is able to prepare the land cover input file, corresponding emission factor inventory and input meteorological data [120].

The BEIS model has been applied in the early studies of biogenic VOC emission estimation from forests in North America and sensitivity studies of BVOC impact on atmospheric pollution (e.g. [112]), [18]). Nowadays, the third generation of BEIS model together with the SMOKE system is widely used in atmospheric chemistry modelling as a useful tool for emission invenotry preparation.

Recently, a modelling system **MEGAN**(Model of Emissions of Gases and Aerosol from Nature) for estimation of net terrestrial biogenic VOC and aerosol rates has been developed [54]. The MEGAN system includes the input land cover database and emission rate data as well as the core modelling software which is again based on the model method of *Guenther et al.*. An extention of canopy-model is included accounting for the canopy effects on meteorological conditions. Leaf-level emission rates are upscaled to canopy-level using canopy environmental model which is dependent on leaf area index, current environmental conditions including solar angle, temperature and light transmission through the canopy, humidity, soil moisture, wind speed etc. The MEGAN model is designed for both regional and global application and has global coverage with approximately 1 km^2 spatial resolution. It can be used as a stand-alone model for generating emission inventory but is also being incorpoated into chemistry transport model systems.

Results of MEGAN model were compared with formaldehyde column measurements from remote sensing observation of the North America and showed good consistency in spatial as well as temporal isoprene predictions [121]. Lately, MEGAN model has been applied in many studies focusing on analysis of biogenic VOC emissions and chemistry (e.g. [122], [123], [124]).

The process-based modelling approach of *Niinemets et al.* has been employed in the model framework **LPJ-GUESS** which combines the dynamic global vegetation model LJP with the general ecosystem simulator GUESS [84]. This model framework has recently been applied in studies investigating the relation between biogenic VOC emissions and CO_2 concentrations (e.g. [84], [125]).

4.6.3 Global and regional BVOC emissions inventories

As soon as the imporatnce of biogenic VOCs in the atmospheric chemistry and composition has been discovered, a significant interest has arisen in quantifying the magnitude of BVOC emissions. The early attempts of regional and even global estimations led to inaccurate results with high uncertainties. As the measurements and knowledge of processes connected with BVOC emissions improved, the invenotries improved as well.

The first well described global estimate of non-methane BVOC emissions was presented by [47]. Applying the *Guenther et al.* model approach the annual inventory of isoprene, monoterpene, group of other reactive volatile organic compounds (ORVOC) and group of other volatile organic compounds (OVOC) with spatial resolution of 0.5° x 0.5° has been calculated. The total annual global VOC flux was estimated to be 1150 Tg C, consisting of 44% isoprene, 11% monoterpenes, 22.5% of ORVOC and 22.5% of OVOC. Spatial distribution of isoprene and monoterpenes during winter (January) and summer (July) are presented in Figure 4.4 and 4.5. The results highlighted tropics as the highest contributor to global BVOC total. The emissions of isoprene are concentrated over areas of high percentage of deciduous forest such as tropical regions, south-eastern part of the United States. Monoterpenes are thought to be connected primarily with coniferous forest therefore areas of high monoterpene concentrations are also located in the nothern part of the North America and Europe.

Aside from the global estimates, focus has been concentrated also on continental and regional emission inventory studies. In the work presented by [126] annual non-methane VOCs released from biogenic sources in the North America are estimated to equal 84 Tg C, consisting of isoprene (35%), terpenoids (25%) and other VOCs (40%). As the dominant source of natural VOCs (out of 98%) has been determined vegetation.

The recent emission inventory for Europe based on the single-tree species database incorporating model algorithm of MEGAN modelling system estimates annual biogenic VOC emissions to be about 12 Tg. Total VOC amount mainly consists of group of other VOCs (4.5 Tg). Monoterpenes are estimated to contribute with 4 Tg and isoprene with 3.5 Tg [127]. Emissions of OVOC were found to originate mainly from agriculture.

Many regional studies can be found in the literature, the main interest focuses on areas in North America, Europe, Asia and the tropics. A decadal study of forest VOC emissions in Germany has been performed by [128]. Isoprene and monoterpene emissions in France were modeled and tested for the impact on regional air pollution by [129]. Temporal variation of biogenic and anthropogenic VOC emissions were measured and modeled for the surroundings of Barcelona and Catalonia region in Spain ([130], [131]). Emissions of BVOC from African savanna and woodland were estimated in the work of [132]. In the work of [133] emissions of isoprenoids from natural sources in China were estimated and compared to emissions of anthropogenic origin.

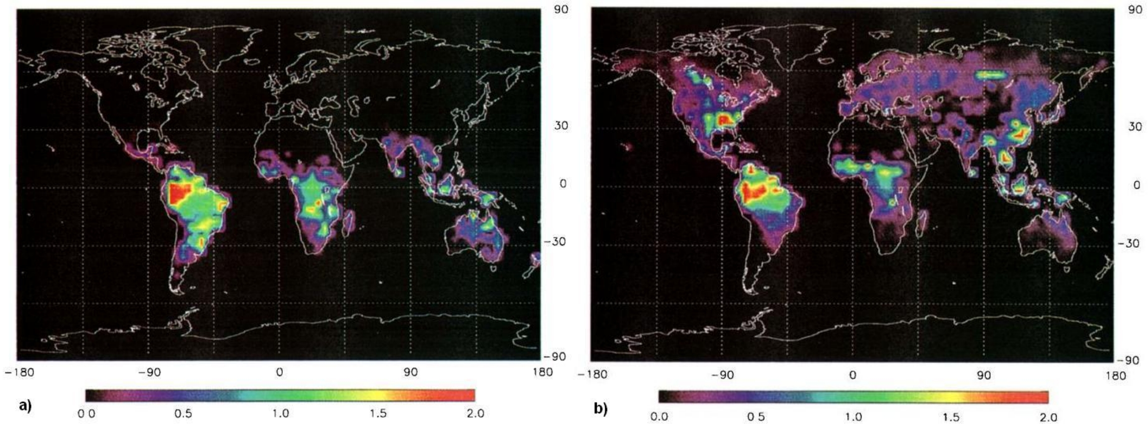


Figure 4.4: Global distribution of isoprene emission rates ($gC.m^{-2}.month^{-1}$) a) in January and b) in July (adapted from [47])

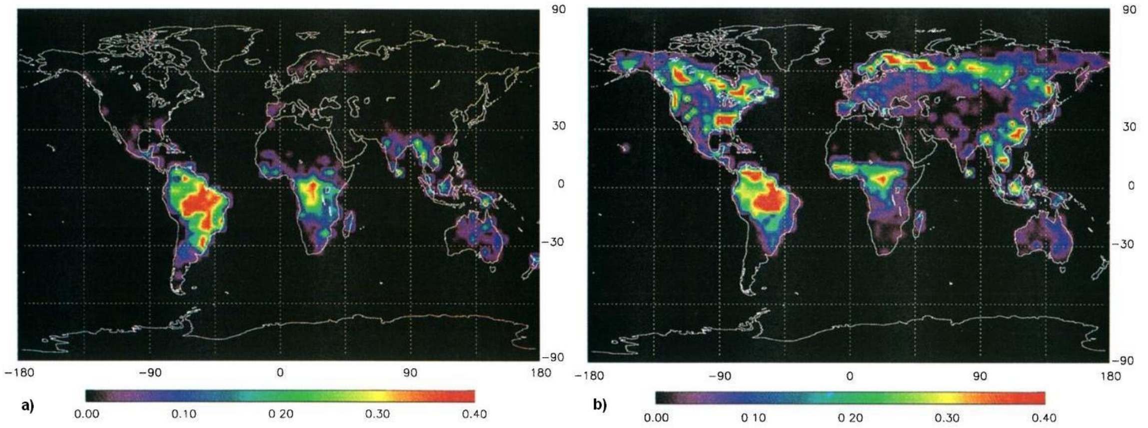


Figure 4.5: Global distribution of monoterpene emission rates ($gC.m^{-2}.month^{-1}$) a) in January and b) in July (adapted from [47])

Various emission databases are being organized into emission portals where the data are available for further utilization of users from atmospheric chemistry modelling community. One such data portal is handled by Global Emission Inventory Activity (GEIA) [134]. GEIA is part of International Geosphere-Biosphere Program (IGBP) and focuses on development and distribution of global gas and aerosol emission inventories from natural and anthropogenic sources.

Valuable dataset of emission potentials and land cover classes for the area of Europe are reported by the NatAir (Improving and Applying Methods for the Calculation of Natural and Biogenic Emissions and Assessment of Impacts on Air Quality) project inventory [135].

Chapter 5

Estimation of BVOC emissions in the area of the Czech Republic

The amount of biogenic volatile organic compounds emitted in the area of the Czech Republic has so far been quantified only within the studies focusing on the BVOC estimation on European level (e.g. [108]). These results were basically based on generalized land cover categories with relatively low resolution (not higher than 10km). The aim of the work presented in this Chapter was to obtain a spatially and temporally resolved emission fluxes of isoprene, monoterpenes and group of oxygenated VOC species on the domain of the Czech Republic by applying a methodology of BVOC estimation using high resolution land cover data which comprised detailed information of single tree species.

5.1 Model algorithm

The approach of *Guenther et al.* [8], whose basis has already been described in Section 4.6.1, has been utilized in this study to estimate hourly fluxes of isoprene, group of monoterpenes and group of oxygenated VOCs per surface area.

Isoprene is considered to be dependent on leaf temperature and on solar radiation. Due to lack of data, the leaf temperature has been approximated by the temperature of ambiet air. The isoprene flux F_{iso} ($\mu g.m^{-2}.h^{-1}$) released from the unit surface covered by land cover category l was therefore calculated as

$$F_{iso} = D_l.\epsilon_{iso,l}.\gamma_{LT} \tag{5.1}$$

where D_l is biomass density assigned to the land cover category l ($g(LDW).m^{-2}$), $\epsilon_{iso,l}$ is isoprene emission factor ($\mu g.g(LDW)^{-1}.h^{-1}$), i.e. isoprene emission under standard conditions of temperature and PAR (for more detail see Section 4.6.1) assigned to land cover category l and γ_{LT} is dimensionless correction factor accounting for light and temperature conditions (defined in Section 4.6.1).

As it has been discussed in the preceding chapter, several studies have proven that emissions of monoterpene species are for some plants controlled by temperature as well as by light depending on the character of monoterpene production.

Monoterpenes stored in reservoir organs are thought to volatilize into the ambient air with respect to temperature only while some plants are able to produce monoterpene species in the similar manner as isoprene and it is accounted that these monoterpenes are emitted from the plant in dependence to temperature and light as well. Thus, the emission flux of monoterepnes F_{mono} ($\mu g.m^{-2}.h^{-1}$) was calculated as a sum of temperature dependent $F_{mono,T}$ and temperature and light dependent $F_{mono,LT}$ fluxes released from a surface area covered by land cover category l

$$F_{mono} = F_{mono,T} + F_{mono,LT} = (D_l.\epsilon_{mono,l,T}.\gamma_T) + (D_l.\epsilon_{mono,l,LT}.\gamma_{LT}) \tag{5.2}$$

Each land cover category has been assigned both emission factors ϵ_T and ϵ_{LT}, although for categories that are not known to emit monoterpenes right after its production the emission factor for light and temperature equaled zero. Parameter D_l is again biomass density of the land cover category. Environmental correction factors γ_T and γ_{LT} are defined in Section 4.6.1 in expessions (4.8) and (4.5), respectively.

Group of Oxygenated VOCs (OVOC) mainly consists of methanol, acetone, ethanol, acetaldehyde, formaldehyde and acetic and formic acids. Emissions of OVOC are thought to depened on temperature only and therefore the OVOC emission flux F_{ovoc} released from the area covered by land cover category l was modeled in the following way

$$F_{ovoc} = D_l.\epsilon_{ovoc,l}.\gamma_T \tag{5.3}$$

with D_l being the biomass density of land cover category l, ϵ_{ovoc} the emission rate of OVOC of assigned land cover category and γ_T temperature correction factor as defined in expression (4.8).

The input data used for the BVOC emission estimation are described in the following sections.

5.2 Model input data

5.2.1 Land cover description

The land cover data are crucial in the modelling of BVOC emissions as they carry the information about the vegetation composition in the modeled domain. The most important BVOC emitters are forest ecosystems. However, many land cover databases offer only generalized categories of broadleaf, coniferous and mixed forests. As it has been discussed in Chapter 4., basal BVOC emissions can vary even within the species of the same genus, as for example some oak species are considered to be high isoprene emitters while other oak species emit only negligible amounts of isoprene. Due to high variation in emission rates of different tree species, the generalized forest categories can then be significant source of inaccuracies. Owing to advancements in remote sensing over the last decades, high resolution data of the Earth's surface became available. The satellite data serve as a base for development of land cover databases on global or continental scale which distinguish between tree families or even single tree species.

In this study, the land cover database developed under the **GHG AFOLU Project** (GreenHouse Gases in Agriculture, Forestry and Other Land Uses) has been used. AFOLU project is maintained by the Climate Change Unit of the Institute for Environment and Sustainability, Joint Research Centre of the European Commission (Ispra, Italy). The project aims to support and harmonize the efforts of European Member States in inventorying greenhouse gas emissions and to perform reasearch activities in order to understand and quantify the role of agriculture and forestry in climate change mitigation, as well as the impact of climate change on terrestrial ecosystems [136].

AFOLU project provides the tree species ditribution maps for the area of Europe in the resolution of 1km by 1km. AFOLU database consists of total number of 137 land cover categories, 115 out of which are categories of single tree species that can be found in european forests. The rest includes one additional forest category for areas where the forest composition was not available and 21 categories describing non-forest classes. The full list of AFOLU database categories can be found in Appendix A. The data are available in the form of ArcGIS shapefile maps for each category giving the percentage of the category in single grid cells. Examples of shapefile maps for four most abundant tree species in Europe - Scots pine, white birch, Norway spruce and European beech, are given in Figure 5.1.

The AFOLU database was created on the basis of three pan-european data sets. The spatial distribution of the forest in the most parts of Europe was adopted from the CORINE land cover data set. For countries which are not included in the CORINE database domain, data from the PELCOM project (Pan-European Land Cover Mapping) were used. Tree species distribution in the forest areas was obtained from the measurement network of the transitional survey of forest condition in Europe - IPC Forest Level I. Within this project crown conditions were screened annually in a grid of sample plots ($\approx$ 0.5 ha of size) in different areas of the European domain [137].

The composition of European land cover according to AFOLU database is depicted in Figure 5.2. Agricultural surfaces and arable land dominate with aproximately 36% of the surface coverage together with forest ecosystems which comprise about 33%. It can be seen that among forested areas coniferous species prevail.

Land cover data set for the domain of the Czech Republic have been compiled based on the AFOLU database. Shapefile maps of all AFOLU categories were merged together using the ArcGIS software. The land cover category with highest percentual coverage have been assigned each cell of the domain grid. The data compilation resulted in final data set of land cover in the Czech Republic consisting of 37 land cover categories including 19 categories of single tree species. The full data set description is presented in Appendix A. In areas where AFOLU data were not available, category from Euroasia land cover database of USGS (U.S. Geological Survey) have been selected [138].

As can be seen in Figure 5.3, major land cover type in the area of the Czech Republic is agricultural and arable land reaching 60% coverage of total area. Approximately 30% of the domain is covered by forest ecosystems dominated by conifers. The forest composition is indicated in Figure 5.4 showing a list of tree species oc-

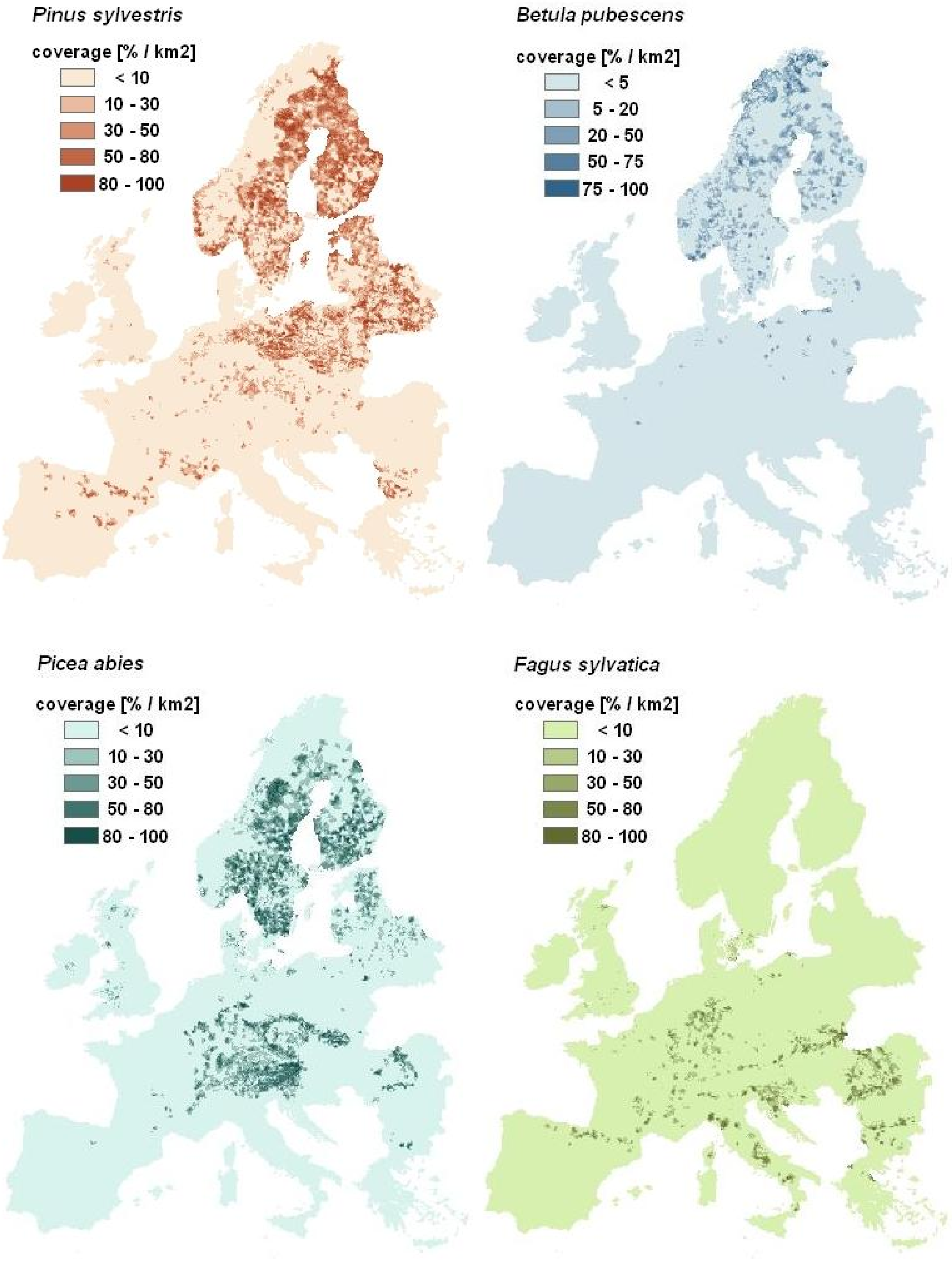


Figure 5.1: Spatial distribution of four most abundant tree species in Europe - Scots pine (*Pinus sylvestris*), white birch (*Betula pubescens*), Norway spruce (*Picea abies*) and European beech (*Fagus sylvatica*). Shown is the percentual coverage in the grid cell.

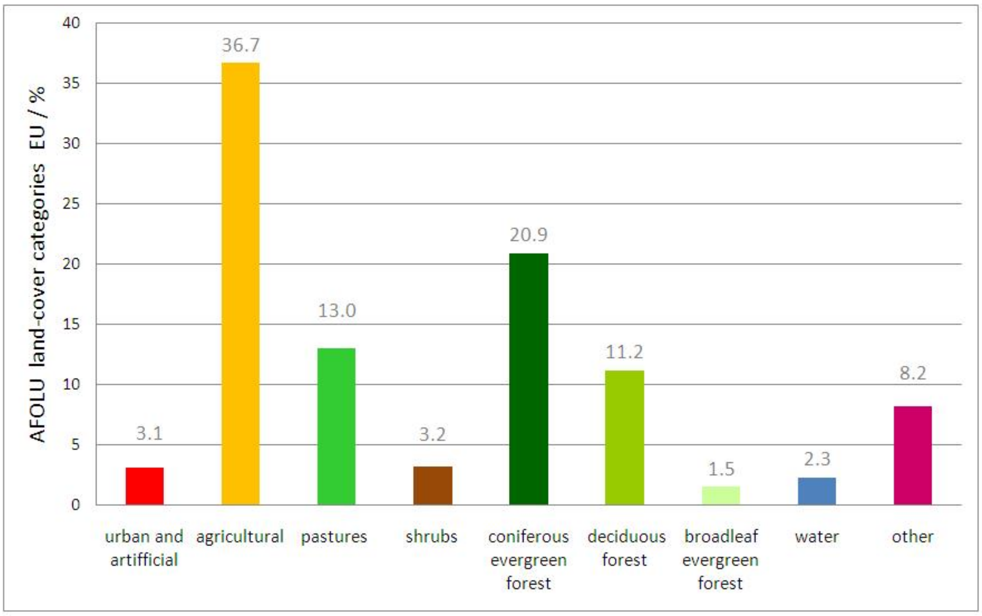


Figure 5.2: Percentual composition of European land cover according to AFOLU and USGS databases.

curing in the model area. By far, forest ecosystems in the Czech Republic are dominated by spruce species (*Picea abies*) monocultures. Considerable is coverage by other coniferous species - pine (*Picea abies*) and broadleaf beech (*Fagus sylvatica*) and oak (*Quercus* sp.) species. Around the coverage of 1% are larch (*Larix decidua*), hornbeam (*Carpinus betulus*) and birch (*Betula pendula*) species. To illustrate the spatial distribution of land cover types in the area of the Czech Republic, original 37 categories were combined together to form general categories listed in Figure 5.5.

5.2.2 Emission factor data

Basal emissions (emission factors) of a chemical compound are emission fluxes from a specified source under standard conditions of light and temperature (for more detail see Section 4.6). Emission factors are not only dependent on environmental conditions such as light, leaf temperature, chemical composition of ambient air, but also vary with respect to actual plant conditions (plant damage), age, developmental stage and even the geographic location. Despite numerous experimental surveys in the laboratory as well as in the field published in the literature studying basal emissions of wide range of plant species, this parameter is still the main source of uncertainties in the BVOC modelling.

In order to acquire as precise input data as possible, the emission factors for isoprene and monoterpenes for five tree species common in the Czech Republic were measured during two week experiment of enclosure measurements funded by the VOCBAS project of the European Science Foundation [139]. The experiment took place in the IBAF−CNR laboratory in Rome, where 3-year-old plants grown in the Czech Republic were analyzed using PTR−MS (Proton Transfer Reaction Mass Spectrometer).

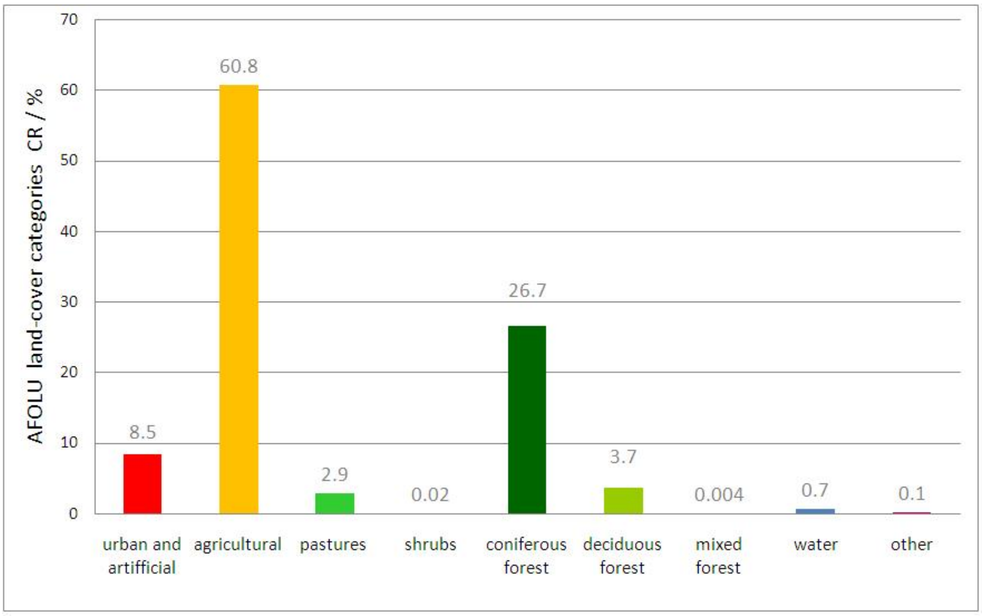


Figure 5.3: Percentual composition of land cover in the Czech Republic according to AFOLU and USGS databases.

Laboratory measurements of net photosynthesis, leaf transpiration, stomatal conductance and VOC emissions were performed on the following plants: *Picea abies* (spruce), *Fagus sylvatica* (beech), *Carpinus betulus* (hornbeam), *Fraxinus excelsior* (ash) and *Alnus glutinosa* (alder). Three samples of each plant were maintained in growing chambers for 12 hours under non-stressing conditions of light and temperature. Experiments were conducted in two different environmental light conditions (day and night).

Gas exchange system described by [140] was used for on-line detection of complex mixture of emitted VOCs. In this system a portion of leaf of selected plant is enclosed in a 0.5 l cuvette and flushed with synthetic air whose composition can be manipulated. The cuvette (Waltz) is made of Plexiglas and its interior is covered with thin film of Teflon to prevent absorption of chemical compounds on the walls inside. The air temperature in the chamber as well as the ambient light intensity (PAR) can be controlled and for the basal VOC emission measurements were set to obtain a leaf temperature of $30°C$ and PAR of $1000\mu mol.m^{-2}.s^{-1}$. One part of the cuvette outflow was directed into an Infra Red Gas Analyzers (LICOR 6262) to determine CO_2 and water fluxes. The other part of the air exiting the cuvette was directed into a Proton Transfer Reaction Mass Spectrometer (PTR-MS, Ionicon) where the amount of VOCs released by the plant was analyzed. PTR-MS measurement allowed a fast response analysis of isoprene and monoterpenes, but it couldn't discriminate between isobaric compounds (e.g. monoterpene species), since it measures molecules only according to their protonated molecular weights (for further details see [141]).

To obtain background concentration of isoprene and monoterpenes, the PTR-MS analysis was daily performed also with empty cuvettes, and the data obtained were successively subtracted to the sample. A calibration was performed with a

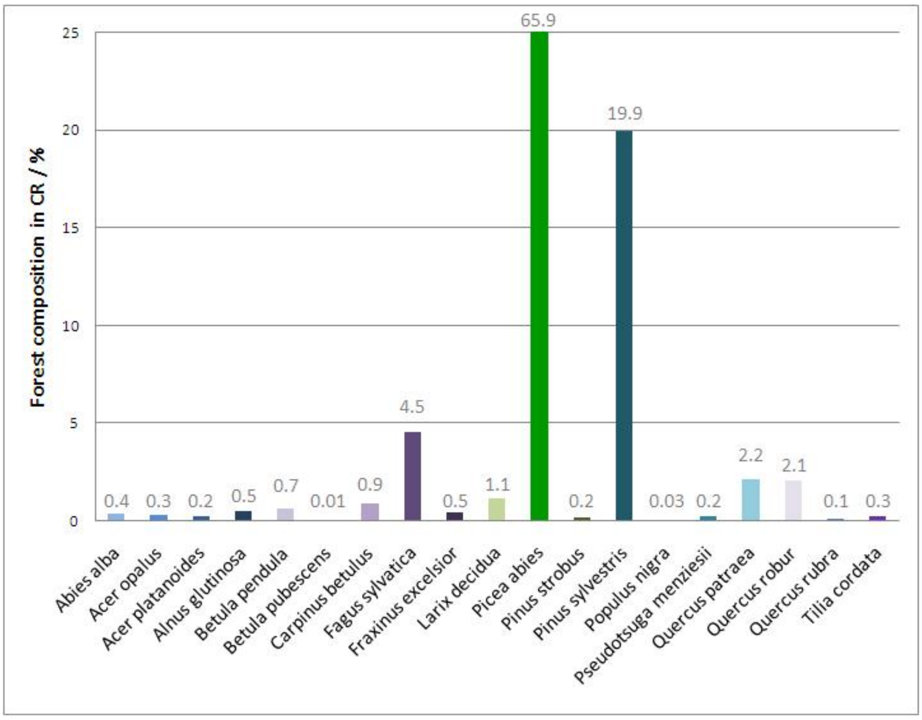


Figure 5.4: Tree species composition of forest ecosystems in the Czech Republic accoring to AFOLU and USGS land cover databases.

mixture of standard gases at the concentration of 50 ppb. Once the concentration of the sample was established, calculation of fluxes was performed according to

$$\Phi_{VOC} = \frac{F}{A_L}.VOC_{PPB} \tag{5.4}$$

where Φ_{VOC} is the flux of VOCs expressed in $nmol.m^{-2}.s^{-1}$, F is the flux of air through the cuvette ($L.min^{-1}$), A_L is the leaf area of the leaf enclosed (m^2) and VOC_{PPB} is the VOC concentration measured by PTR-MS (ppb).

Emission factors of isoprene and monoterpenes measured in the laboratory study are shown in Table 5.1. When compared with emission factors from previous studies and emission databases the measured monoterpene data fit into range of values from the literature while the isoprene data reach lower values. However, not many studies of isoprene emissions of these plants are available.

The emission factors for other common tree species and ecosystem categories in the Czech Republic were taken from the literature ([114], [12], [108], [142], [115]). A complete list of emission factors used in the BVOC model is presented in Appendix A.

5.2.3 Leaf biomass density

Leaf biomass density is a parameter which alows to upscale the leaf level basal emissions to the level of the ecosystem. It represents the amount of dry leaf weight

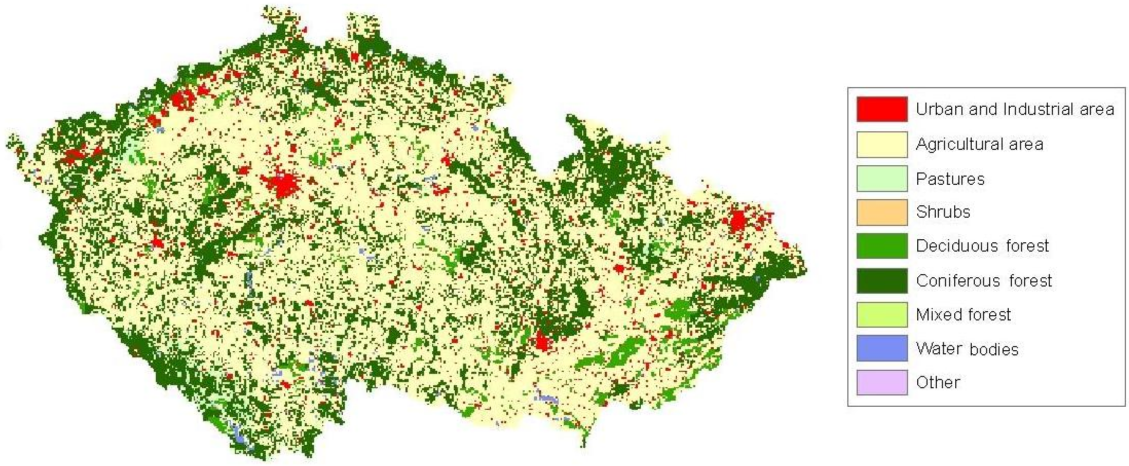


Figure 5.5: Distribution of land cover categories in the Czech Republic based on the data from AFOLU and USGS databases.

of individual ecosystem type being a potential BVOC emitter per surface area. Leaf biomass density has been assigned to each land cover category and the full list is shown in Appendix A.

Further, leaf biomass density has been employed to capture the seasonality of model emissions. Land cover categories have been divided into three leaf type classes - a) coniferous/broadleaf evergreen, b) coniferous/broadleaf deciduous, c) mixed. Values for deciduous tree species were assigned as their maximum value for the period from May to September, half of this value for April and October, and zero for the periods January−March and November−December. The foliar densities of evergreen trees were maintained at the same value throughout the year. The foliar densities of mixed forest were calculated as the average of the deciduous and evergreen densities.

5.2.4 Meteorological data

The estimation of BVOC emissions presented in this chapter is based on the meteorological data obtained from regional climate model RegCM [143] which is being run under the Cecilia Project, part of the Sixth Framework Programme of the European Union (1.1.6.3.I.3.2.). RegCM model supplied hourly data of surface temperature (K) and global solar radiation ($W.m^{-2}$) for year 2000 on the grid covering the domain of the Czech Republic with spatial resolution of 10 km by 10 km. Data of global solar radiation were used as a substitution for PAR applying the assumption that PAR equals twice the value of global radiation (e.g. [144]).

5.3 BVOC model results

Biogenic emissions of isoprene and monoterpene were estimated for each 1km x 1km grid square of the mesh that covers the entire area of the Czech Republic. Figure

Tree type		Experiment	Hewitt	Kess.	Simps.	Wiedin.
Isoprene / $\mu g.g(LDW)^{-1}.h^{-1}$						
Picea abies	Norway spruce	0.03	0.34-1.8	0.34-1.8	1.0	0.34-1.8
Fagus sylvatica	European beech	0.01	< 0.1	< 0.1	0.1	-
Carpnus betulus	European hornbeam	0.02	-	-	0.1	-
Fraxinus excelsior	European ash	0	-	-	0.1	-
Alnus glutinosa	European alder	0.02	-	-	0.1	-
Monoterpenes / $\mu g.g(LDW)^{-1}.h^{-1}$						
Picea abies	Norway spruce	0.9	0.2-7.8	0.2-7.8	1.5	0.2-7.8
Fagus sylvatica	European beech	0.6	0.24-0.47	0.25-5	0.65	-
Carpnus betulus	European hornbeam	0.2	0.04	0.04	0.65	0.04
Fraxinus excelsior	European ash	0	-	-	-	-
Alnus glutinosa	European alder	1.2	5.39	-	1.5	5.39

Table 5.1: Emission rates of isoprene and monoterpenes from laboratory enclosure measurements under standard conditions (temperature 303 K, PAR flux 1000 $\mu mol.m^{-2}.s^{-1}$) and their comparison with values from the literature (Hewitt, [114]; Kess., [12]; Simps., [108]; Wiedin., [115]).

5.6 shows monthly variations in the sum of emissions over the entire domain. Isoprene emissions decrease to zero during winter because of the loss of foliage of deciduous trees (these species, especially oaks, are the main isoprene emitters), and because of reduced temperature and sunlight hours.

Monoterpene emissions remain at significant levels over the entire year, as these compounds are mainly emitted by conifers; however, emissions are reduced during winter because of lower temperatures.

Following recommendations from the literature, the emission factors for OVOC were set to more or less same values for all land cover categories and equaled approximately 2 $\mu g.g(LDW)^{-1}.h^{-1}$. The group of OVOC comprises relatively high number of various compounds and therefore the total emission of OVOC is also relatively high throughout the year. Similarly to isoprene and monoterpenes, emissions of OVOCs follow the annual profile of temperature.

The spatial distribution of total annual emissions of isoprene (Fig. 5.7), monoterpenes (Fig. 5.8) and OVOCs (Fig. 5.9) is in consistance with land cover distribution in the model domain (Fig. 5.5). The isoprene sources are mainly located in the southeast region of the Czech Republic and several spots of high isopene emissions are visible in the central parts of Bohemia. High isoprene emissions are connected to locations dominated by oak trees. Monoterpene and OVOC emitters are approximately uniformly distributed over entire area. The total annual emissions of isoprene, monoterpenes and OVOCs from the entire domain are approximately 30, 86 and 150 kt, respectively.

The following figures display the differences in the wintertime and summertime emissions of isoprene (Figs. 5.10 and 5.11), monoterpenes (Figs. 5.12 and 5.13) and OVOCs (Figs. 5.14 and 5.15). Isoprene emissions increase from negligible values in winter to values in order of tons in summer, whereas monoterpene and OVOC emissions remain relatively high throughout the year.

Up to now, no previous study specially focused on the estimation of BVOC

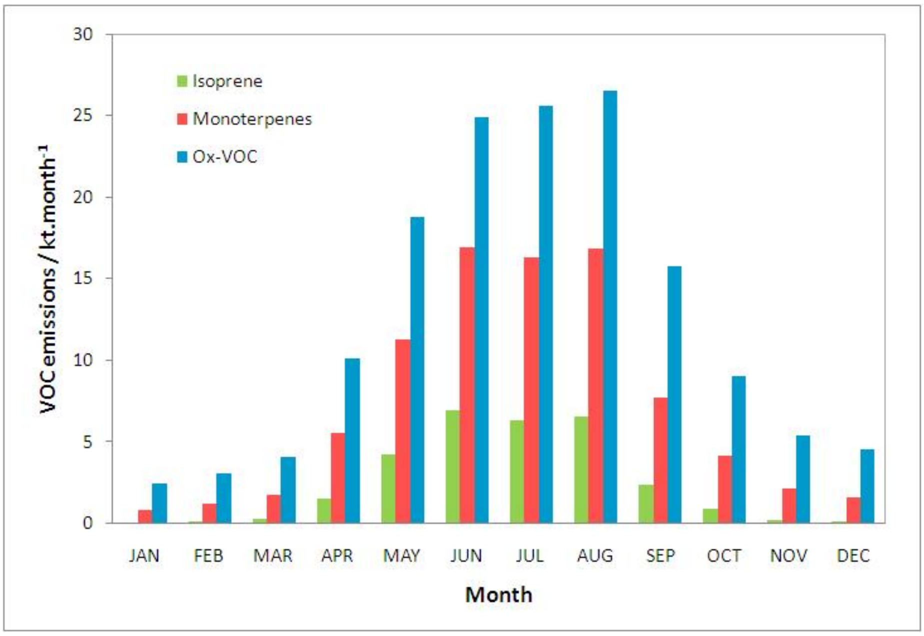


Figure 5.6: Estimated monthly mean emissions of isoprene, monoterpenes and OVOCs from ecosystems in the Czech Republic for the year 2000.

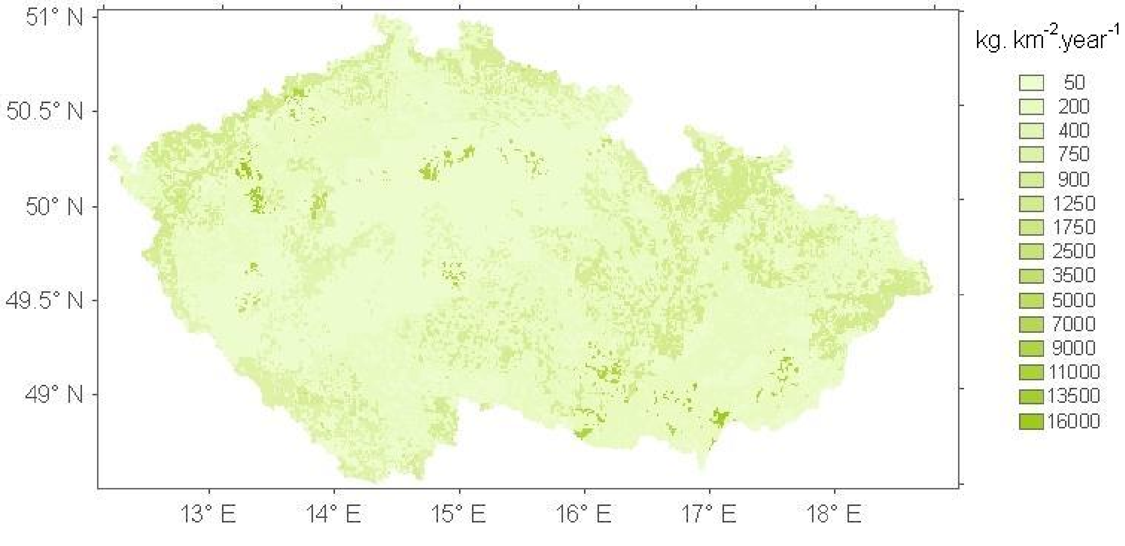


Figure 5.7: Spatial distribution of modeled annual emissions of isoprene in the Czech Republic for the year 2000.

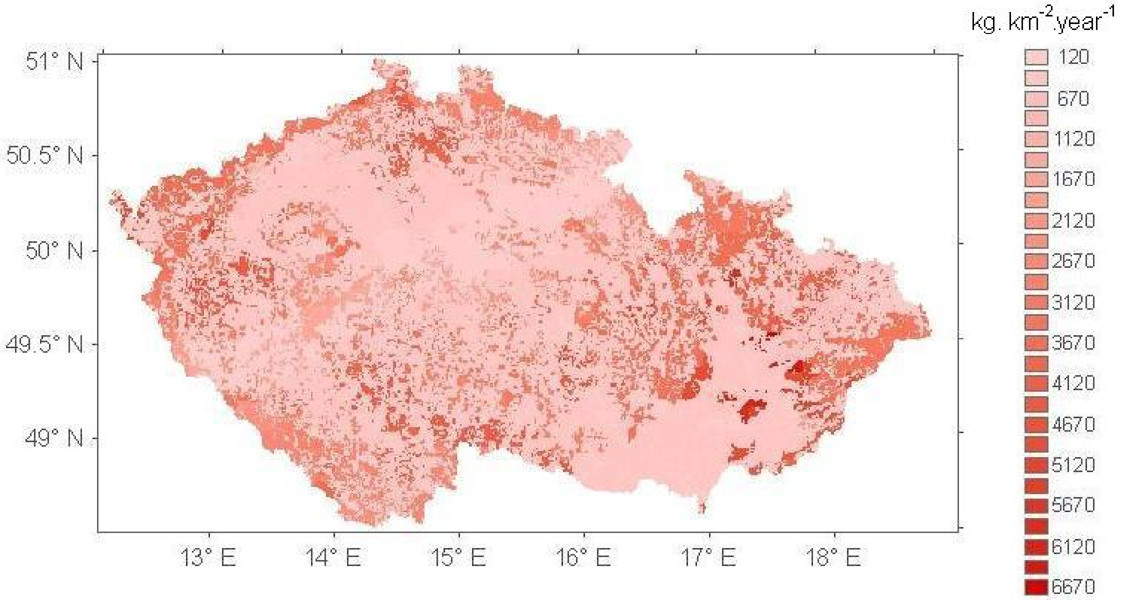


Figure 5.8: Spatial distribution of modeled annual emissions of monoterpenes in the Czech Republic for the year 2000.

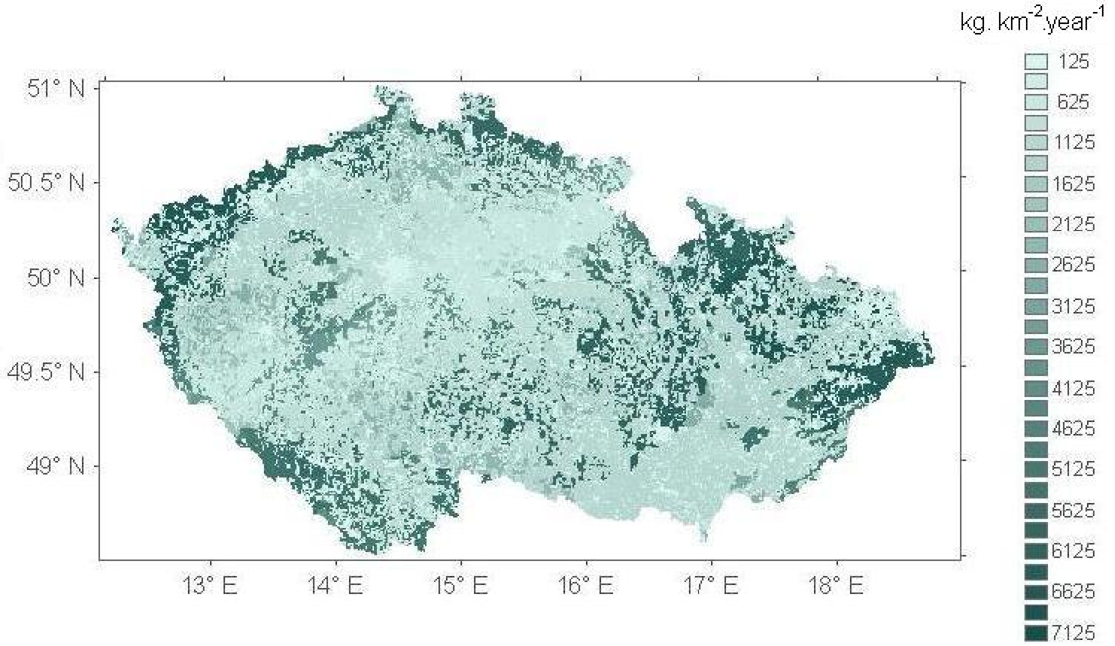


Figure 5.9: Spatial distribution of modeled annual emissions of oxygenated VOCs in the Czech Republic for the year 2000.

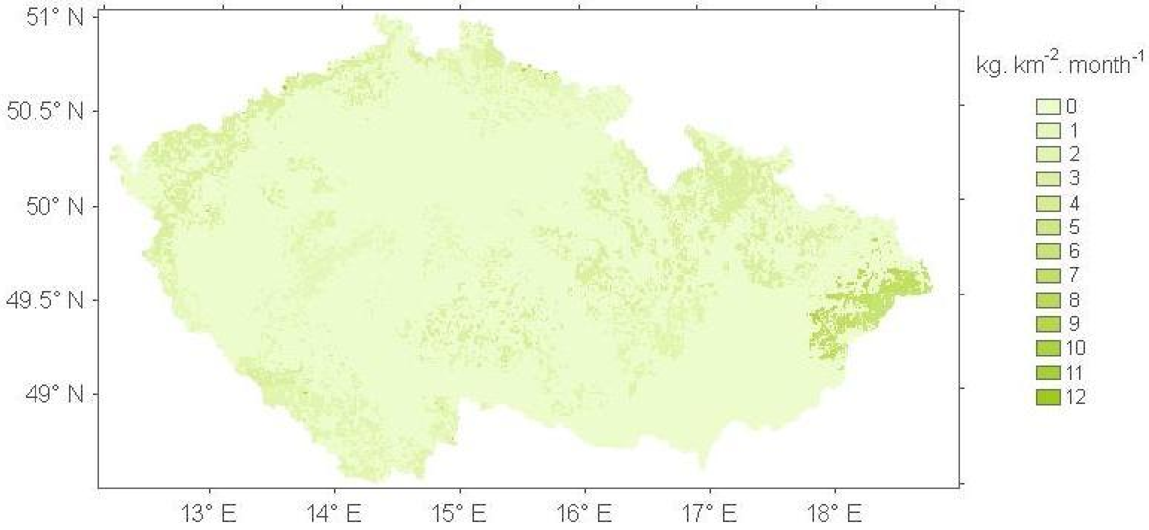


Figure 5.10: Monthly totals of estimated biogenic emissions of isoprene in January 2000.

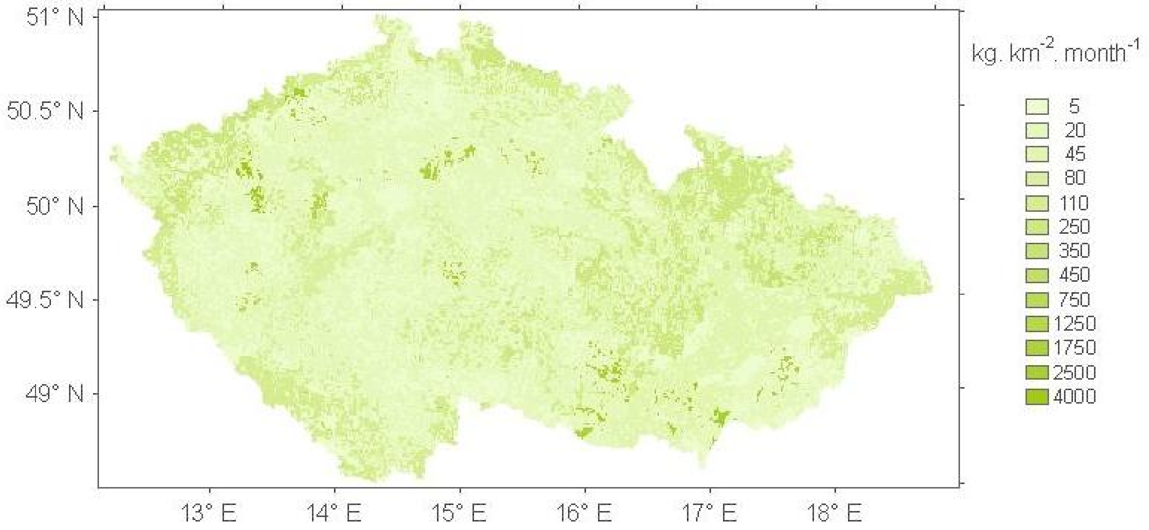


Figure 5.11: Monthly totals of estimated biogenic emissions of isoprene in July 2000.

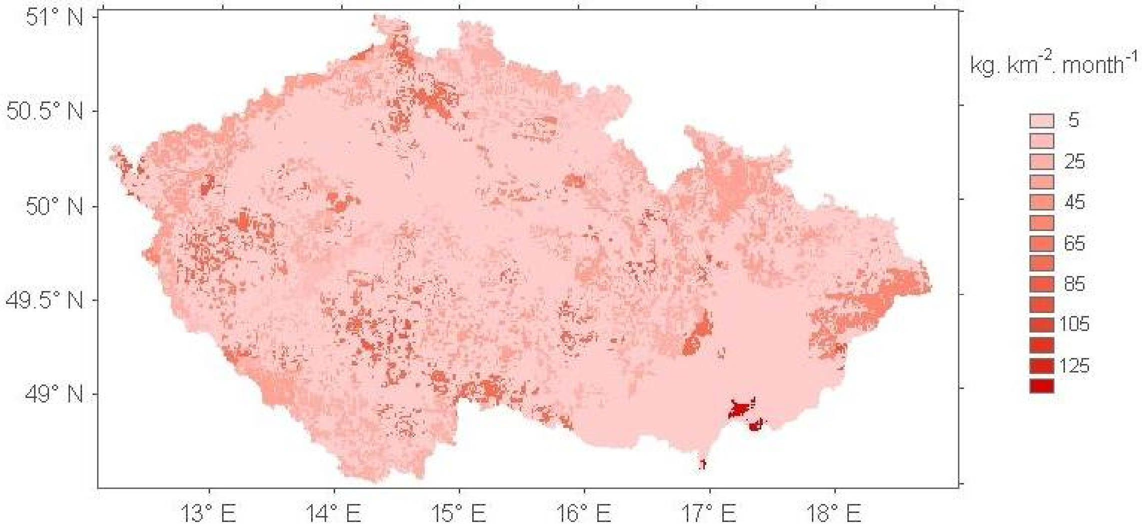


Figure 5.12: Monthly totals of estimated biogenic emissions of monoterpenes in January 2000.

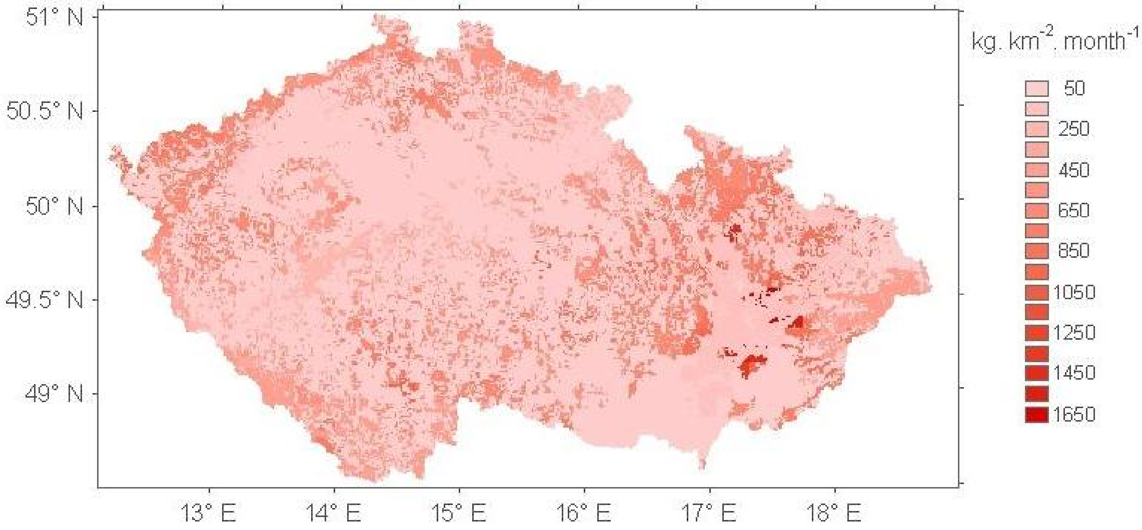


Figure 5.13: Monthly totals of estimated biogenic emissions of monoterpenes in July 2000.

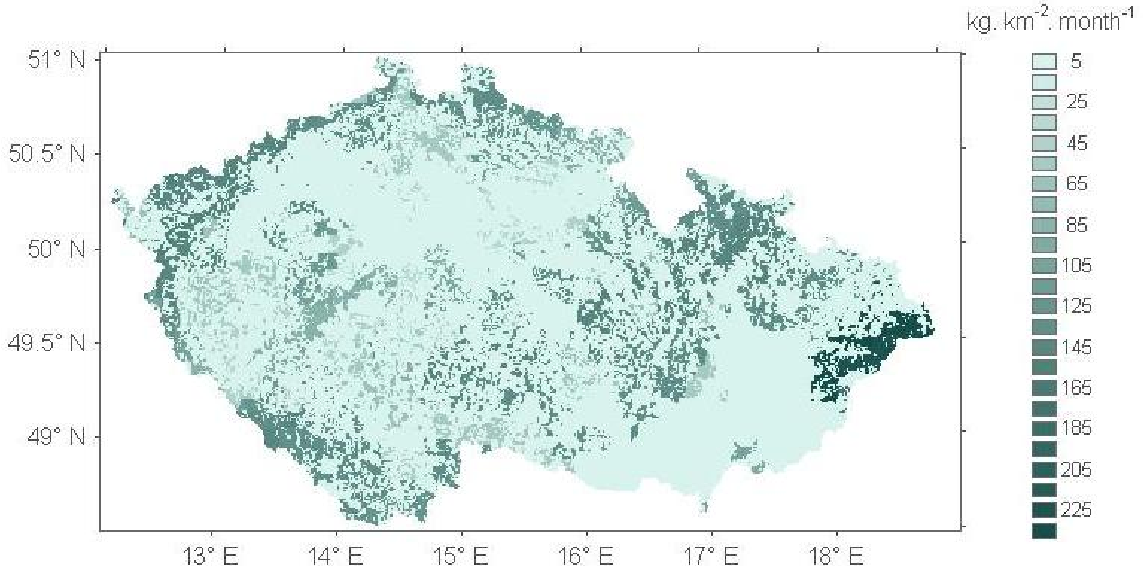


Figure 5.14: Monthly totals of estimated biogenic emissions of oxygenated VOCs in January 2000.

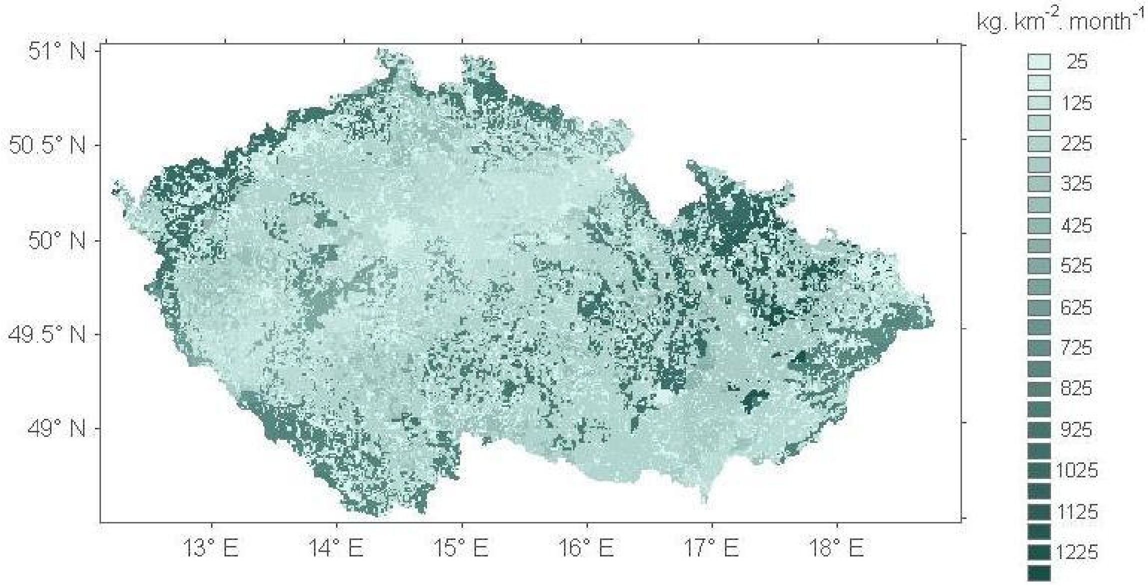


Figure 5.15: Monthly totals of estimated biogenic emissions of oxygenated VOCs in July 2000.

emissions in the region of the Czech Republic. BVOC estimates for this region have been previously presented only as a part of european studies. In recent work of [142] emissions of isoprene, group of monoterpenes and group of oxygenated VOC originating from biogenic sources were evaluated on european domain and contributions of individual states were listed. BVOC emissions in the Czech Republic were estimated to reach values from 158 $kt.yr^{-1}$ to 190 $kt.yr^{-1}$. Emissions were calculated based on the single tree species land cover database with spatial resolution of 10 km x 10 km. The range of resulted estimate is related to the uncertainty of the calculation. BVOC emissions totals estimated in this study equal to 266 $kt.yr^{-1}$. The discrepancy between result of presented model and study of [142] can be caused by higher spatial resolution of the model domain of the Czech Republic which is connected to more precise description of emitting plant species.

Nevertheless, presented BVOC estimate is connected to significant uncertainty as well. The main source of inaccuracies are emission factor data. The effort has been made to minimize the error arising from emission factors of five tree species common in the Czech Republic by measuring the emission potentials of isoprene and monoterpenes of these species in the laboratory study. It has to be noted, however, that these measurements themselves are connected with an uncertainty since only two samples of each plant were investigated. Emission factors of other species were obtained from the literature. Main emission potential inventories and databases were included in the survey in order to select as precise data as possible, but the majority of available data sources is based on measurements from North America and applicability of these data in Europe is still subject of research. Special consideration deserve estimates of oxygenated VOCs. Published emissions factor inventories concentrate mainly on isoprene and monoterpenes as these are the most abundant and most reactive BVOC species. Precise measurements of OVOC emission potentials are not yet available.

Chapter 6

Comparison of BVOC emission estimates with anthropogenic VOC emission data

Several studies have indicated that on regional as well as on global scale amounts of VOCs released from biogenic sources are equal or even higher than those of anthropogenic origin. Global estimates of total VOCs from anthropogenic sources range from 120 - 190 $Tg.yr^{-1}$ (e.g. [39], [40], [145]). When we compare these estimates with the result of [47] who estimated global annual emissions of BVOCs to be as high as 1150 $Tg.yr^{-1}$ we see that on global scale the biogenic VOC emissions are almost 10 times higher than the man made VOCs. Both biogenic and anthropogenic emissions vary with location as well as in time. The highest ratio of BVOCs to anthropogenic VOCs (AVOC) can be expected in tropical forest regions since these are the major BVOC sources. In other regions the dominance of BVOCs is not so striking; however, the quantities are still significant. For example, it has been estimated that in the USA biogenic VOC emissions exceed those from anthropogenic sources by a factor of 1.5 [116] while in France level of biogenic VOCs is 50% lower than that of anthropogenic origin [146].

6.1 National inventory of athropogenic emissions

For the area of the Czech Republic emissions of air pollutants are centralized in the National emission-inventory system (REZZO) which is being maintained by the Czech Hydrometeorological Institute ([147]) and is part of the national Informational system of air quality (ISKO). The inventory system comprises stationary as well as mobile sources and is divided into four source categories (REZZO1 to REZZO4).

The stationary sources are classified depending on the output of heat and on the degree of technological process impact on air quality. The first group REZZO1 includes large stationary point sources of pollution with output of heat higher than 5 MW. These facilities are evaluated to have serious influence on the ambient air quality. Emissions released from intermediate stationary point sources of pollution with output of heat in range of 0.2 to 5 MW are comprised in the group REZZO2. Examples of such facilities are surface coal mines, potential area sources of burning products and resuspension. REZZO3 group comprises stationary area sources with output of heat less than 0.2 MW. Within this group of sources belong household heating facilities whose emissions are estimated based on the model approach, together with VOC emissions from areal use of solvents, emissions of NH_3 from non-monitored livestock breeding and handling of animal manure.

The last group of REZZO4 covers the main mobile sources such as road and railway traffic, aerial and shipping transportation. Concerning the aerial transport, acounted for are only emissions from the airplane operational mode on the ground. Included is also an off-road transport as for example emissions from agricultural and building machines. Emissions are calculated following a methodology based on the transport statistics, annual fuel consumption and registry of vehicle types in use [147].

6.2 VOC data comparison

Calculated annual emission fluxes of isoprene and monoterepenes, representing the most reactive VOC species, in the area of the Czech Republic (as described in Chapter 5.) were compared to anthropogenic VOC emissions inventored in the REZZO system. Since REZZO system provides emission totals emitted from individual administrative regions in the Czech Republic (Figure 6.1) modeled BVOC emission data of 1km x 1km were summed to give a total amount for each region.

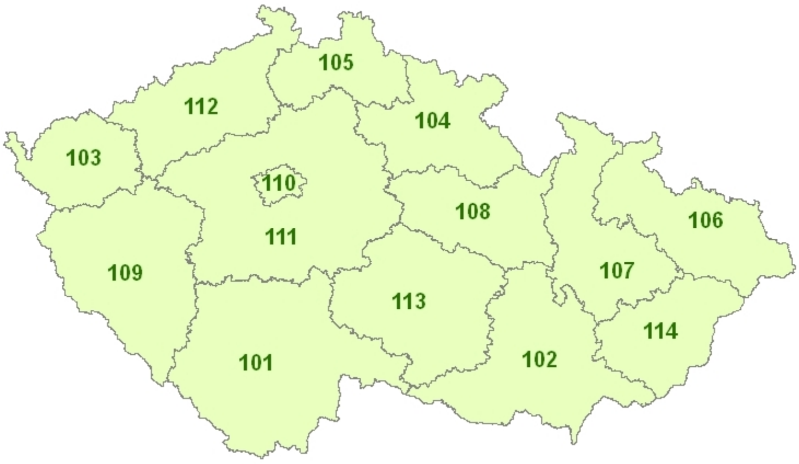


Figure 6.1: Map of administrative regions in the Czech Republic.

BVOC emissions were first compared region by region to the inventory of all anthropogenic emissions (REZZO1˘4) and then with emissions from stationary sources only (REZZO1˘3). This approach was applied to distinguish between stationary and mobile anthropogenic emissions. Terrestrial ecosystems are similar to the sources contained in the first three inventories (i.e. stationary point and area sources); consequently, it is desirable to compare them separately from mobile sources. Furthermore, the methodology used to prepare traffic−emission data differs from that used for the data in inventories REZZO1˘3. It must be acknowledged, however, that emissions from mobile sources make an important contribution to total anthropogenic emissions, and therefore must be included in any comparison with BVOCs. Although both biogenic and anthropogenic emissions experience interannual variability in this study we compare the estimate of BVOC emissions based on the year 2000 with the anthropogenic emission inventory for the year 2006 since when the methodology of emission estimation has been updated and especially the emissions from mobile sources have been calculated more precisely.

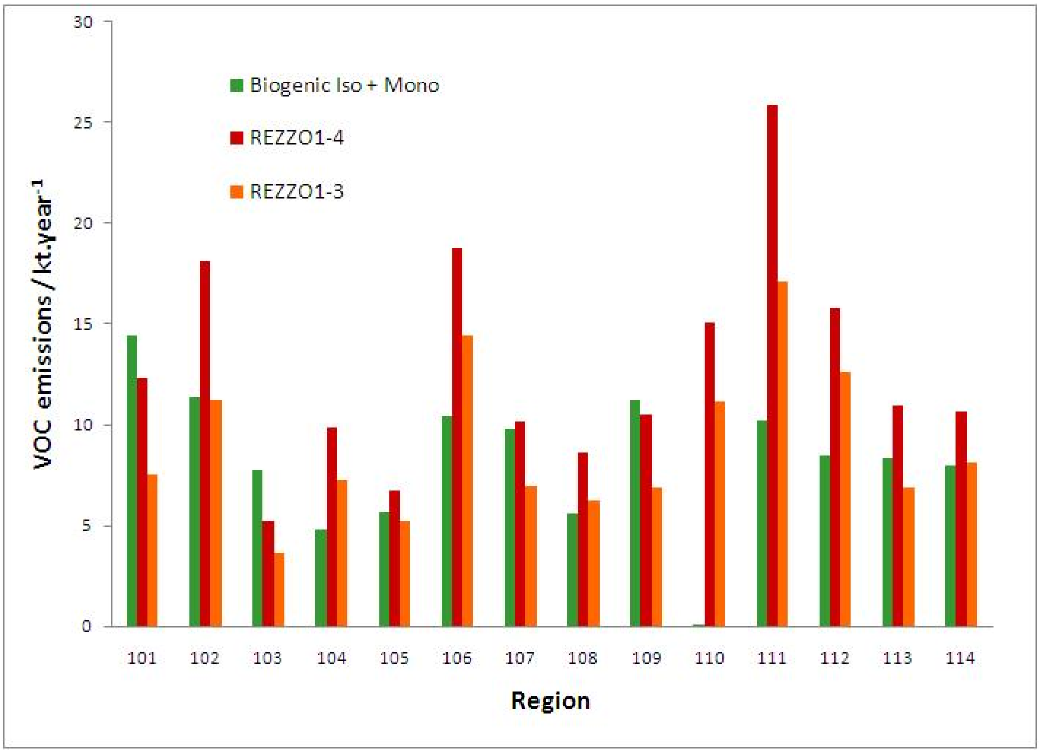


Figure 6.2: Comparison of VOC emissions from anthropogenic sources with biogenic emissions of isoprene and monoterpenes. Shown are two anthropogenic inventories: REZZO1˘4 (including mobile sources) and REZZO1˘3 (excluding mobile sources).

Figure 6.2 shows that the biogenic and anthropogenic emissions are of comparable magnitude in all regions except region no. 110 (Prague, the capital of the Czech Republic). Even in this region, however, nonzero BVOC emissions are recorded because there exist several large forested areas and parks, and many smaller parks with trees, although the total amount of annual BVOC emissions is relatively small (0.07 $kt.yr^{-1}$) and the intensive nature of human activity in this region means that anthropogenic emissions far exceed BVOC emissions. In contrast, in region no. 101, no. 103 and no 109. (southern and south-western Bohemia) the BVOC emissions exceed the sum of anthropogenic emissions (including emissions from traffic). High amounts of biogenic emissions originate from large forested areas located in these regions as can be seen in Figure 5.5. In half of the other regions the BVOC emissions are of the same magnitude or even exceed those from stationary sources. Visible are regions of high anthropogenic activity (no. 111, no. 106, no. 112) where large industrial facilities are concentrated.

Chapter 7

Study of BVOC emission influence on tropospheric ozone formation

The modelling study of tropospheric ozone concentration with special focus on influence of biogenic VOC emissions on ozone formation is described and discussed in this chapter. Ozone concentration fields are calculated using chemical transport model CAMx based on the meteorological input data from prognostic model WRF. Both models are briefly described in the following sections.

The simulations are carried out during the ozone episode in spring 2007. Selection of period for model simulations was dependent on availability of precise meteorological data from prognostic model. Regrettably, the data for summer period, when the ozone concentration reaches its annual maxima and also the effect of biogenic VOC emissions is expected to be the highest, were not available. Nevertheless, meteorological conditions during the selected period were favourable for ozone formation as well as for emissions of BVOCs, even though this time period falls into the first part of the growing season.

Presented are results of three model runs. In the first run, the biogenic VOC emissions were not included at all, model took into account anhropogenic VOC emissions only. In the second run, BVOC estimates based on the simple approach of generalized land cover categories were included into model input emission data. Finally, the third model run took into consideration estimates of BVOC emissions calculated on the basis of high resolution tree-species resolved land cover database.

Obtained model results were compared to meteorological conditions and to ozone concentration measurements. The comparison of modeled and measured data is presented in the last section of this chapter.

7.1 Chemical transport model CAMx

The Comprehensive Air quality Model with Extensions (CAMx) is an Eulerian photochemical dispersion model which can handle a variety of inert and chemically active pollutants, including ozone, particulate matter (inorganic and organic PM2.5/PM10), mercury and other toxics and is applicable in whole range of scales, starting from sub-urban up to the continental [148]. CAMx model has been developed by ENVIRON corp. and is publicly available.

CAMx model simulates emissions, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species on a system of nested three-dimensional grids. Within each grid cell of the model domain the model calculates space and time variation of the pollutant concentration due to horizontal advection and vertical transport together with the sub-grid scale tubulent diffusion. Chemistry is treated by simultaneously solving a set of reaction equations defined from specific chemical mechanisms. Processes of pollutant removal include both dry deposition on the surface and wet deposition through precipitation.

The model domain can be flexibly defined in vertical as well as horizontal direction in order to fit the domain of meteorological model whose data are employed in the CAMx model simulations. Model allows application of various nesting grid procedures dependent on the user needs. At any point during the course of simulation user can introduce and/or remove model grid with actual desired specifications.

Regarding the chemical reactions included in the model, user has an option to select one of the predefined chemical mechanisms (Carbon Bond chemical mechanism IV or V, SAPRC chemical mechanism) or can define his own chemical mechanism, if a less complex application of the model is intended. CAMx model system includes detailed algorithms for the relevant science processes of particulate matter, such as aqueous chemistry, inorganic aerosol thermodynamics and secondary organic aerosol formation. The particulate chemistry mechanism utilizes products from gas-phase photochemistry for production of sulfate, nitrate, condensable organic gases, and chloride.

CAMx model includes applications for apportionment of ozone and PM sources. By tracking the source contributions to predicted pollutant concentrations in individual grid cells, CAMx identifies distribution of ozone and ozone precursors with source category or source region. Part of the CAMx model system is also a postprocessing tool (Process Analysis) which is designed to provide analyses of physical and chemical processes in air quality model [148].

7.2 CAMx model input data

7.2.1 Meterological data from prognostic WRF model

Simulations of CAMx model were driven by meteorological data fields from Weather Research & Forcasting Model (WRF). It is a mesoscale numerical weather prediction system featuring multiple dynamical cores, a 3-dimensional variational (3DVAR) data assimilation system, and a software architecture allowing for computational parallelism and system extensibility. Data fields for this study were provided by Institute of Computer Sciences, Academy of Sciences of the Czech Republic.

Model has been operated on three nested domains D01, D02, and D03, whose extent and location are illustrated in Figure 7.1. The horizontal spatial resolutions of the domains are 27 x 27 km, 9 x 9 km and 3 x 3 km, respectively. Each domain has 16 vertical layers distributed along half-sigma levels. This study concentrated on the spring ozone episode in year 2007 (1.4. - 14.5). Provided were hourly meteorological fields of all nescessary meteorological parameters for CAMx model simulation in this time period.

Model predictions of temperature at 2m height above the ground and global solar radiation during modelling period were compared to observations at sample of stations in the Czech Republic. Comparison of daily average values are shown in the following Figures 7.2 and 7.3.

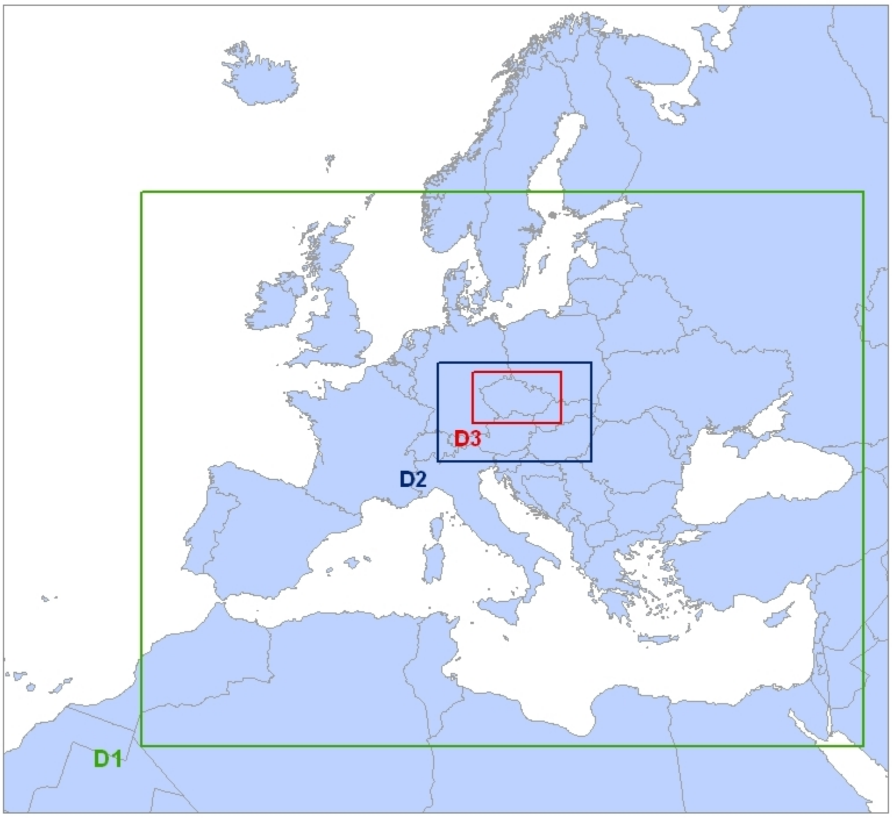
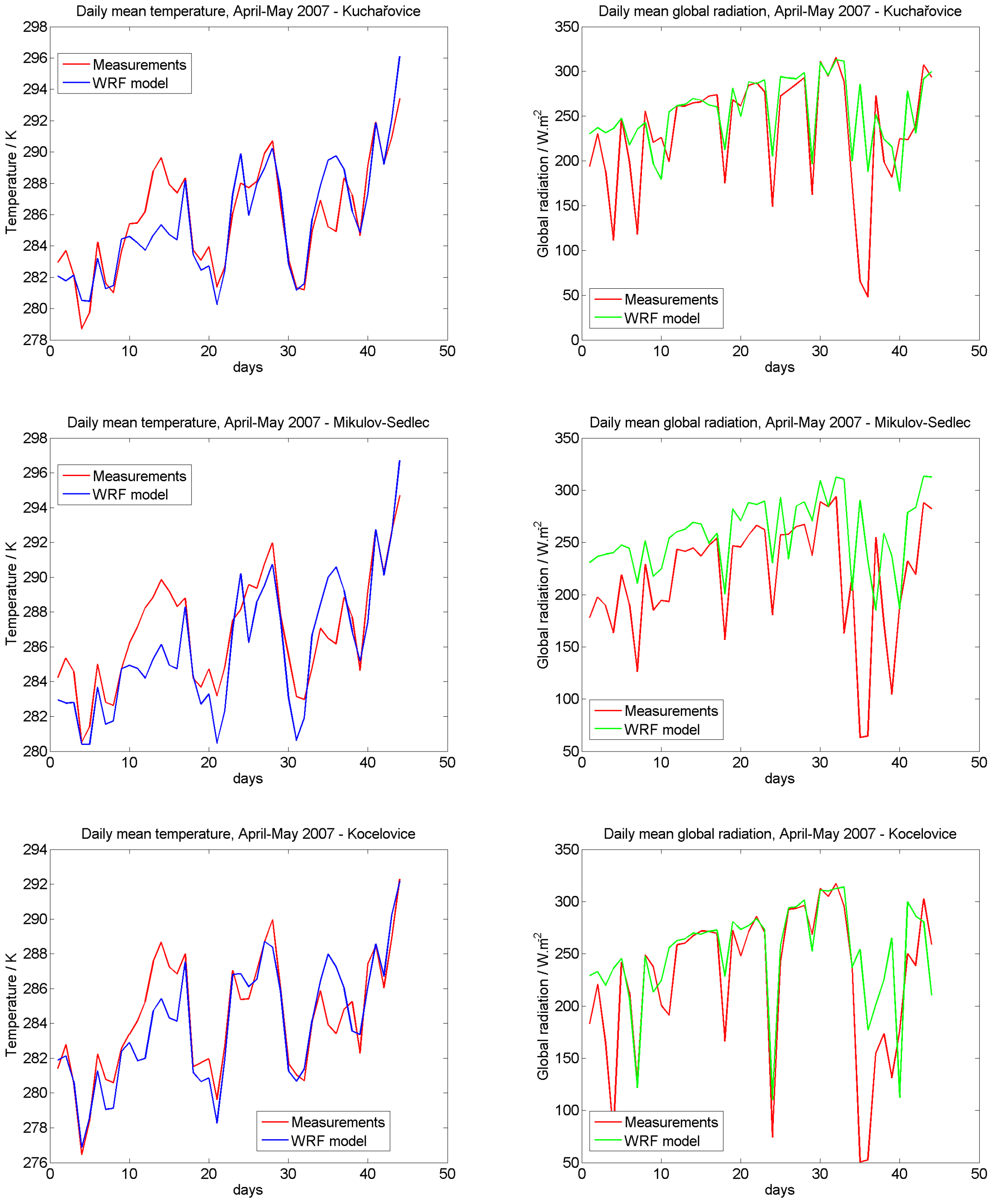


Figure 7.1: CAMx model domains.

7.2.2 Athropogenic emission inventory

Anthropogenic emissions of atmospheric pollutants for this study were obtained from the MEGAPOLI project of the 7th Framework Programme of the European Comission [149]. MEGAPOLI project encompasses all european countries. The base year of the inventory is 2005 and the data are provided in the spatial resolution of 1/8° longitude times 1/16° latitude, which, depending on the location, roughly equals to resolution of 6 km x 6 km. The substances taken into consideration in the inventory are acidifying compounds, ozone precursors ($SO_2, NO_x, NH_3, CO, NMVOC, CH_4$) and particulate matter (PM). The majority of the information in the inventory is



Daily mean temperature, April-May 2007 - Kuchařovice

Daily mean global radiation, April-May 2007 - Kuchařovice

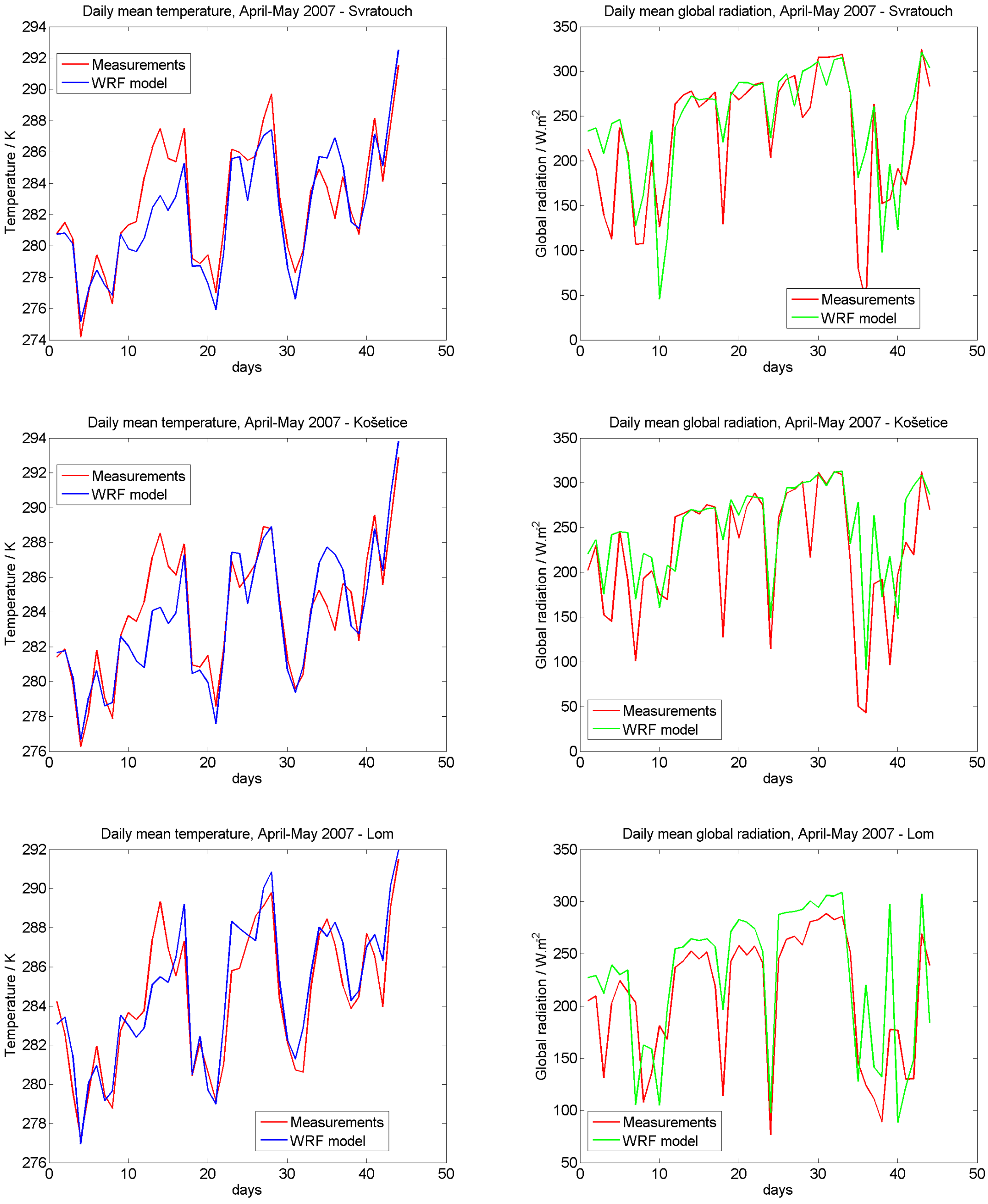
Daily mean temperature, April-May 2007 - Mikulov-Sedlec

Daily mean global radiation, April-May 2007 - Mikulov-Sedlec

Daily mean temperature, April-May 2007 - Kocelovice

Daily mean global radiation, April-May 2007 - Kocelovice

Figure 7.2: Comparison of temperature (K) and global solar radiation ($W.m^{-2}$) from WRF model with observations from stations Kuchařovice, Mikulov-Sedlec and Kocelovice.



Daily mean temperature, April-May 2007 - Svratouch

Daily mean global radiation, April-May 2007 - Svratouch

Daily mean temperature, April-May 2007 - Košetice

Daily mean global radiation, April-May 2007 - Košetice

Daily mean temperature, April-May 2007 - Lom

Daily mean global radiation, April-May 2007 - Lom

Figure 7.3: Comparison of temperature (K) and global solar radiation ($W.m^{-2}$) from WRF model with observations from stations Svratouch, Košetice and Lom.

based on the national emission data that each country submits to the EMEP network (European Monitoring and Evaluation Programme). Missing data were completed using information from alternative databases under european projects or were filled applying the RAINS model (Regional Air Pollution INformation and Simulation model). The national emission data from EMEP were first spatially distributed over the emission inventory domain, and subsequently were divided into individual emission source sectors and seperated into area and point source types.

7.2.3 Biogenic emission inventory

Effect of two emission inventories of BVOCs, prepared on the basis of different data sources, on tropospheric ozone levels was evaluated in the presented study.

In the model run entitled **EXP0** estimates of biogenic VOCs based on the generalized land cover categories of the USGS database were used. Data from the USGS land cover database were merged together into the categories of broadleaf forest, coniferous forest, grassland and category standing for other land cover types. The original dataset with spatial resolution of 1 km x 1 km has been recalculated into the resolutions of model domains (27km, 9km and 3km) preserving the information about the land cover of each grid cell as a percentual area coverage of the grid cell by individual land cover categories.

Each category has been assigned an emission factor of isoprene and monoterpenes following the recommendations of [150]. Emission fluxes of isoprene and monoterpenes were simulated on the basis of the model approcach of *Guenther et al.* [47].

Second run of the CAMx model, entitled **EXP1**, accounted with the BVOC emission inventory obtained from the utilization of land cover database presented in Section 5.2.1. This database has been prepared from the data provided by the AFOLU project and by the USGS land cover database. List of landcover database categories is presented in Appendix A. The AFOLU database covers most of the European domain and describes land cover with categories of single tree-species together with generalized non-forest categories in the resolution of 1 km x 1 km. Areas outside the AFOLU database domain were described by categories of USGS database. The distribution of land cover categories on CAMx model domains D01 and D03 is presented in Figures 7.4 and 7.5. Land cover maps give a general impression of distribution of the main ecosystem types, for the sake of better visualization, the single tree-species categories were aggregated into the generalized forest categories. A conspicuous difference in land cover type is visible in Figure 7.4 close to the western border of Russia where category of mixed forest seems to be extensive. This discontinuity happens on the edge of AFOLU and USGS data sets and is caused by different land cover description used in both databases. While in AFOLU database most of the forest species can be seperated into broadleaf or coniferous forest type, the main forest category of USGS database is mixed forest.

Similarly to BVOC inventory of EXP0 model run, the original dataset of spatial resolution 1 km x 1 km has been recalculated into the resolutions of CAMx model domains (27km, 9km and 3km) and each grid cell has been assigned the percentual area coverage of the grid cell by individual land cover category.

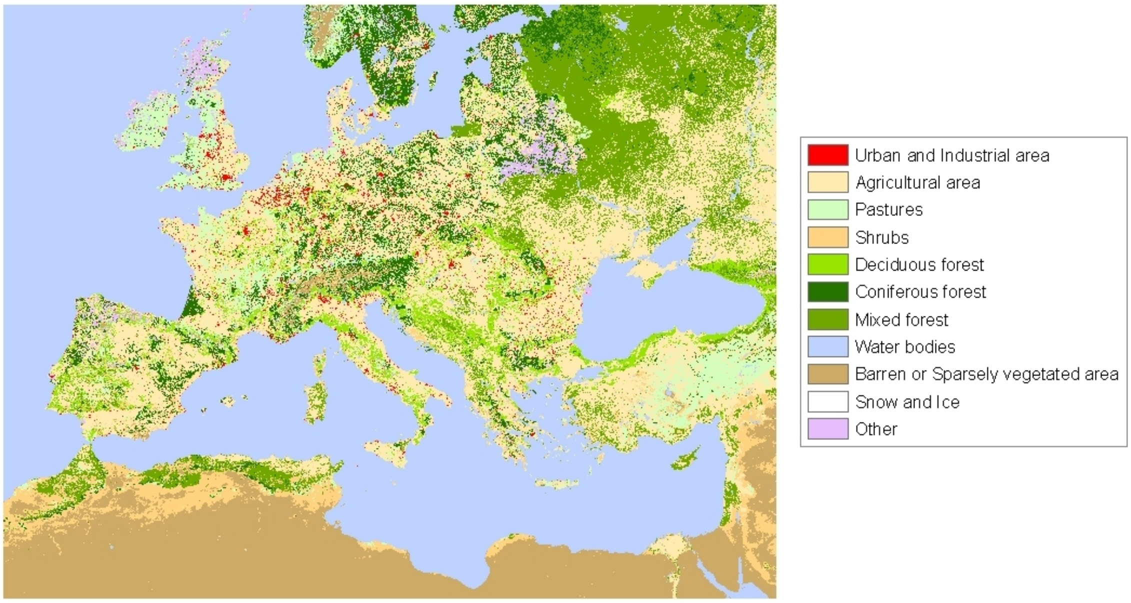


Figure 7.4: Distribution of land cover categories on model domain D01.

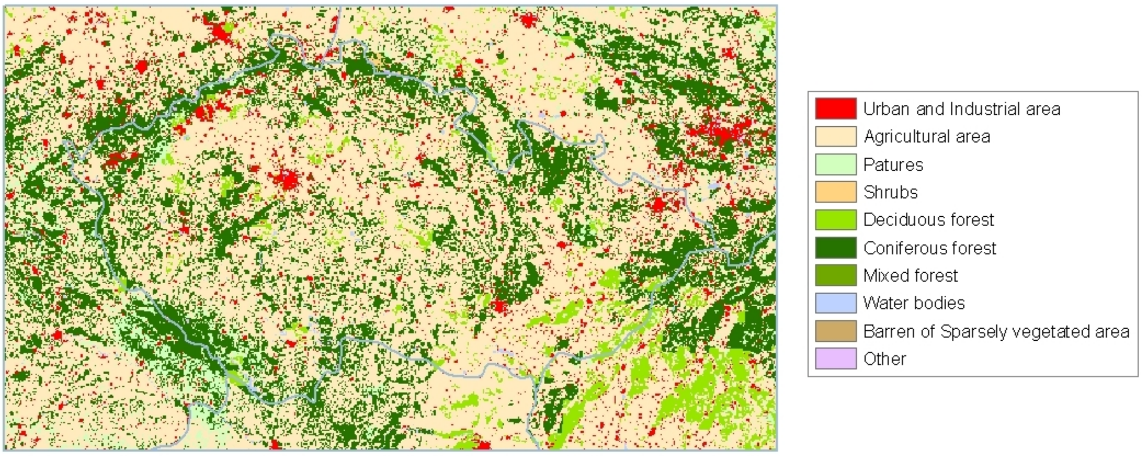


Figure 7.5: Distribution of land cover categories on model domain D03.

Emission fluxes of isoprene, monoterepenes and group of OVOCs were calculated in the similar manner as already described in Chapter 5. However, due to insufficient information about the light dependence of monoterpene emissions of involved land cover categories, it had to be assumed that monoterpene emissions of all ecosystem species depend on temperature only and monoterpene emission potentials assigned to land cover categories were adjusted to fit this assumption.

Both presented biogenic VOC inventories were calculated utilizing actual meteorological data from WRF model simulations.

7.3 Results of CAMx model simulations

Comparison of three CAMx model runs simulating levels of tropospheric ozone is presented in this section. The model calculations were concentrated on evaluation of influence of biogenic VOC emissions on ozone formation on European domain as well as in the region of the Czech Republic during the period of elevated ozone concentrations in Spring, 2007.

CAMx model runs were divided into three cases. In the first base case simulation (BC) only anthropogenic emissions of VOCs were taken into account. This simulation serves as the reference. In other two CAMx runs, entitled EXP0 and EXP1, biogenic VOC emissions prepared on the basis of two different data sources (decribed to more detail in the preceding section) were implemented into model inputs. All three modelling cases were operated on nested domains D01, D02 and D03.

7.3.1 Surface distribution of modeled ozone concentration

Concentration fields of tropospheric ozone were calculated on the hourly basis for each model case on all three model domains. Ozone concentrations ($\mu g.m^{-3}$) averaged over the whole modelling period are presented for the model cases BC, EXP0 and EXP1. Surface ozone concentration maps for the model domain covering whole European region (D01, spatial resolution 27km x 27 km) are followed by results obtained from the domain of the Czech Republic (D03, spatial resolution 3 km x 3 km).

European model domain (D01)

Maps of spatial distribution of mean ozone concentration calculated in model simulations BC, EXP0 and EXP1 on domain D01 are presented in Figures 7.6 to 7.8. Locations of highest ozone concentration are situated in remote areas over the sea and ocean where there are no significant sources of nitrogen oxides and therefore ozone tends to reside in the atmosphere. Nevertheless, in Mediterranean sea a track of shipping traffic is visible as the ozone concentration decreases due to trace of NOx emissions from ship exhausts that lead to titration of ozone.

Ozone concentrations over the continent reach lower values when compared to concentrations over sea. Spots of lowest concentrations are located close to the areas

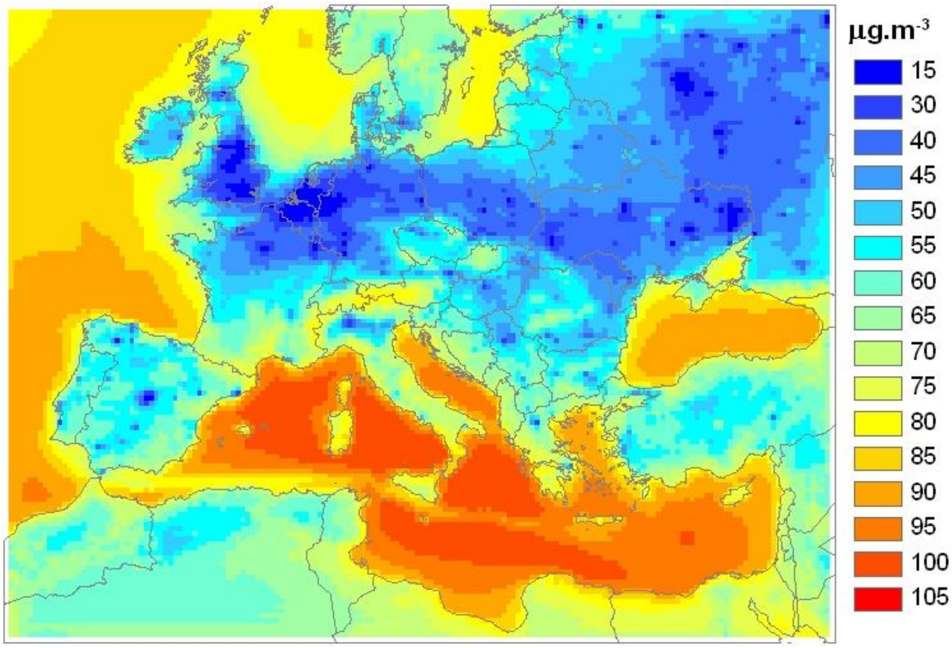


Figure 7.6: Spatial distribution of daily mean ozone concentration ($\mu g.m^{-3}$) averaged over the modelling period calculated in the BC model run on D01 model domain.

of extensive human activities, urban and industrial areas. Well visible are for example Madrid region in Spain, Milan region and Po valley in northern Italy and the areas of high density population and industry in states of Benelux and south-eastern part of the Great Britain.

Although differences between individual model runs are relatively small, one can see that inclusion of biogenic VOC emissions in the model run EXP0 as well as in EXP1 leads to increase in averaged ozone concentration. The differences between model simulations including BVOC emissions (EXP0, EXP1) and the reference run BC are evaluated in Figures 7.9 and 7.10. In Figure 7.11 the difference between both simulations with BVOC emissions is demonstrated.

Addition of BVOC emissions into model run EXP0 increased average ozone concentration over the whole domain with 1.7 $\mu g.m^{-3}$, which compared to average ozone concentration of BC simulation represents 2.5% increase over the whole domain. Maximal growth of ozone levels are visible particularly on Iberian peninsula and in the region of former Yugoslavia. These locations well correspond to stands of dense vegetation where supply of biogenic VOC emissions is the highest. Ozone concentration in these locations increased with approximately 10 $\mu g.m^{-3}$, meaning 18% rise of ozone levels when compared to BC model run.

Amounts of BVOC emissions averaged over the whole domain in model run EXP1 almost doubled in magnitude when compared to BVOC estimates in EXP0. It is due to more detailed description of land cover, revision of emission potentials and addition of oxygenated VOCs which are not included in EXP0 model run. This

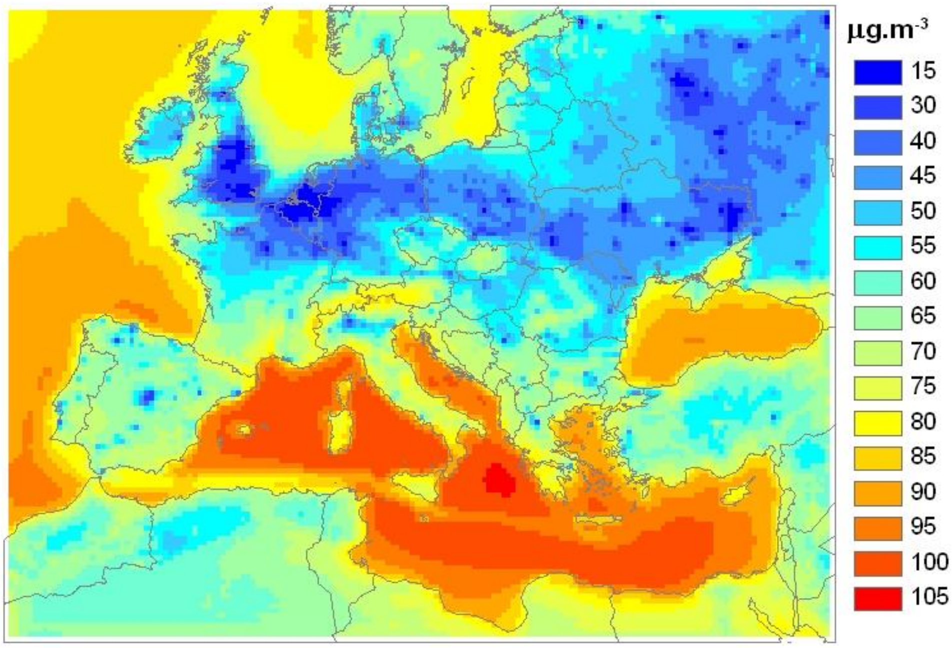


Figure 7.7: Spatial distribution of daily mean ozone concentration ($\mu g.m^{-3}$) averaged over the modelling period calculated in the EXP0 model run on D01 model domain.

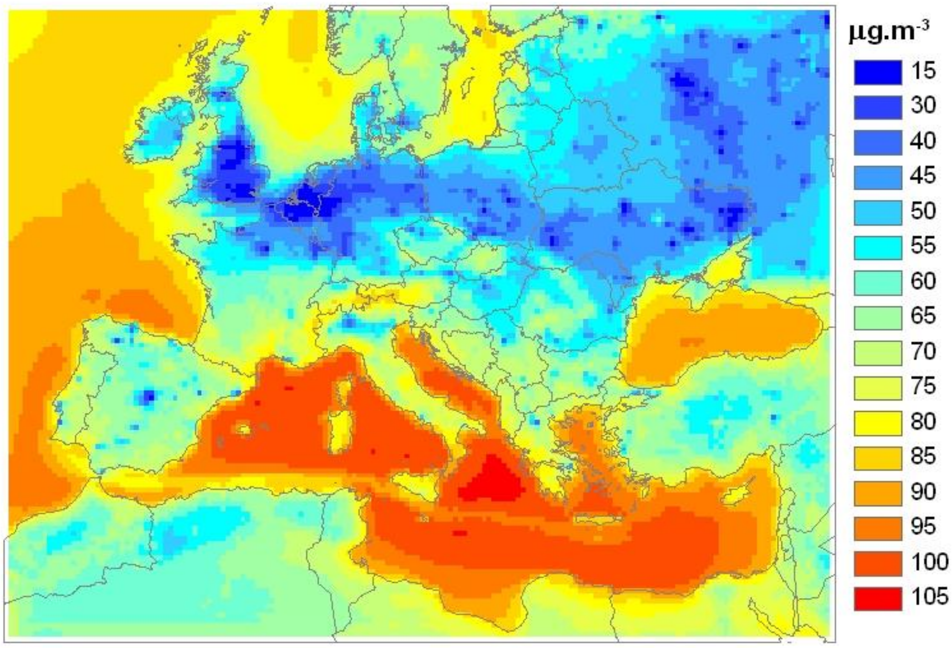


Figure 7.8: Spatial distribution of daily mean ozone concentration ($\mu g.m^{-3}$) averaged over the modelling period calculated in the EXP1 model run on D01 model domain.

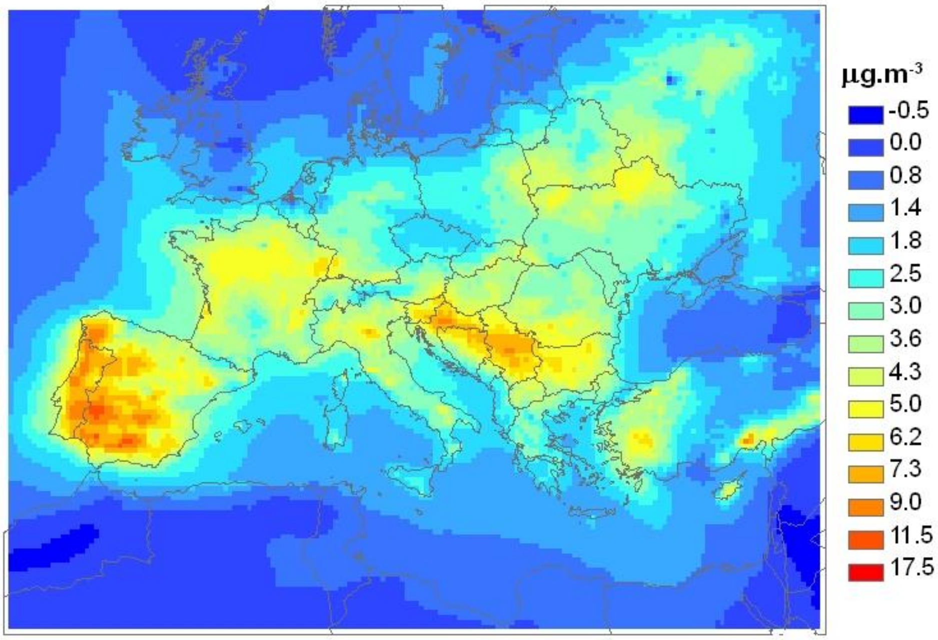


Figure 7.9: Differences between daily mean ozone concentrations ($\mu g.m^{-3}$) calculated in the EXP0 and BC model runs averaged over the modelling period on D01 model domain.

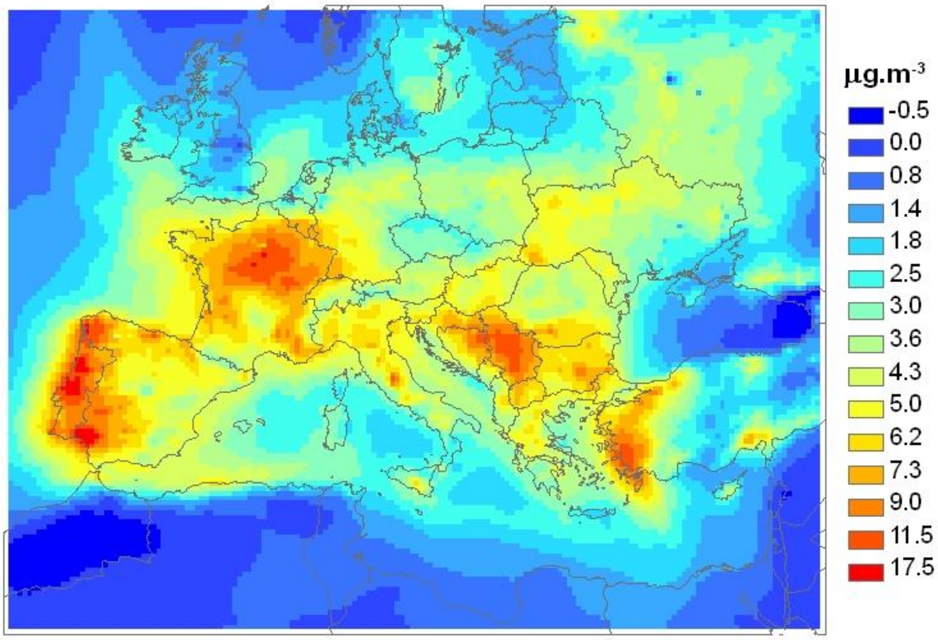


Figure 7.10: Differences between daily mean ozone concentrations ($\mu g.m^{-3}$) calculated in the EXP1 and BC model runs averaged over the modelling period on D01 model domain.

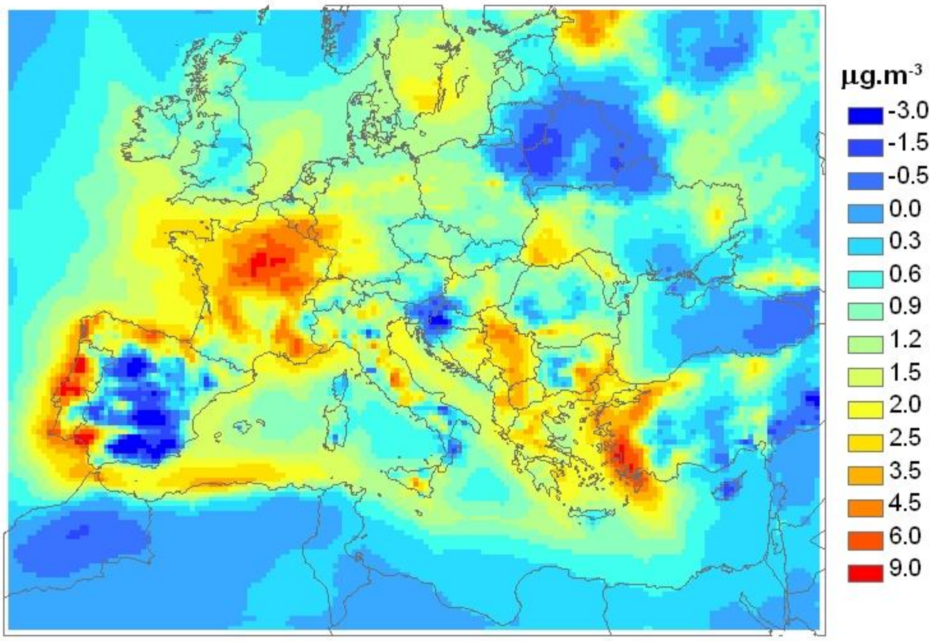


Figure 7.11: Differences between daily mean ozone concentrations ($\mu g.m^{-3}$) calculated in the EXP1 and EXP0 model runs averaged over the modelling period on D01 model domain.

increase in VOC emissions is reflected in overall growth of ozone concentration in this model run. On average, the ozone levels over the whole domain incresed with 2.5 $\mu g.m^{-3}$ (i.e. +3.7% compared to BC model run).

Owing to better resolved forest composition description additional high emitting locations showed up. Beside western part of Iberian peninsula and former Yugoslavia, also central and southern France, central Italy and western Asia Minor. Increase in BVOC emissions again well corresponds with elevation of ozone levels. Maximal effect of BVOCs can be seen in Portugal and western parts of Spain. These spots are more bounded than in previous case and are situated in stands of broadleaf forests composed mainly by oaks which are high isoprene emitters. The effect of BVOCs in these areas is enhanced by significant NOx sources such as sites of Lisboa, Porto and Sevilla. Difference in these locations between ozone concentration from EXP1 simulation and reference run reach values around 17 $\mu g.m^{-3}$, which means approximate 30% increase in ozone levels compared to BC model run.

Comparison of model results obtained from the utilization of different sources of BVOC inventories is given in Figure 7.11. Depicted is a difference between averaged ozone concentration calculated on the basis of BVOC emissions in EXP1 simulation and EXP0 model run. The application of more detailed BVOC emission inventory in EXP1 led to an overall increase of ozone levels which is most significant in areas of highest ozone concentrations described in the previous paragraph. However, at certain locations such as central Iberian peninsula, Slovenia and Belarus, ozone concentration in EXP1 simulation decreased with almost 3 $\mu g.m^{-3}$ when compared to EXP0 model run. This decrease is caused by lesser values of BVOCs emissions calculated from more detailed land cover database than the ones based on the generalized categories.

Model domain of the Czech Republic (D03)

Ozone concentrations ($\mu g.m^{-3}$) averaged over the modelling period simulated in reference model runs and in EXP0 and EXP1 model runs on the domain focused on the Czech Republic are shown in Figures 7.12 to 7.14. Again, visible is increase of ozone levels when the BVOC emissions were included in model simulations. Areas of highest ozone concentrations are situated in remote locations of Šumava, Krkonoše and Jeseníky mountains in the Czech Republic and in areas of Velká and Malá Fatra in Slovakia. Ozone sinks can be recognized close to urban and industrial regions of Prague, north-western Bohemia and conurbation in northern Moravia which continues to urban regions in Poland. Well visible are also spots of urban aglomerations of Brno, Pardubice, Hradec Králové, Karlovy Vary and the industrial triangl on the border of the Czech Republic, Poland and Germany.

Similarly to results obtained on the European domain, inclusion of BVOC emissions into model simulations led to overall increase of ozone levels on the domain of the Czech Republic as well. Differences between model runs which included BVOC emissions and the reference run are shown in Figures 7.15 and 7.15. The effect of BVOC emission inclusion in EXP0 and EXP1 simulations is compared in Figure 7.17.

The areas of highest difference between EXP0 and reference model run lie outside the Czech Republic, mainly in southern part of the model domain. Inclusion of biogenic VOC emissions in EXP0 simulation led to increase of mean ozone concetration on the whole model domain with 1.9 $\mu g.m^{-3}$ (i.e. +3.6% of the mean value obtained in BC model run). Maximal difference on the whole domain reached values around 3 $\mu g.m^{-3}$ (i.e. +4.9% of the mean value obtained in BC model run). However, mean increase in ozone levels due to BVOC emissions in EXP0 simulation in the area of the Czech Republic is lower, reaching values around 1.6 $\mu g.m^{-3}$ which means 3% increase of ozone concentration compared to reference case.

As it has been already shown on the European domain, inclusion of BVOC emissions in EXP1 model run enhanced further growth of ozone concentration also on domain D03. Emissions of BVOCs were elevated of about 30 % in average when detailed land cover database was applied. The difference in mean ozone concentration between EXP1 simulation and the reference model run is for overall domain approximately +2.7 $\mu g.m^{-3}$, giving 5% increase of ozone levels compared to BC simulation.

Similarly to previous case, areas of maximal ozone level increase lie outside the Czech Republic, mainly in north-eastern Austria, where ozone concentration has been elevated with 4 $\mu g.m^{-3}$ (i.e. almost 8% of the ozone concentration from BC model run). Mean increase of ozone levels caused by BVOC inclusion in EXP1 model run on the area of the Czech Republic is around 2.3 $\mu g.m^{-3}$, approximately 4% rise when compared to reference model run.

According to Figure 7.17 it can be stated that the difference between application of detailed BVOC emission inventory and BVOC estimation from generalized land cover data in the region of the Czech Republic is relatively small. Inclusion of BVOC

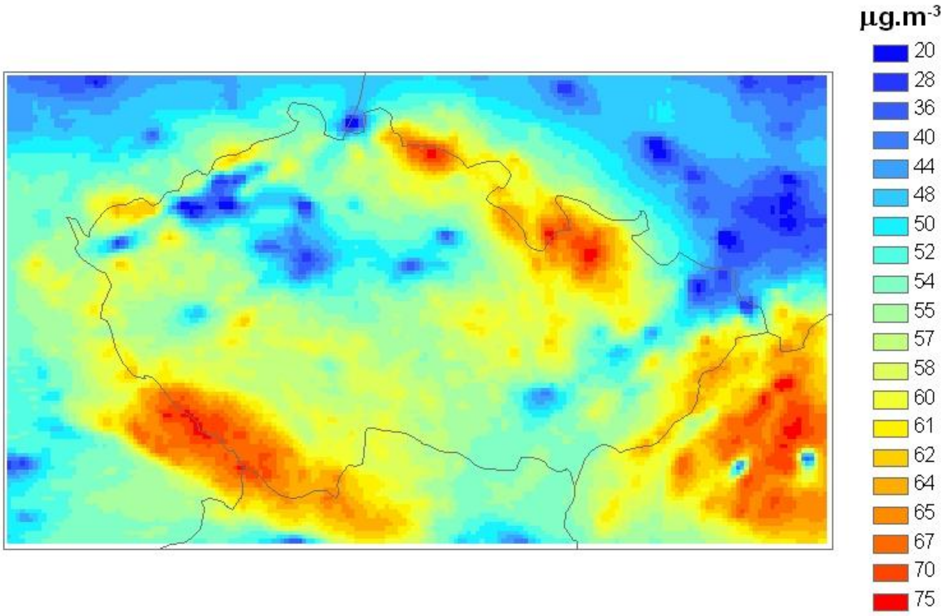


Figure 7.12: Spatial distribution of daily mean ozone concentration ($\mu g.m^{-3}$) averaged over the modelling period calculated in the BC model run on D03 model domain.

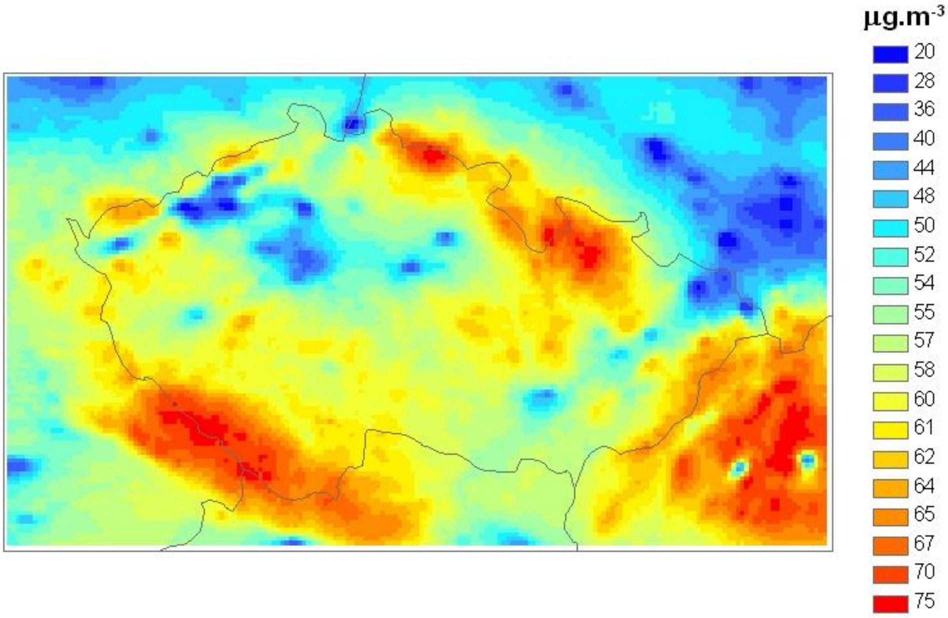


Figure 7.13: Spatial distribution of daily mean ozone concentration ($\mu g.m^{-3}$) averaged over the modelling period calculated in the EXP0 model run on D03 model domain.

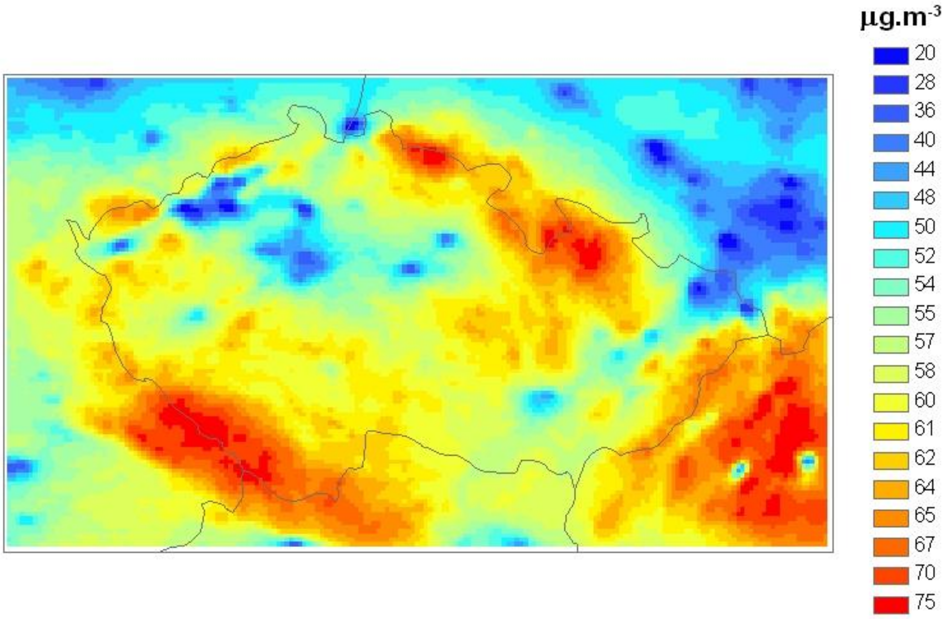


Figure 7.14: Spatial distribution of daily mean ozone concentration ($\mu g.m^{-3}$) averaged over the modelling period calculated in the EXP1 model run on D03 model domain.

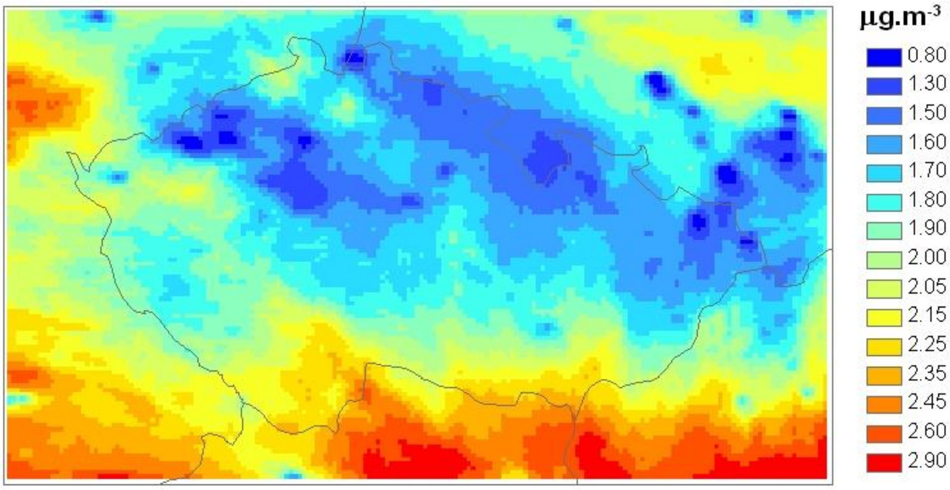


Figure 7.15: Differences between daily mean ozone concentrations ($\mu g.m^{-3}$) calculated in the EXP0 and BC model runs averaged over the modelling period on D03 model domain.

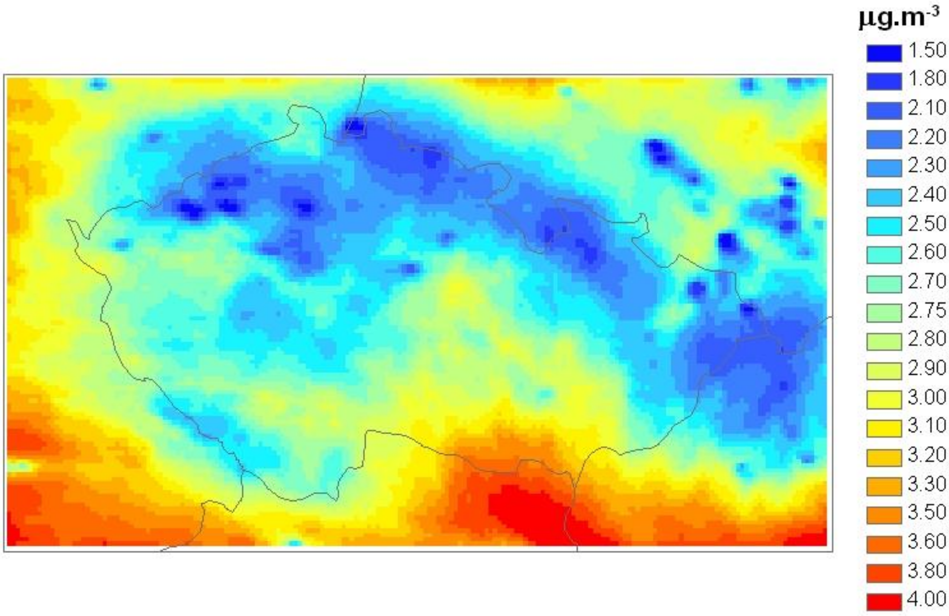


Figure 7.16: Differences between daily mean ozone concentrations ($\mu g.m^{-3}$) calculated in the EXP1 and BC model runs averaged over the modelling period on D03 model domain.

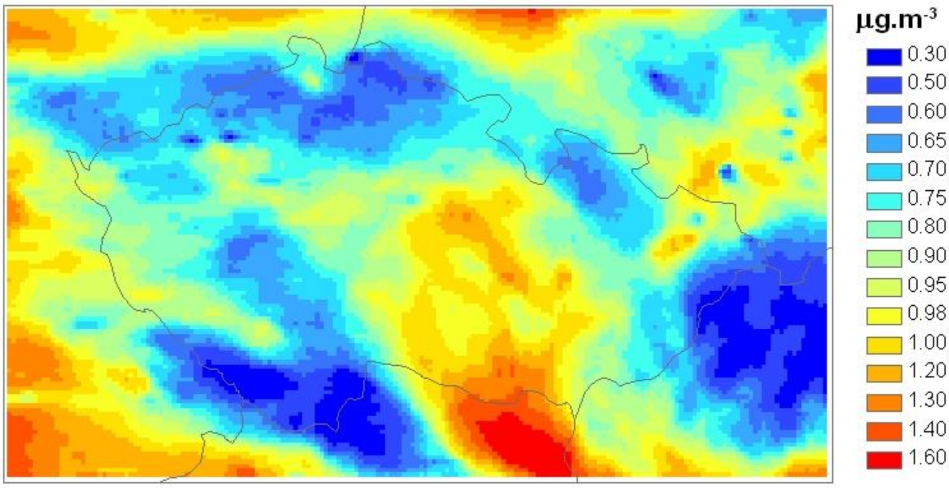


Figure 7.17: Differences between daily mean ozone concentrations ($\mu g.m^{-3}$) calculated in the EXP1 and EXP0 model runs averaged over the modelling period on D03 model domain.

inventory in EXP1 simulation caused increase in mean ozone levels on the overall domain with only 0.83 $\mu g.m^{-3}$ when compared to EXP0 simulation.

Maximal difference between EXP1 and EXP0 model runs is visibe in north-eastern Austria reaching up to 1.6 $\mu g.m^{-3}$. In the area of the Czech Republic, the effect of detailed BVOC inventory in EXP1 simulation is most profound in southern Moravia, eastern Bohemia and in the region in northern Moravia in the vicinity of Ostrava aglomeration. This increase is mainly caused by the increase in isoprene emissions in the BVOC emission inventory of EXP1 simulation from broadleaf forests situated in these locations.

7.3.2 Comparison of model results with observations

Simulated ozone concentrations from all three model runs (BC, EXP0, EXP1) were compared to measured values. Selected were 6 measuring stations on European domain (D01) available in EMEP database and located in areas indicating significant differences between individual model runs. Modeled data of ozone concentration from all three model runs operated on domain of the Czech Republic (D03) were compared to measurements from 36 local measuring stations. Results of comparison of modeled and measured ozone concentration data with meteorological parameters (temperature, global radiation) are also presented.

Model results and observations on European domain (D01)

Daily mean ozone concentrations ($\mu g.m^{-3}$) from 6 european measuring stations were compared with model simulations. Measured data were retrieved from the EMEP network database.

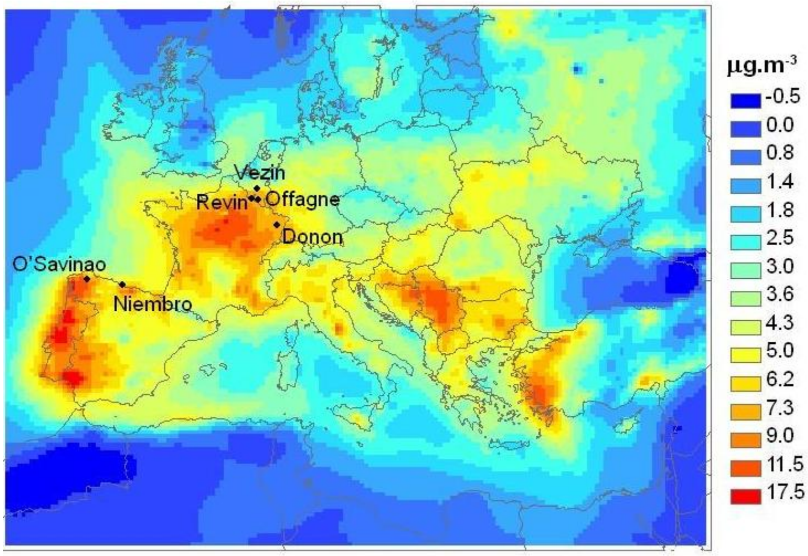


Figure 7.18: Differences in mean ozone concentration ($\mu g.m^{-3}$) calculated in EXP1 simulation and in reference model run; location of EMEP stations.

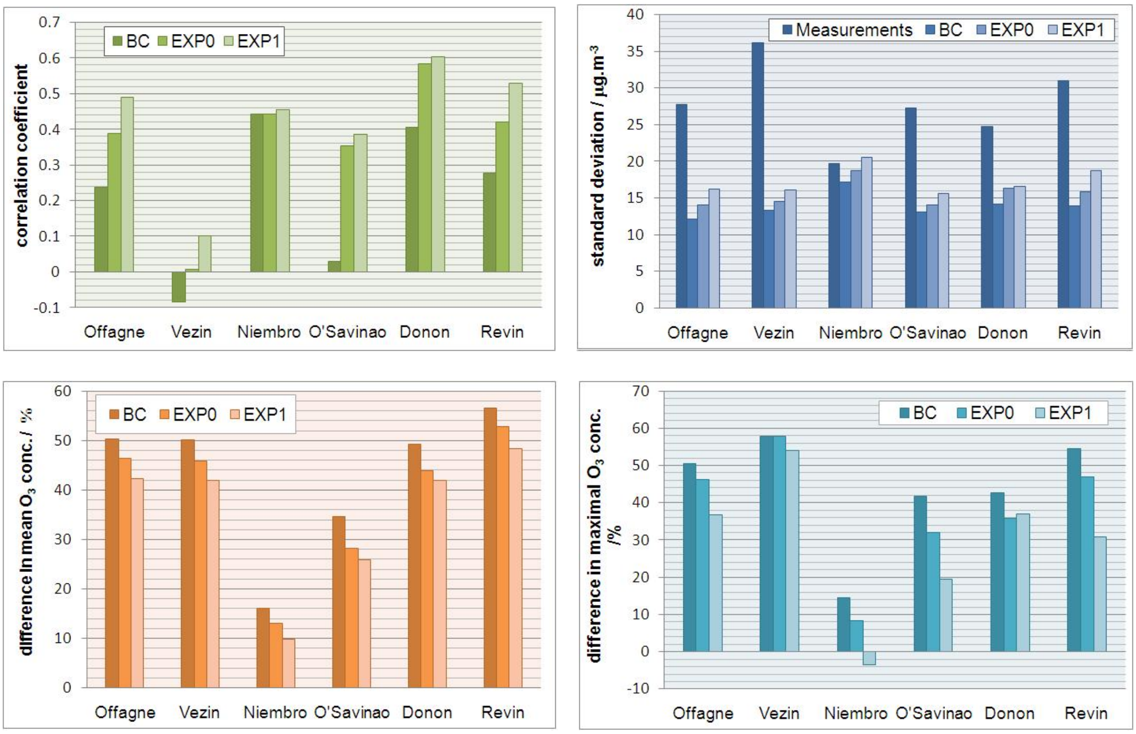


Figure 7.19: Basic statistics performed on ozone concentration data from model simulations and from observations on EMEP measurement stations.

EMEP (European Monitoring and Evaluation Programme) is a cooperative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe [151]. All participating countries provide EMEP network with data from their national measurement networks, these are being processed and offered freely available for scientific comunity. For this study, data from two stations located in Spain (O'Saviñao, Niembro), two located in Belgium (Offagne, Vezin) and two located in France (Donon, Revin) were used. The location of EMEP stations is depicted in Figure 7.18.

Simple statistical analysis has been applied on the modeled and measured hourly ozone concentration data on selected EMEP stations. Obtained correlation coefficients of CAMx simulations and measurements, standard deviations of measurements and model simulations, differences between measured and modeled mean ozone concentration together with differences between measured and modeled maximum ozone concentration are presented in Figure 7.19. Differences between modeled data and measurements are expressed as a percentage of the measured value.

It can be seen that the correlation between measured and modeled data increased at all stations with inclusion of BVOC emissions into the chemical model. In all cases the best correlation has been achieved with results of EXP1 simulation, even though difference between EXP1 and EXP0 simulations at Niembro, O'Saviñao and Donon are small. The most significant improvement of the model results after the inclusion of BVOCs can be observed at O'Saviñao station. As is visible from Figure

7.18, out of all six selected EMEP stations this station is located in area of highest dfference between EXP1 simulation and the reference model run.

Graph of standard deviations indicate that the chemical model is not able to capture the variability of the measurements, nevertheless, variability of the model slightly improves with inclusion of biogenic VOCs into model input data and again the best performace can be observed at results of EXP1 model run.

Analysis of absolute values of ozone concentration average presented as a difference between measured and modeled data expressed as a portion of measured value show model underestimation at all observed stations. Similar results are obtained for maxima of ozone concentration with the exception of Niembro station where data from EXP1 simulation are 3% higher than the measurements. Model values get closer to measurements with the inclusion of BVOC emissions into model simulations.

Profiles of daily mean ozone concentrations along the modelling period (1.4.-14.5. 2007) from all three model simulations were compared to profiles of daily mean ozone levels measured at EMEP stations and the comparison is shown in Figures 7.20 to 7.25.

Also these graphs suggest general underestimation of simulated data when compared to measurements. Well visible is rise of ozone concentration after inclusion of BVOC emissions. Underestimation of model results and inconsistencies between model results and observations can arise from the spatial resolution of the model (27 x 27 km) which is relatively low and the model is not able to capture precisely all processes getting involved in ozone formation and destruction. However, model is relatively well capable to simulate temporal evolvement of ozone concentration.

Model results and observations on domain of the Czech Republic (D03)

Similar analysis as performed in the previous section has been applied on data obtained from model run operated on domain of the Czech Republic (D03). Daily mean concentrations of ozone ($\mu g.m^{-3}$) simulated in all three model runs (BC, EXP0, EXP1) were compared to measured data from 36 stations located in the Czech Republic. Measured data were obtained from the measurement network of the Czech Hydrometeorological Institute and the station locations are shown in Figure 7.26. All selected stations are classified either as backround-rural or backround-suburban.

Hourly ozone concentration data from measurement as well as from model simulations were used to calculate following statistical parameters. Correlation coefficients of model runs and measurements were calculated at each station and are depicted in Figure 7.27, standard deviation of observations and model simulations is given in Figure 7.28 and the differences in averages and maximal values of ozone levels between measurements and model runs expressed as a portion of measured values are shown in Figures 7.29 and 7.30, respectively.

According to Figure 7.27 the best correlation between measured and modeled data is achieved at stations located mainly in remote areas far from the main sources of pollution (e.g. Svratouch, Churáňov, Krokonoše Rýchory, Šerlich, Sněžník). At all stations, the correlation between observations and model increases with inclusion of BVOC emissions into the model inputs. Even though the differences between EXP1

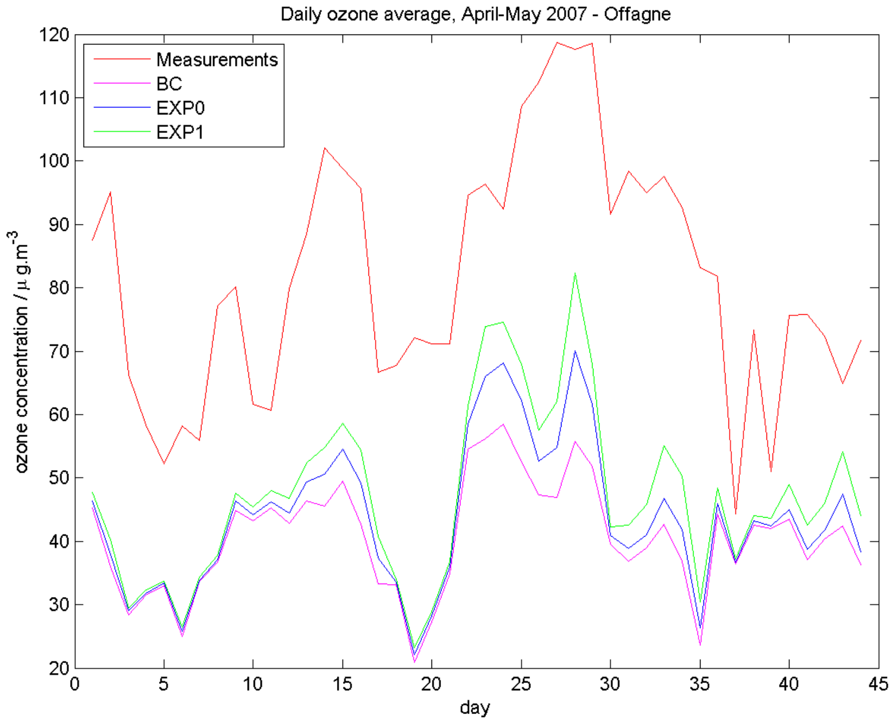


Figure 7.20: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Offagne station compared to model simulations.

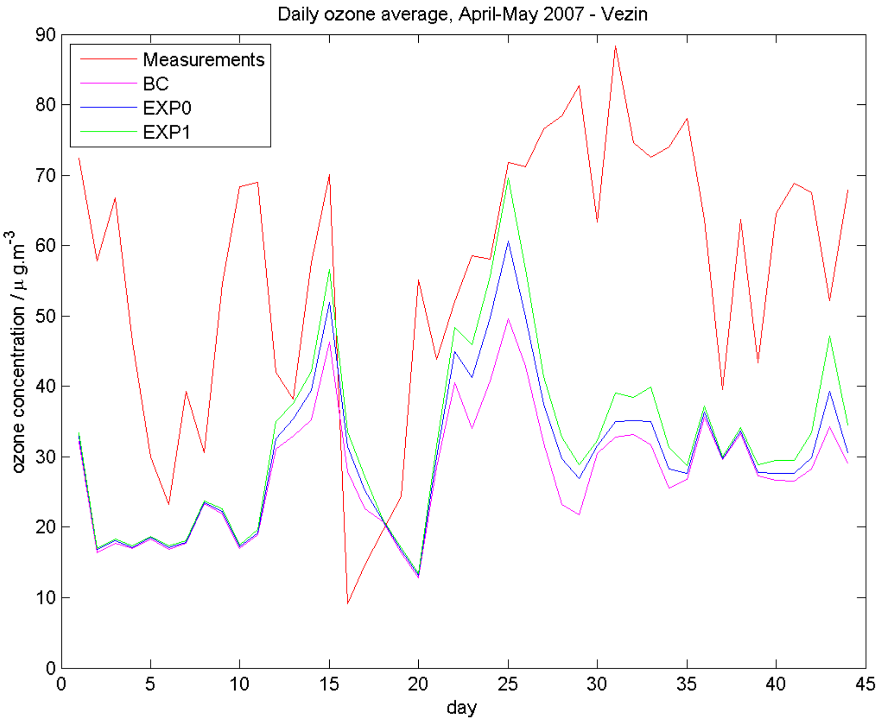


Figure 7.21: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Vezin station compared to model simulations.

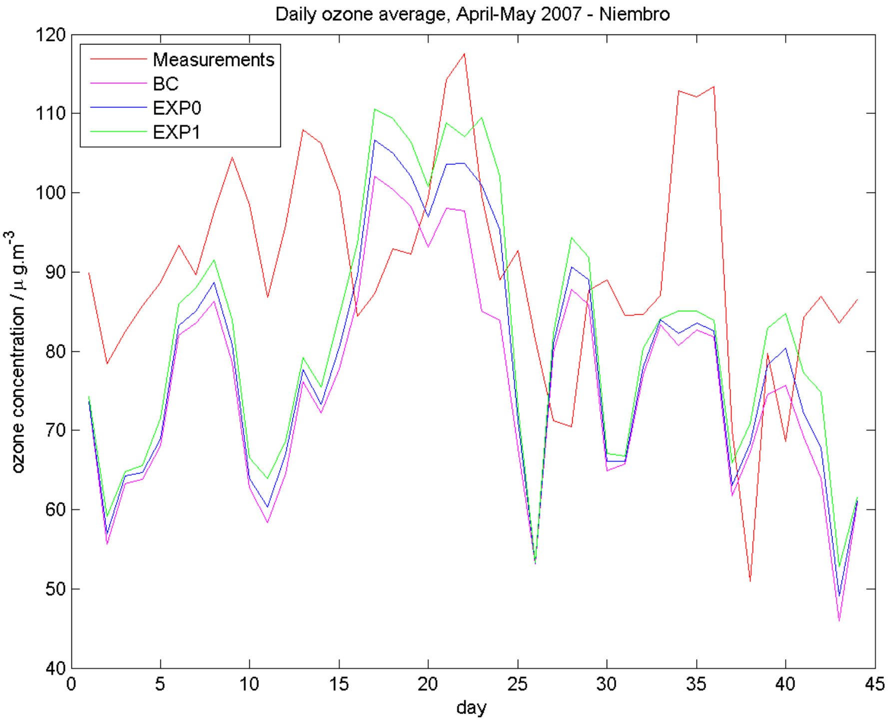


Figure 7.22: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Niembro station compared to model simulations.

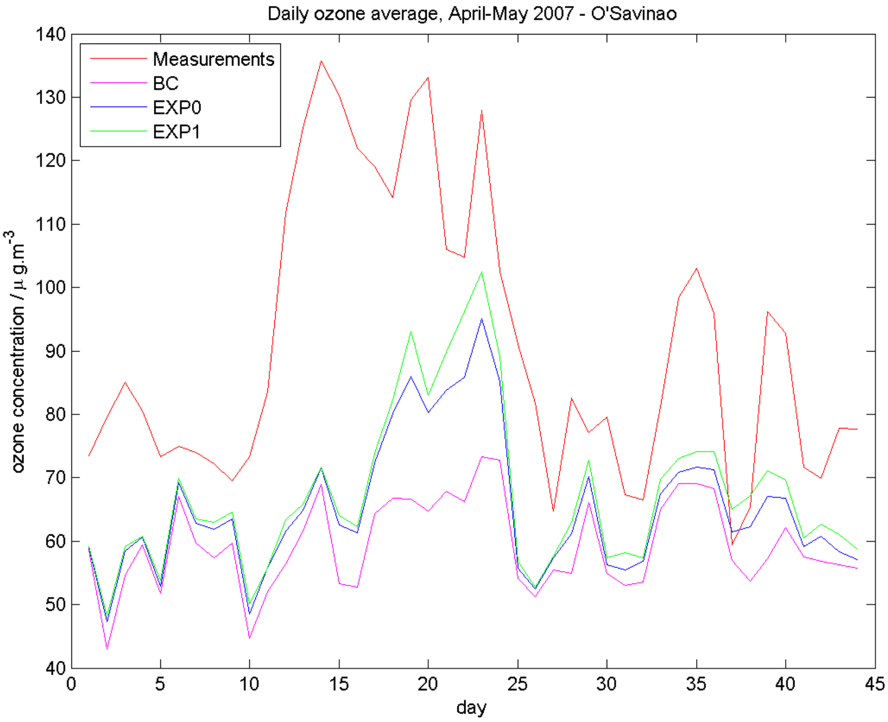


Figure 7.23: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at O'Saviñao station compared to model simulations.

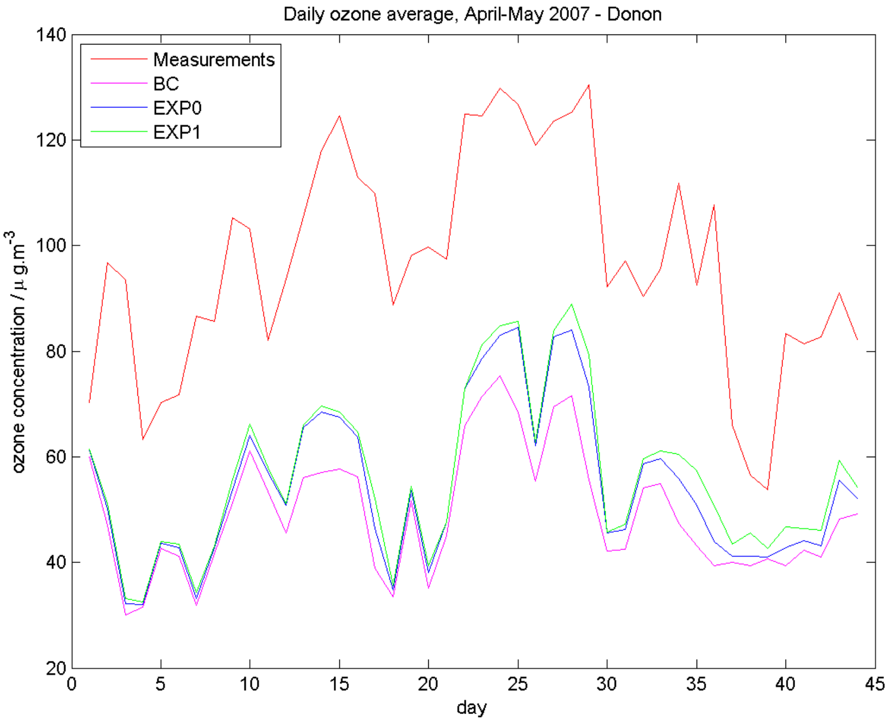


Figure 7.24: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Donon station compared to model simulations.

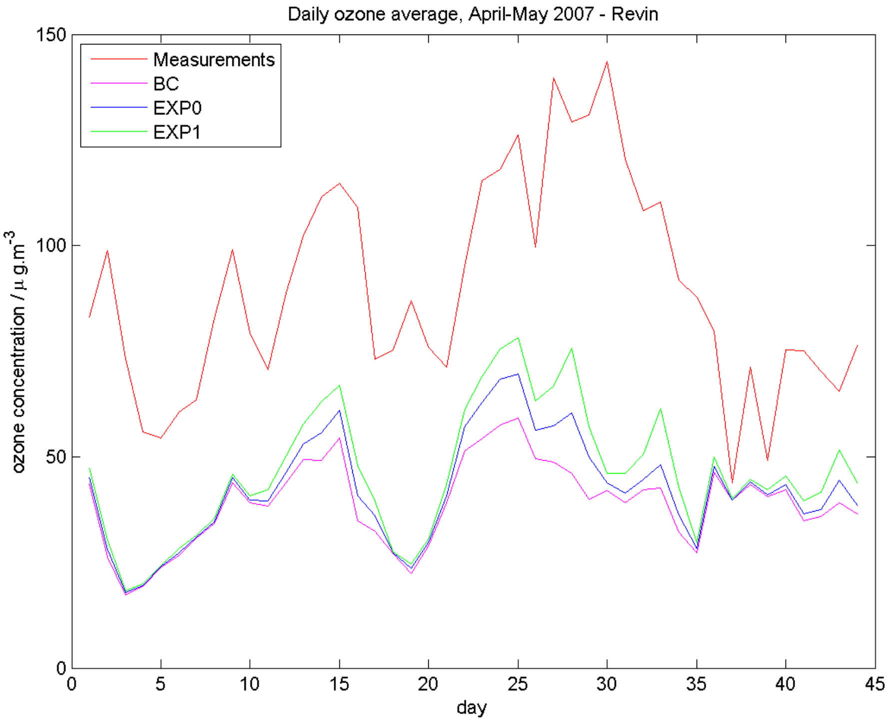


Figure 7.25: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Revin station compared to model simulations.

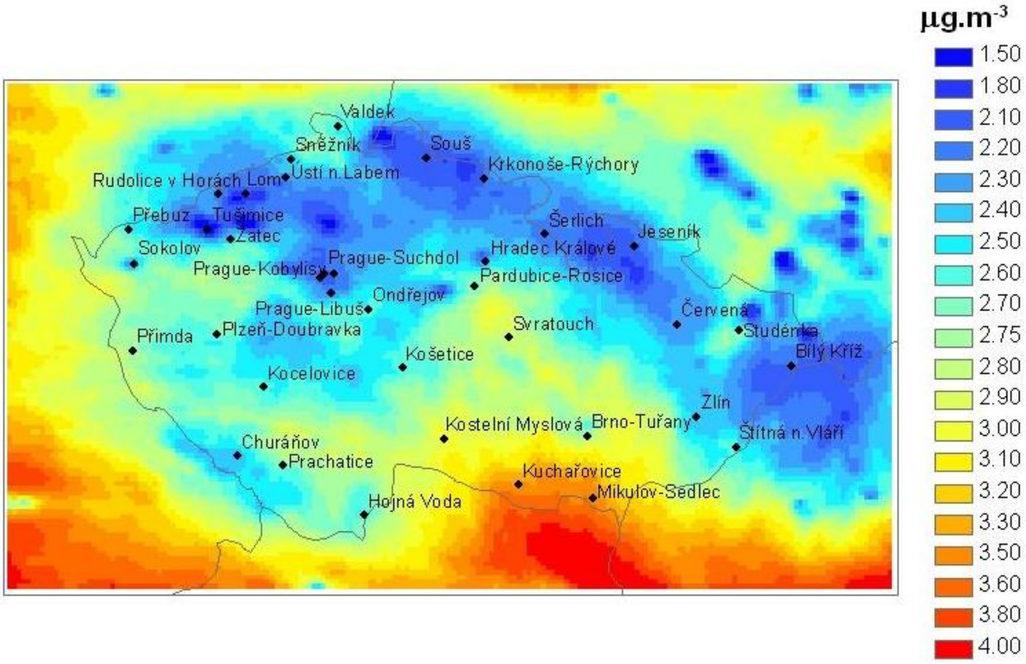


Figure 7.26: Differences in mean ozone concentration ($\mu g.m^{-3}$) calculated in EXP1 simulation and in reference model run; location of measurement stations in the Czech Republic.

and EXP0 model runs are rather small, the best performace at most of the stations give data from EXP1 simulation.

On the other hand, lowest differences in averaged values between observations and model simulations (Fig. 7.29) are found at suburban stations or at stations in the vicinity of industrial areas (e.g. Prague-Kobylisy, Pardubice-Rosice, Plzeň-Doubravka, Lom). The difference continues to dicrease after the inclusion of biogenic VOC emissions into the model simulation.

Similarly to results obtained on the European domain, graph of standard deviations (Fig. 7.28) suggests that chemical model is not capable of capturing the level of variability of measured data, but at most of the stations the variability increases in simulations involving BVOC emissions.

Both Figures 7.29 and 7.30 indicate that also in this smaller domain with higher spatial resolution (3 km x 3 km) model tends to underestimate ozone concentrations. This fact is also visible in the following Figures 7.31 to 7.36 depicting comparison of daily averaged data of ozone concentration from model calculations and from measurements at six selected stations in the Czech Republic, presented over the whole modelling period. Presented profiles of daily ozone concentrations indicate that the CAMx model relatively well follows the trend in measured ozone concentrations, however, mostly doesn't reach the observed ozone levels.

As it has already been discussed in the Section 7.3.1, the effect of BVOC emissions inclusion in model simulations on the domain of the Czech Republic is not as noticable as it has been in particular areas on the European domain. Presented comparison of model runs with observations show differences between individual model simulations ranging in the scale of units of $\mu g.m^{-3}$. Nevertheless, it is visible that

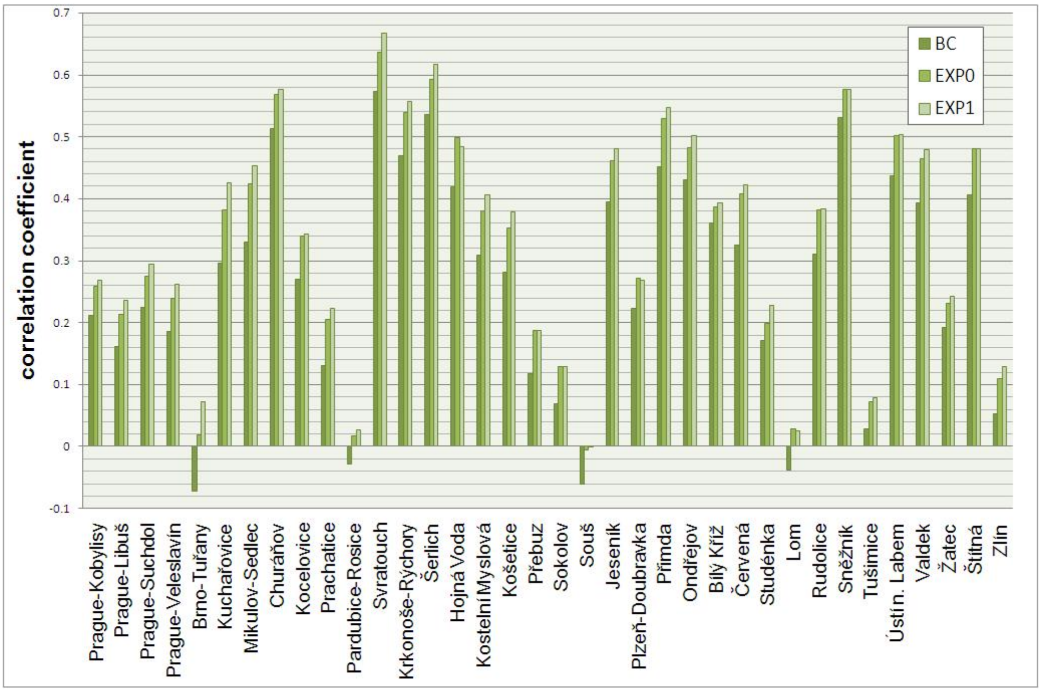


Figure 7.27: Correlation coefficients of CAMx model simulations and measurements calculated from hourly ozone concentrations.

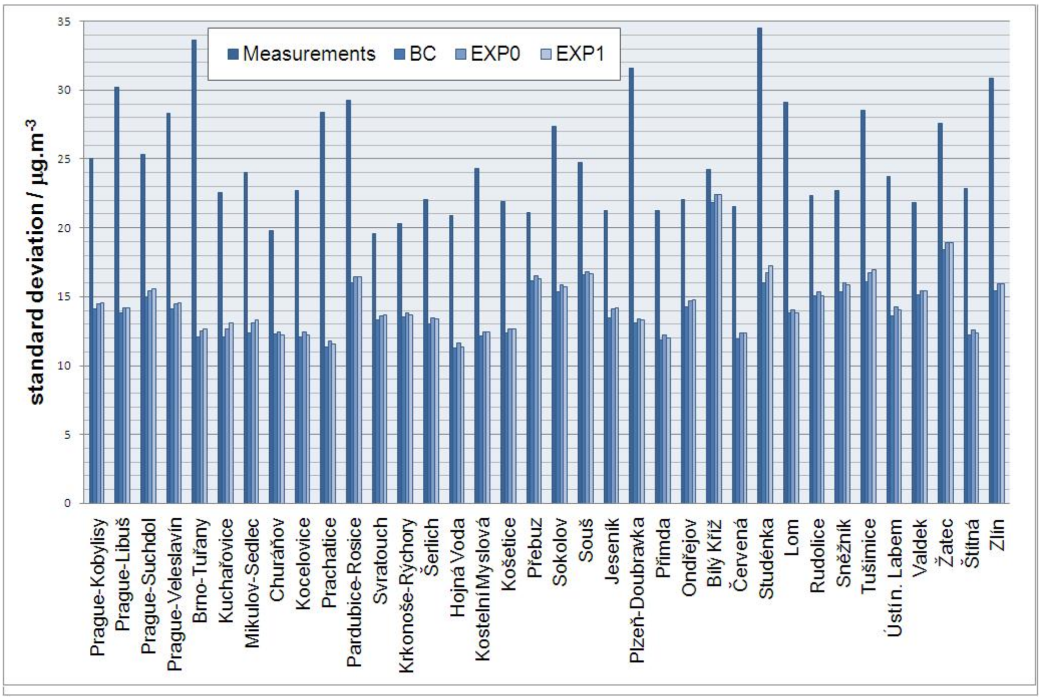


Figure 7.28: Standard deviation of CAMx model simulations and measurements calculated from hourly ozone concentrations.

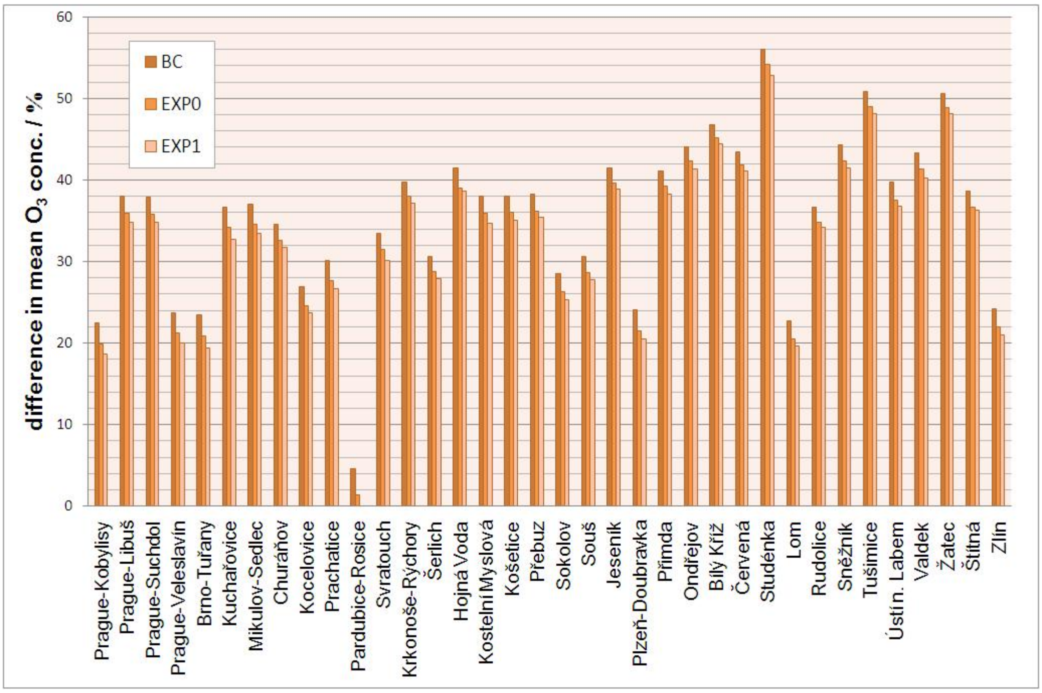


Figure 7.29: Differences of ozone concentration averaged over the modelling period between CAMx model simulations and measurements.

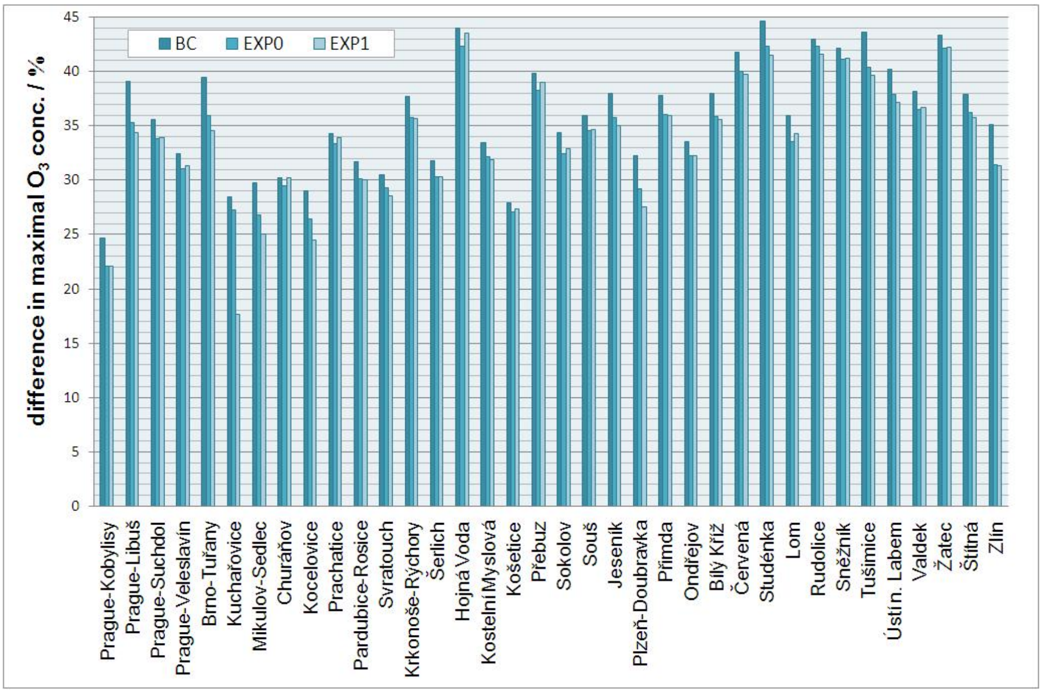


Figure 7.30: Differences of maximal ozone concentration over the modelling period between CAMx model simulations and measurements.

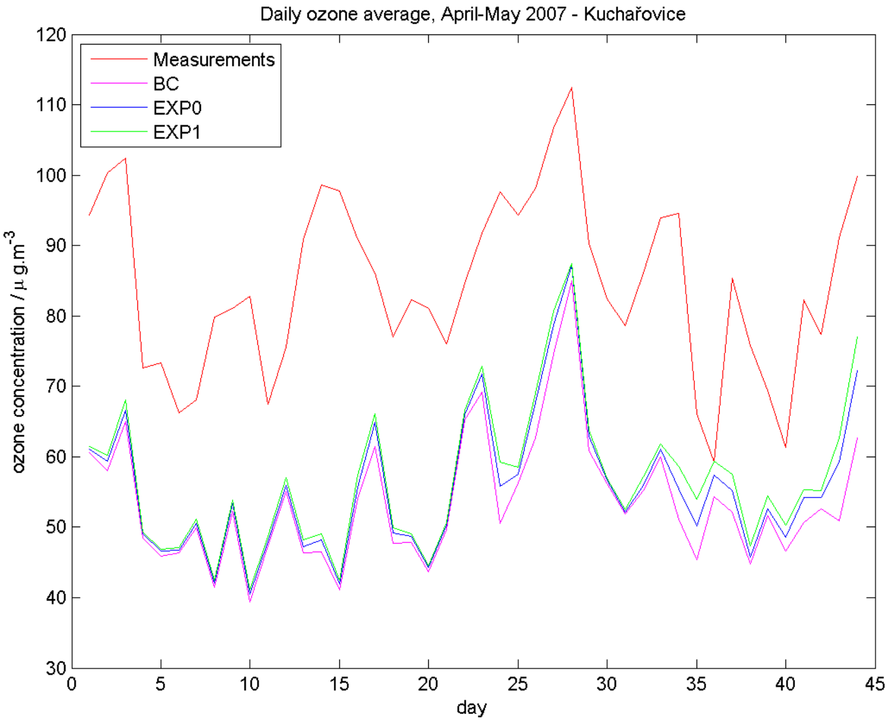


Figure 7.31: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Kuchařovice station compared to model simulations.

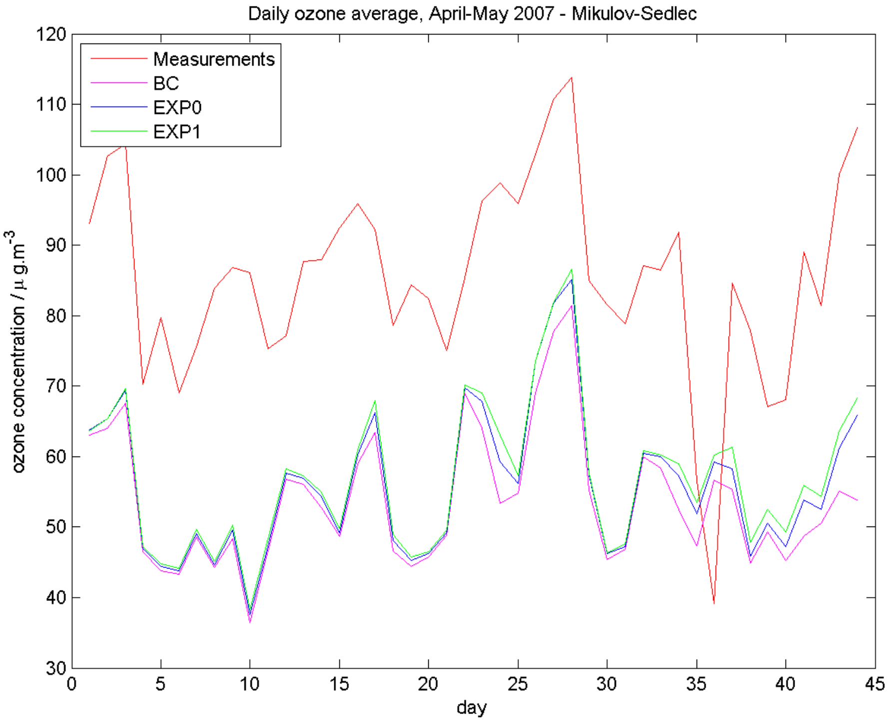


Figure 7.32: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Mikulov-Sedlec station compared to model simulations.

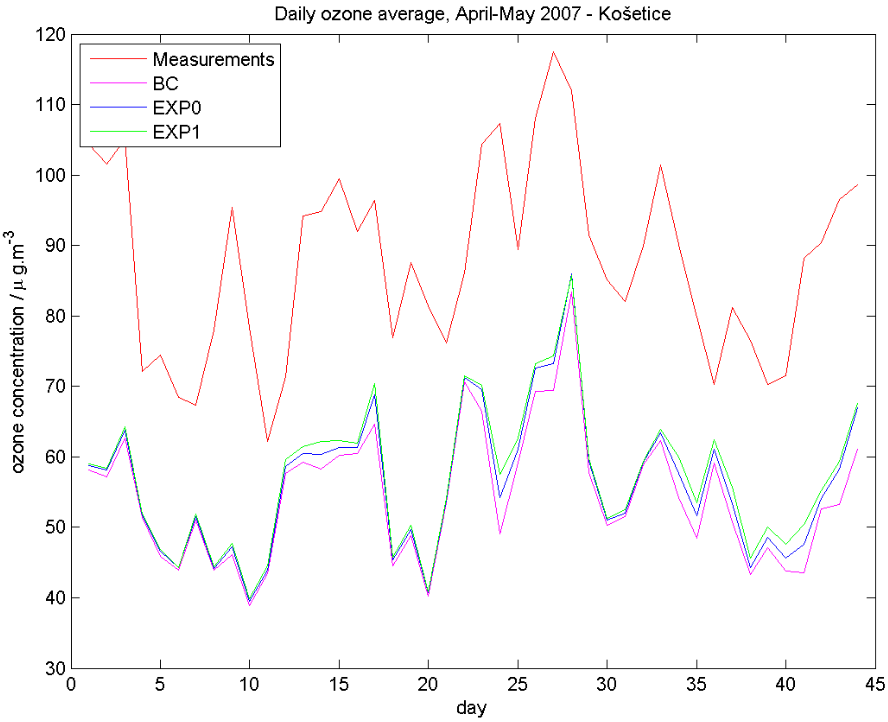


Figure 7.33: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Košetice station compared to model simulations.

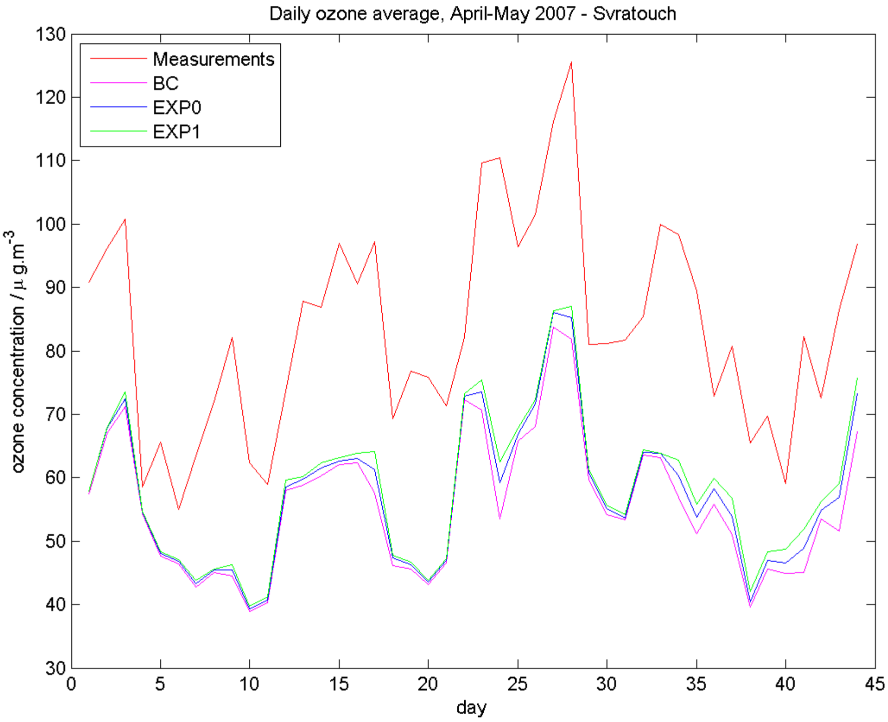


Figure 7.34: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Svratouch station compared to model simulations.

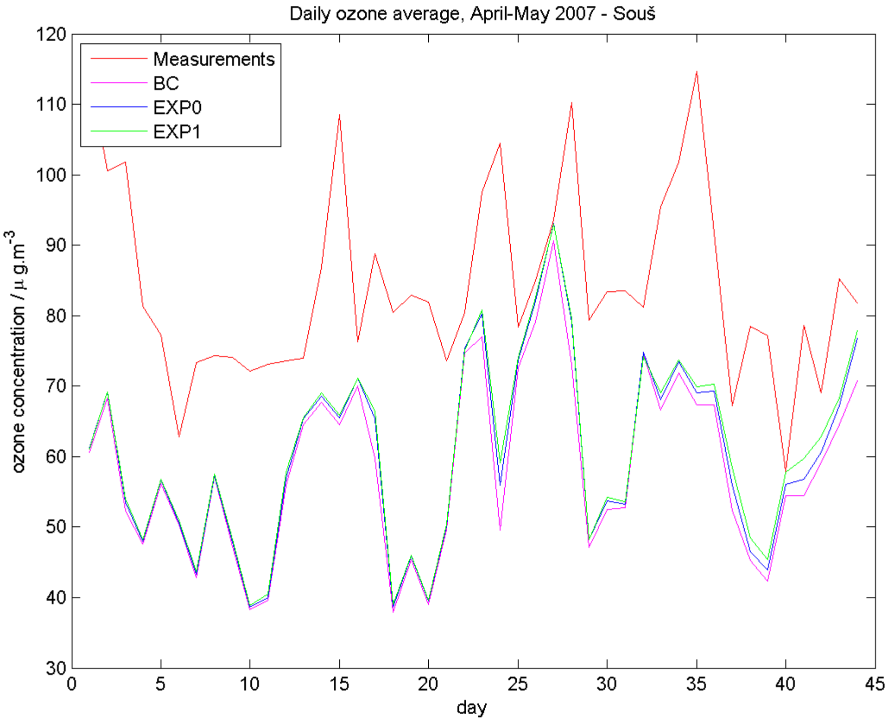


Figure 7.35: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Souš station compared to model simulations.

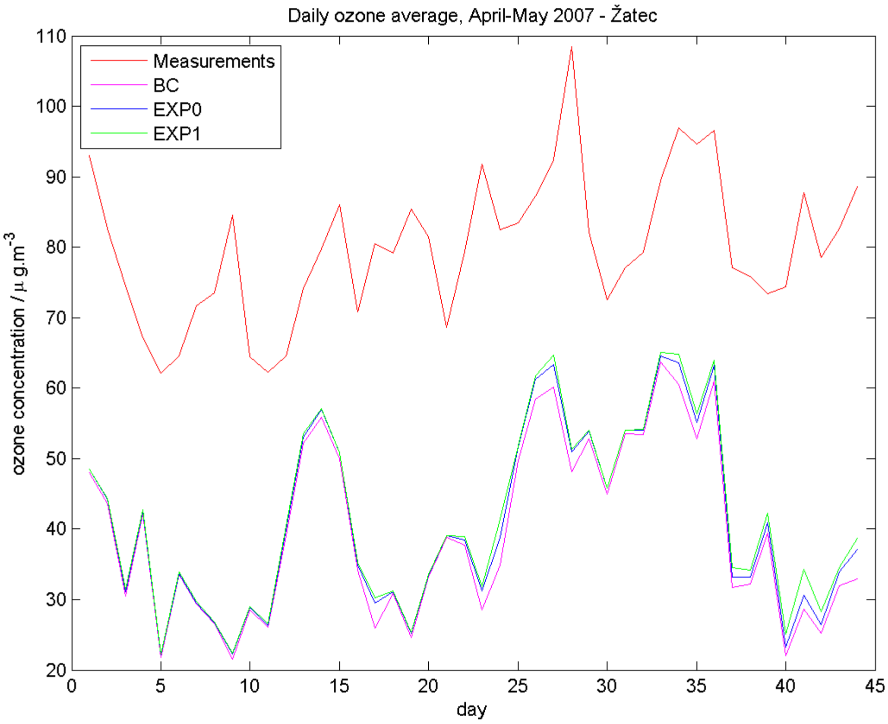


Figure 7.36: Daily mean ozone concentration ($\mu g.m^{-3}$) measured at Žatec station compared to model simulations.

at all stations ozone concentration rises when biogenic VOC emissions are taken into account. The increase is even more profound in the second half of the simulated period when meteorological conditions were more favourable for ozone formation as well as for emissions of BVOCs.

Daily mean ozone concentrations from measurements and from EXP1 model run were for selected stations compared to meteorological parameters - temperature at the height of 2 m above the ground and global solar radiation. Meterological data were taken from WRF model simulations which, according to Figs. 7.2 and 7.3, well correlate with observations. Both temperature and solar radiation are known to have positive effect on ozone formation as well as on emissions of biogenic VOCs. This relationship is well visible in presented Figures 7.37 to 7.42. Decrease in global radiation and in temperature is followed by decrease in ozone concentration and vice versa.

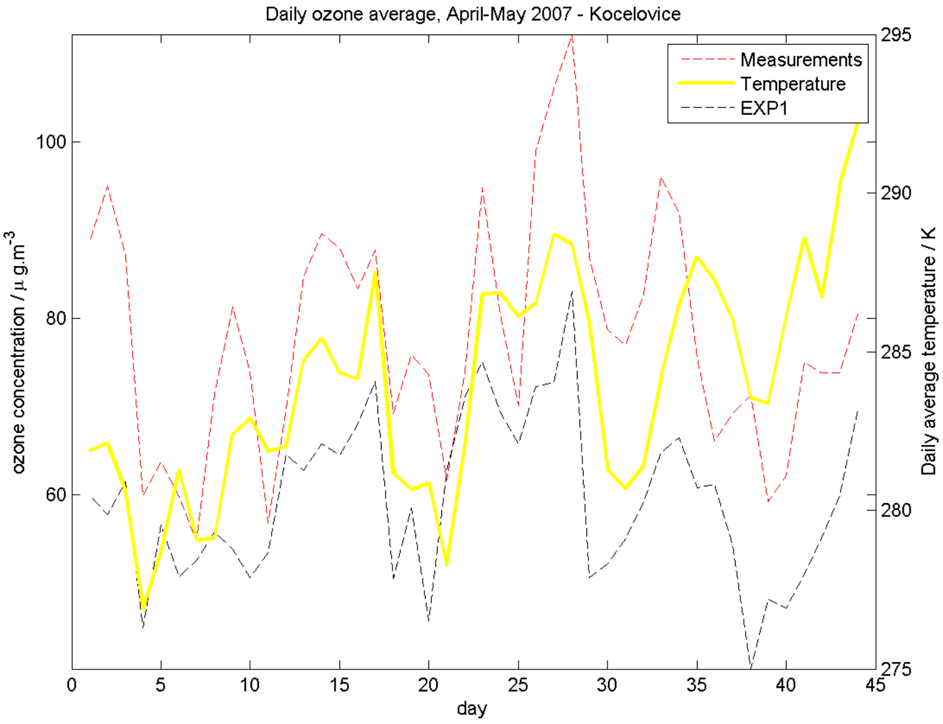


Figure 7.37: Comparison of daily averaged ozone data from model run EXP1 and from measurements with temperature at Kocelovice station.

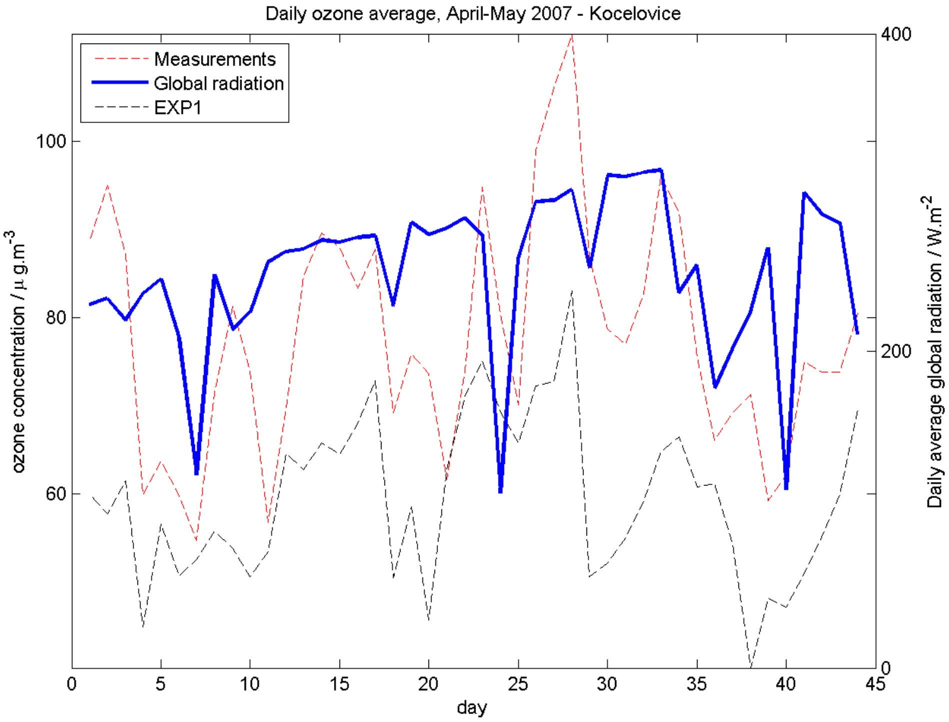


Figure 7.38: Comparison of daily averaged ozone data from model run EXP1 and from measurements with global radiation at Kocelovice station.

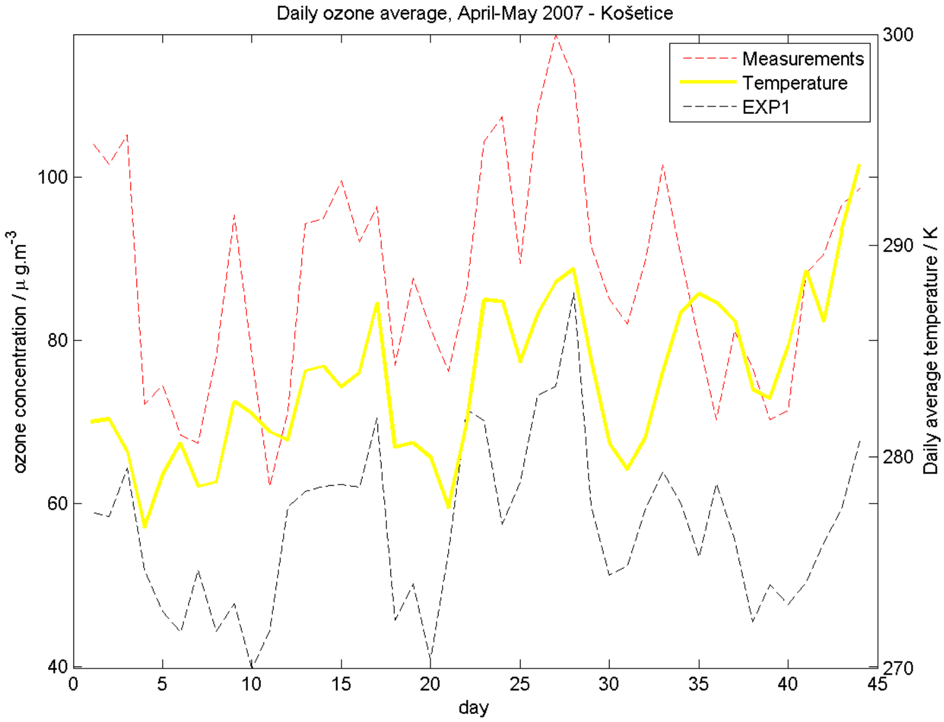


Figure 7.39: Comparison of daily averaged ozone data from model run EXP1 and from measurements with temperature at Košetice station.

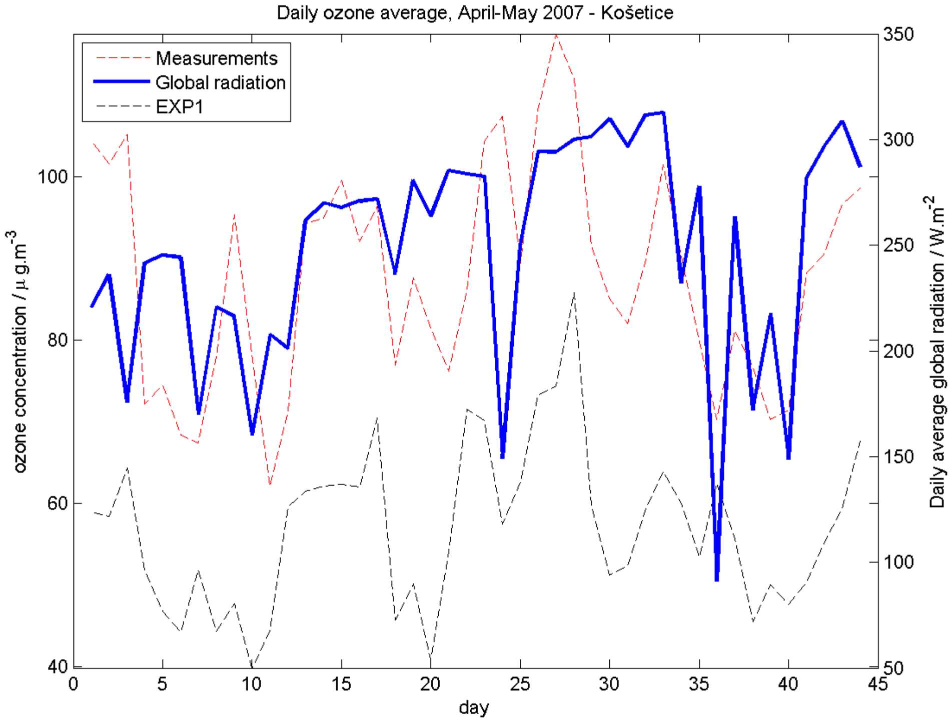


Figure 7.40: Comparison of daily averaged ozone data from model run EXP1 and from measurements with global radiation at Košetice station.

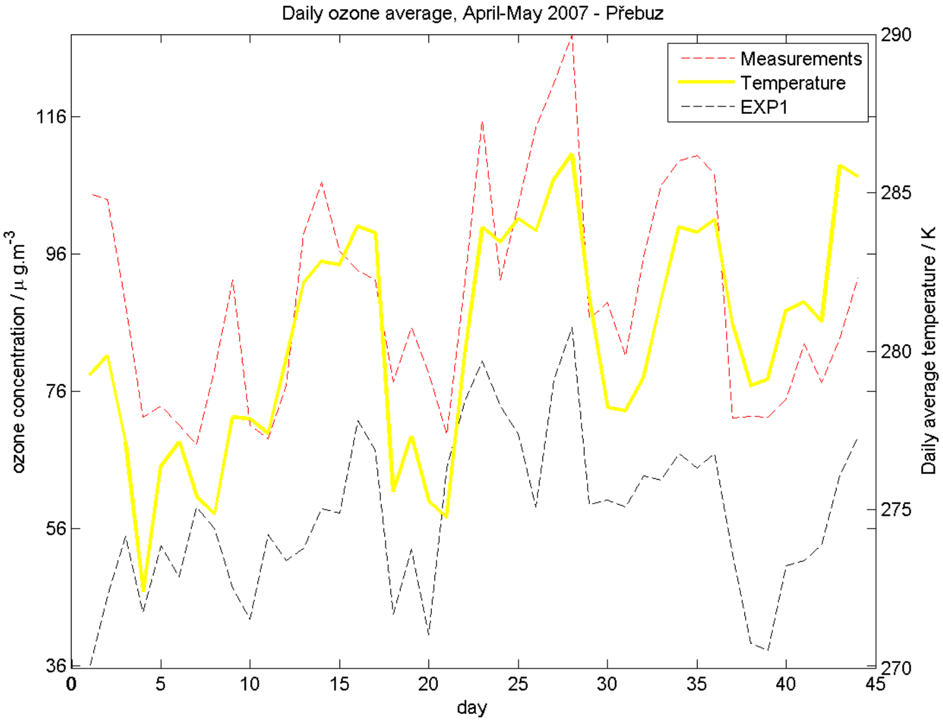


Figure 7.41: Comparison of daily averaged ozone data from model run EXP1 and from measurements with temperature at Přebuz station.

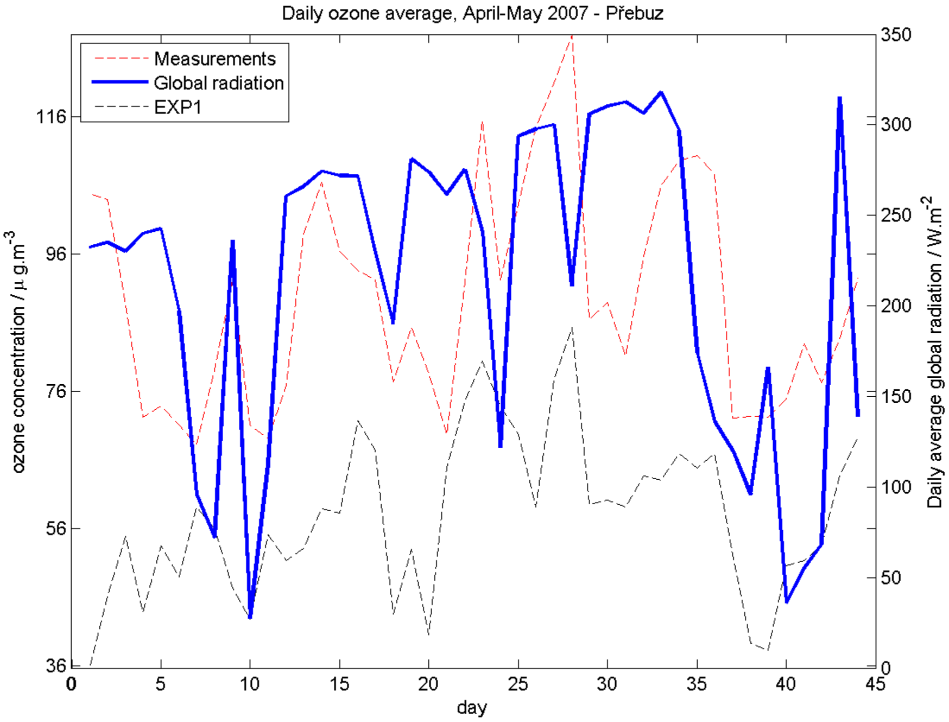


Figure 7.42: Comparison of daily averaged ozone data from model run EXP1 and from measurements with global radiation at Přebuz station.

Chapter 8

Conclusions

Presented thesis aimed to investigate the relationship between emissions of volatile organic compounds of natural origin and formation of tropospheric ozone. As it has been previously shown (e.g. [6]), significant amounts of highly reactive VOC species can be emitted from biogenic sources, especially from vegetation. Biogenic VOCs then enter complex system of atmospheric chemistry and beside other consequences can effect concentrations of low-level ozone.

Processes connected to VOC biosynthesis inside plants and factors influencing VOC release were studied together with ecophysiological functions of these chemical compounds. Special attention has been paid to methods of biogenic VOC emission measurement and simulation.

Emission fluxes of biogenic VOCs were estimated for the area of the Czech Republic. Approach of *Guenther et al.* [47] has been adapted to simulate emissions of isoprene, group of monoterpenes and group of oxygenated VOCs. The estimate is based on the high spatial resolution land cover database (1 km x 1 km) comprising information about distribution of single tree species. Emission potentials of simulated chemical species assigned to each land cover category were partially obtained from survey of up-to-date emission factor databases and publications, and partially from laboratory measurement study when emission fluxes of five tree species grown in the Czech Republic were measured using Proton-Transfer Reaction Mass Spectrometer. By employing these input data an emission inventory of BVOCs in the Czech Republic for the year 2000 has been created. Annual totals of isoprene, monoterpenes and OVOC were calculated together with the annual profile of monthly averages. Presented was the spatial distribution of individual chemical species over the area of the Czech Republic. Differences between emissions in winter and summer were discussed as well as the uncertainties connected with the estimates. Obtained emission inventory or compiled database of land cover categories and emission potentials can be further utilized in regional studies implementing VOCs from biogenic sources (e.g. tropospheric chemistry modelling, secondary organic aerosol formation).

Modeled emissions of isoprene and monoterpenes, the most reactive VOC species, were compared to data from national inventory of anthropogenic VOC emissions. Following the data format of anthropogenic VOC emissions, total annual emissions of BVOCs were summed within individual administrative regions in the Czech Republic and compared to two categories of man-made VOCs. First category included only stationary sources of pollution (point and surface), second category comprised stationary and mobile sources as well. The comparison suggested that in all regions biogenic emissions are comparable in magnitude to man-made emissions. Biogenic sources exceed all anthropogenic sources in areas of dense vegetation (south and south-west Bohemia) and in approximately half of regions biogenic emissions are of comparable magnitude or even higher than anthropogenic emissions from stationary sources.

Effect of biogenic VOCs on tropospheric ozone formation was investigated applying chemical transport model CAMx on the whole European domain and then on domain focused on region of the Czech Republic. Period of the simulations was dependent on the availability of prognostic model data and selected was an episode of elevated ozone concentration in Spring, 2007. Model simulations tested two different inventories of biogenic VOCs and the results were afterward compared to reference model run accounting with anthropogenic emissions only, and to ozone concentration measurements.

First BVOC inventory (included in model run EXP0) was calculated on the basis of generalized land cover categories distinguishing only between deciduous, coniferous and mixed forest. Second BVOC inventory (included in model run EXP1) was created by utilizing more precise, species specific land cover categories. Inventory of EXP0 simulation included emissions of isoprene and monoterpenes, while EXP1 simulation included group of OVOCs in addition. In average, biogenic emissions of EXP1 simulation reached twice the values of emissions of EXP0 simulation, and even triple the value of EXP0 in areas of maximal emissions. The increase in released BVOCs can be assigned to better correspondance of EXP1 emissions to vegetation distribution and higher emission factors of certain land cover categories.

Locations of highest BVOC emissions are situated in Portugal, area of former Yugoslavia, central France and Asia Minor. These locations are represented by dense vegetation, especially broadleaf forest consisting of oak species which are high isoprene emitters. Furthermore, meteorological conditions at these sites, i.e. high surface temperatures and sufficent solar radiation, favor emissions of BVOCs.

Results of ozone concentration simulations showed that inclusion of BVOC emissions in the model caused overall increase in ozone levels. The largest effect of BVOCs is best visible in locations of highest BVOC emissions and is even more profound in the vicinity of major sources of nitrogen oxides. Increase in ozone concentration as a consequence of increase in BVOC emissions suggests that most of the domain is in the "VOC limited" state. Modeled ozone concentrations were compared to measurements at six european stations. The best agreement with measurements was obtained with EXP1 simulation, although model has a tendency for underestimation of ozone levels.

When focused on the region of the Czech Republic, increase in ozone concentration as a result of BVOC emissions inclusion to model run was detected as well. However, the growth in this region was relatively small (less than 5 %). Estimate of biogenic VOCs based on more detailed land cover database brought only slight improvement. Even though the differences between EXP1 and EXP0 model runs are small, comparison of modeled data with observations at 36 stations in the Czech Republic proved best performace of EXP1 model run. Model better captured course of ozone concentration in remote areas, wherease in absolut values better agreement with measurements was visible at suburban stations close to potential sources of nitrogen oxides.

In general, presented results suggest that CAMx model tends to underestimate ozone concentrations but relatively well follows the ozone temporal course. There are several potential sources of inconsistencies between model and measurements. They partially lie in approximations of chemical and dynamical processes represented in the model and are partially given by the resolution of input model data which doesn't allow model to capture effects of local sources and regional meteorological conditions.

Outlooks of future work involve testing the effect of BVOC emissions on ozone concentration during summer period when BVOC fluxes are expected to reach highest values and when the conditions are most favourable also for ozone formation. It is desirable to improve the biogenic emissions model with module for more sophisticated representation of emitting biomass which would also account for effects of canopy layer on micrometeorology.

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