Modeling of ozone and nitrogen oxides pollutions in urban air environments

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Abstract

As the air quality in urban environments is a rising problem, a deeper understanding of how air pollution is dependent on different factors is necessary. In these environments, there are different parameters that effect how the chemical reactions of the pollutants are proceeding. Here the parameters solar radiation, temperature, humidity, emission factors and background concentrations of gaseous air pollutants are at focus. They were chosen as they all contribute to the reactions in the air and results with different outcomes. In the study a box model taking 608 chemical species and 1923 reactions into account is used to simulate how these parameters effects the processes of ozone and NO_x (NO and NO_2). The model that was used was a merge of a Master Chemical Mechanism (MCM) and Kinetic Pre-Processor (KPP) solver. The effect of each parameter was studied by changing one of them and keeping the rest constant. This was performed for all the parameters. All the simulations was based on a case from London. Even though there are many air pollutants contributing to the poor air quality the ones that this study have its focus on is ozone, nitrogen oxides and some hydrocarbons. This is due to the fact that they all occur naturally, that they are made through the reactions caused by industrial and traffic combustion, that they all interfere with each other, that they contribute to unhealthy environment and that most of them increases the greenhouse effect. The aim is to investigate the sensitivity of urban atmospheric chemistry with respect to different parameters and gain general insights in these important chemical systems and better understanding of in what conditions simpler or more complex modeling schemes can or must be used to reproduce the systems.

It was found that the temperature was important for the processes of ozone and NO_x as the rate of significant reactions are highly dependent on temperature. This resulted in both decrescent, in low temperatures, and increasing, in high temperatures, of ozone concentration. Here the humidity also played a role as it at high temperatures contribute to more production of OH radicals which is an important part of the tropospheric chemistry. This as OH is a sink for NO_x so an amplified production of OH decreased the NO_x. Solar radiation acted expected as a support for ozone production when NO_2 is photolyzed. Different ratios of NO_2/NO_x acted differently on the ozone concentration. When NO_2/NO_x consisted of mostly NO the concentration of ozone decreased and when NO_2/NO_x consisted of mostly NO_2 it increased. Different ratios did not affect the end concentration of the total NO_x. When hydrocarbon compounds and CO was studied an increase produced more ozone and decrease the concentration of NO_x. The result was the same when all the volatile organic compounds with CO and when only the non-methane volatile organic compounds was changed.

Contents

1 Introduction

1.1 Background

In the world's urban environments there is a growing problem of poor air quality. Even though this is concerning the entire globe, the quality of the air is especially an exceptional problem for large cities in Asia. This is severe as urban air pollution is causing serious effects on human life. As the World Health Organization (WHO) states that 91% of the world's population lives in places where air pollution exceeds WHO guideline limit and that there are 4.2 million deaths every year as a result of exposure to ambient air pollution [1]. The consequences are alarming and hence a deeper understanding of the physical and chemical aspects of the processes of air pollutions is in focus.

In this work it is studied how the concentrations of ozone (O_3), nitrogen oxides (NO and NO_2, together defined as NO_x) and some hydrocarbons are altered in the troposphere. These species are chosen as they are typical urban pollutants and due to the chemical interplay between them. Also because they influence human health [2] and most of them contribute to increase the greenhouse effect. It is studied how the progress of these species concentrations are affected when different parameters are changed. This is of interest as the chemical system of urban air pollution is a complex system that is sensitive to external factors; such as solar radiation, humidity, temperature, emission factors, and background concentrations of gaseous air pollutants. A box model is used to simulate the processes of the air pollution. The startup case for the model has been presented by Bright et al. [3]. With their case this study used a Master Chemical Mechanism (MCM) that comprise 608 species and 1923 reactions together with a Kinetic Pre-Processor (KPP) solver.

1.2 Aim

As these air pollutants have an effect on both humans and the environment a deeper understanding of how they behave in urban environments is wanted. Here is where the aim of the thesis lies, to investigate the sensitivity of urban atmospheric chemistry with respect to different parameters such as named in Section 1.1. This investigation is preformed to study the individual effects of the different parameters. The point is to gain general insights in these important chemical systems and better understanding of in what conditions simpler or more complex modeling schemes can or must be used to reproduce the systems.

2 Theory

All over the globe there are human activities that is causing emissions of air pollution. It is clear that these pollutants are resulting in problems for both the environment and humans. The effects are on a scale from climate change and stratospheric ozone loss to regional and local ozone episodes and poor air quality. In cities the main primary emissions are NO_x and hydrocarbons. Here, the hydrocarbons in focus are the volatile organic compounds (VOC), which are all hydrocarbon compounds in gas phase at room temperature. These species are highly significant for the production of surface ozone which hence is a secondary pollutant. Surface ozone is significant for the cause of health problems. All these species are for high concentrations a health risk and all interplay with each other in the troposphere chemistry. [4]

2.1 Tropospheric chemistry

In the atmosphere, about the 8-16 km nearest the ground is called the troposphere. The gas compounds that make the troposphere is a well mix with the average composition of 78% N_2, 21% O_2, 1% Ar, and 0.036% CO_2 [4]. The amount of water vapor varies with temperature and altitude and the majority of trace species is due to emissions at the surface. The trace species are the gas compounds that make up less than 1% of the gas in the troposphere. This is where the NO_x and VOC enter and then go through various complex series of physical and chemical transformations. In the troposphere, gas phase chemistry involves oxidation of organic molecules in the presence of NO_x and solar radiation. These oxidations happen via chains of reactions and can be long and complex.

Even though the concentrations of the trace species are so low in the entire troposphere they are high in urban environments. This as there are many emission sources in these areas which then give a larger concentration number of the trace species here. And due to the combustion emissions there is an increase of NO_x in the urban areas playing a key role as an oxidation medium in the chemistry. Furthermore, ozone is a secondary pollutant. This means that ozone is not emitted directly from the combustion, but is instead a product of the pollutants that are emitted. Hence ozone concentrations is based on the concentration of the other species. However, ozone plays a great role in the cycles of the tropospheric chemistry which can be simplified and summarized as seen in Figure 1.

2.1.1 Nitrogen oxides

The nitrogen oxides (NO_x) that are in focus in this study is defined as the sum of the concentration of nitric oxide (NO) and nitrogen dioxide (NO_2). These species are, just like ozone, harmful for both humans and nature. But they are also important for the tropospheric chemistry as they play a big part of the cycle shown in Figure 1. NO_x are primary pollutants from all combustion and are emissions from for example internal combustion engines such as in cars. When NO_x is emitted it is mostly as NO. Furthermore, NO is very reactive and quickly oxidate and produce NO_2 as shown in Reaction C1.

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad \mathrm{(C\,1)}$$

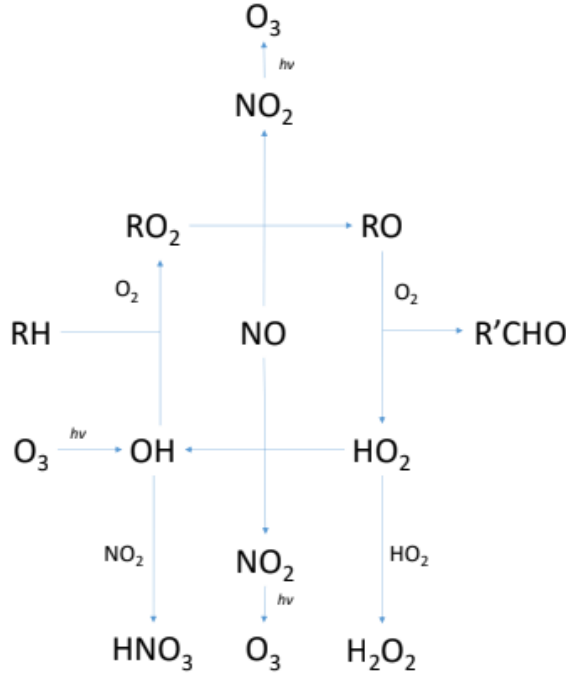However, NO_2 is photolyzed by solar radiation with wavelength up to 424 nm which is

Figure 1: Summary of the tropospheric chemistry. R is any carbon chain and $h\nu$ is photon. (Magnus Joelsson, personal communications, 2018)

just in the spectra of visible light. Hence this photolysis occurs easily with the sunlight. The photolysis is seen in Reaction C2.

$$NO_2 + h\nu \longrightarrow NO + O \tag{C2}$$

where $h\nu$ is the notation for a photon. $h = 6.626 \cdot 10^{-34}$ m^2 kg/s is Planck's constant and ν is the photon's frequency [5]. The oxygen atom that is a result of the photolysis is reactive and will likely react with an O_2 as in Reaction C3.

$$O + O_2 + M \longrightarrow O_3 + M \tag{C3}$$
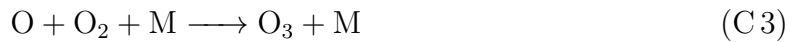
where M is a third body molecule that absorbs the surplus vibrational energy and hence stabilizes the formed O_3 molecule. Reactions C2 and C3 can be summarized to Reaction C4.

$$NO_2 + h\nu \xrightarrow{O_2} NO + O_3 \tag{C4}$$

The chain reaction shown in Reaction C4 is the only significant source of ozone to the troposphere. This is because the photolysis of NO_2 is the only source of the needed O in Reaction C3 [6]. As a result of the cycle of NO_x and O_3 it can be discussed that without sunlight NO_x helps to decrease the concentration of ozone by Reaction C1, but with sunlight NO_x is the source of ozone.

2.1.2 Ozone

The health risks of ozone has been highlighted by, among others, Jacobson [2]. In the troposphere ozone is a directly harmful (even deadly in high concentrations) pollutant. It attacks the respiratory organs and is hence injurious for people suffering of lung cancer.

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It can also hurt children and elderly. Furthermore, it can be a triggering factor for people with other health conditions. High concentrations of ozone can also exacerbate asthma, emphysema and chronic bronchitis. Exposure might as well lead to premature death in heart and lung diseases.

From the production of ozone in the troposphere described in Section 2.1.1 above and with the connection between ozone and NO_x Equation 1 can be formed. It is a steady state approximation that describes how the concentration of ozone is dependent on NO_2 and NO in the troposphere.
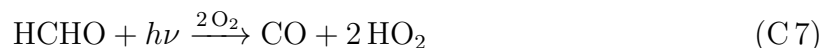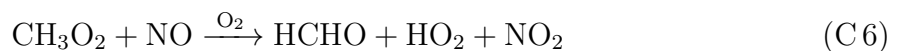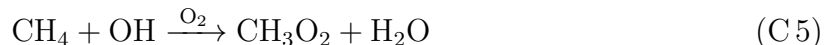
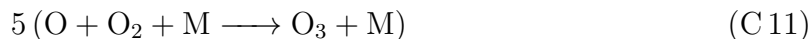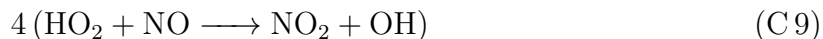$$[O_3] = \frac{j_{NO_2}[NO_2]}{k_{NO}[NO]} \tag{1}$$

where j_{NO_2} and k_{NO} are different reaction rate coefficients. [6] The coefficient j is dependent of the solar radiation and used for reaction by photolysis such as Reaction C2. Photolysis is a first order reaction. k is constant and is used for second order reactions which are the ones that is not dependent of pressure or solar radiation. Example of a second order reaction is Reaction C1. The notation with [ ] is used when discussing concentrations. From Equation 1 it can be seen that the concentration of ozone is dependent of the ratio between NO and NO_2.

2.1.3 Hydrocarbons

Hydrocarbons are a big part of the pollutants emitted by human activity. The hydrocarbons of interest is the compounds that are part of the group known as VOC. Since VOCs are a collection of a great deal of species the focus here will be on ethene C_2H_4, propene C_3H_6, Formaldehyde HCHO, acetaldehyde CH_3CHO, isoprene C_5H_8, Methanol CH_3OH, ethanol C_2H_5OH, peroxyacetyl nitrate PAN and methane CH_4. These are chosen as they are good representative for all of the VOCs in the urban environment. Of all the VOCs methane is the one that is emitted in largest concentrations and also have a significant longer lifetime than the other VOC due to stronger bonds. Even though VOCs mostly is emitted anthropogenically (human reasons) it is substantial to point out that isoprene is by far a biogenic (natural) emission. Isoprene is a result of photosynthesis. Beside the VOCs, carbon monoxide (CO) is also a big part of the emissions and hence of interest in the chemistry in urban environments. This as CO is toxic and as seen in Reaction C8 reacts easily with OH and creates HO_2.

Even though the cycle in Reaction C4 is the only significant source of ozone to the troposphere the VOCs can contribute. As can be seen in Figure 1 the process when RO_2 goes to RO and HO_2 goes to OH, NO comes in producing NO_2 which from above gives ozone. An example of this and when VOC is contributing to the produce of ozone is shown below in the Reactions C5 to C11 [6].

$$CH_4 + OH \xrightarrow{O_2} CH_3O_2 + H_2O \tag{C 5}$$

$$CH_3O_2 + NO \xrightarrow{O_2} HCHO + HO_2 + NO_2 \tag{C 6}$$

$$HCHO + h\nu \xrightarrow{2\,O_2} CO + 2\,HO_2 \tag{C 7}$$

$$CO + OH \xrightarrow{O_2} CO_2 + HO_2 \tag{C 8}$$

$$4\,(\text{HO}_2 + \text{NO} \longrightarrow \text{NO}_2 + \text{OH}) \tag{C 9}$$

$$5\,(\text{NO}_2 + h\nu \longrightarrow \text{NO} + \text{O}) \tag{C 10}$$

$$5\,(\text{O} + \text{O}_2 + \text{M} \longrightarrow \text{O}_3 + \text{M}) \tag{C 11}$$

What this show is theoretically how methane maximized can contribute to the production of ozone by these seven reactions. It can be seen how the reactions start with a OH reacting with a RH (as in Figure 1) and how the cycle then continues. The Reactions C5 to C8 have the primary effect to create HO_2 which will then give more OH and in that step create more NO_2 as in Reaction C9. This step is as mentioned contributing to the cycle in Figure 1. These seven reactions, Reactions C5 to C11, can be described in the net reaction shown i Reaction C12 [6].

$$\text{CH}_4 + 10\,\text{O}_2 \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\,\text{OH} + 5\,\text{O}_3 \tag{C 12}$$
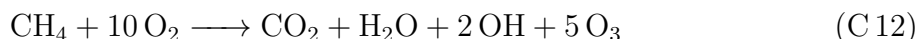
Hence the presence of methane can contribute to the quintuple effect of the production of ozone. This effect apply for all the VOCs in different scales. How the concentration of NO_x and VOC corresponds to each other to produce ozone is shown in Figure 2.
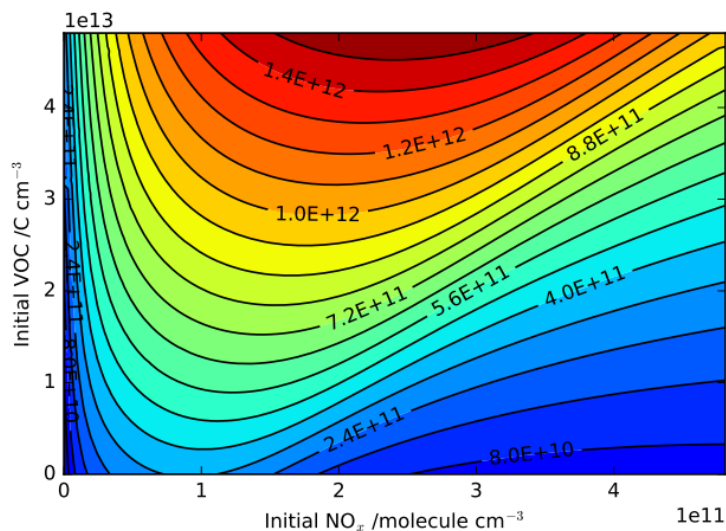

Figure 2: Ozone concentration dependents to concentrations of NO_x and VOCs. Here concentration is given in the unit molecules/cm^3. (Magnus Joelsson, personal communications, 2018)

What this figure shows is how VOC still is important for the production of ozone even though the source of ozone is the NO_2 in Reaction C4. In Figure 2 it can be seen that if only the VOC, along the y-axis, would increase substantially the increase of ozone concentration is small. If only the concentration of NO_x, along the x-axis, would increase the concentration of ozone would even decrease. This is due to that NO_x consist of both NO and NO_2 that will together find an equilibrium which will not change without an external boost such as VOC. So there have to be a collaboration between the NO_x and VOC for the maximum production of ozone. Reactions C5 to C11 is an example of such collaboration and boost which give the maximum ozone concentration seen as red in Figure 2.

2.2 Model

What controls the concentrations for chemical species in the atmosphere is emissions, chemistry, transport, and deposition [7]. To model a perfect simulation of all the chemical and physical processes of an environment is complicated and very time consuming. This as there are a lot of factors within the four types of processes that effects the air. Examples of such factors are winds, ocean currents, atmospheric circulation systems, convective motion, topography, temperature, biogenic and anthropogenic sources and so on. Also different latitudes, longitudes and altitudes plays a part. Since these simulations are so complex and especially so time consuming they are not used in this study. Also as the complex model simulations does not give information about the individual effects of each parameter as they all are modeled to cohere. During this study a box model is instead used. In a box model it is possible to study one parameter at a time and hence increase the understanding of each parameter. A box model is a great simplification from how the reality looks like in a sense of physical verity. This means that all the values of the concentrations produced in the result is not correct in reality. Hence, this study is not a quantitative analysis but a qualitative one. However, since the importance here is to study the relation between the species in an urban environment a box model is more than enough as it has great credibility there.

A one-box model is based on simplifications of the four types of processes mentioned above. The concept is shown in Figure 3 which describe the comprehensiveness of a species X.
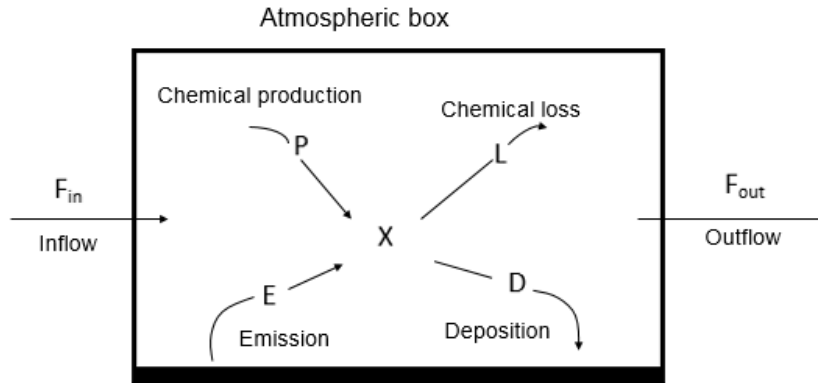

Figure 3: One-box model for an atmospheric species X. (Adopted from [7])

In the atmospheric box, in Figure 3, E is emission, P is chemical production, L is chemical loss, D is deposition, F_{in} is transport of the species X into the box and F_{out} is the transport out. In the one-box model E, P and F_{in} is sources of X and L, D and F_{out} is sinks. It is assumed that the box is well mixed so the computations for sources and sinks get simplified. In the box model there has to be a mass balance. The balance is the change of the comprehensiveness of the species X with time inside the box. Hence, the mass balance is the difference between sources and sinks which is described in Equation 2.

$$\frac{dm}{dt} = \Sigma\text{sources} - \Sigma\text{sinks} = E + P + F_{in} - L - D - F_{out} \qquad (2)$$

The step beyond a one-box model is a multi-box model. The multi-box model is an

assembly of N boxes that exchange mass with each other. This is done by the same mass balance, Equation 2, but the equations is coupled by the F_{in} and F_{out} terms.

In this study a subset from the chemical scheme called a Master Chemical Mechanism (MCM) is used, which is a near-explicit chemical mechanism. The used subset is comprised of 608 species and 1923 reactions describing the processes of gas phase chemicals. This involves in a tropospheric degradation of a series of VOCs. The model uses a Kinetic Pre-Processor (KPP) solver. This results in a collection of differential equations that are formulated from the chemical reactions. Then this is used in a chemical box model with initial values of factors such as solar radiation, humidity, temperature, emission factors, and background concentrations of gaseous air pollutants. This calculates and model the chemical processes in an urban environment. It is then possible to change all of these factors which also are the parameters that were studied. With all of this, the result is a model taking a wide range of ambient conditions and chemical processes in an urban environment and with NO_x and VOC simulates the development of ozone. [8–11]

3   Case studies

The case studies consist of the combining MCM and KPP model described in Section 2.2. Throughout the research there have been several runs where different parameters have been changed. Every run tests the consequences when only one parameter is changed. So for example, when different solar radiations were changed and tested all the other parameters were constant. This was to study all the parameters individually and see how the outcome could change depending on the changes of each parameter. The model then ran for a 30 min simulation, this as it is a relevant timescale when studying urban environments. Furthermore, it is also as most of the species are short lived. This resulted in plots for scenarios of 30 minutes process.

3.1   Bright case

The initial values for all the species concentrations was presented by Bright et al. [3]. Their study was based on a measurement study in London [12] making all initial values to be from measurements in urban environment in London. These values are presented as mixing ratios in Table 1 and are the starting concentration for the runs of the model. It was also performed tests for an extra high NO_x case which describe an scenario of large pollution from combustion emission from carriage. In this high NO_x case the initial values are $[NO] = 1000$ ppb and $[NO_2] = 120$ ppb.

The regular base case is presented in Figure 4. Here it shows how the concentrations develop for a scenario of 30 minutes. In the results it is the values after these 30 minutes that is plotted against the parameter that was tested.

Table 1: Initial mixing ratios used in the model simulations

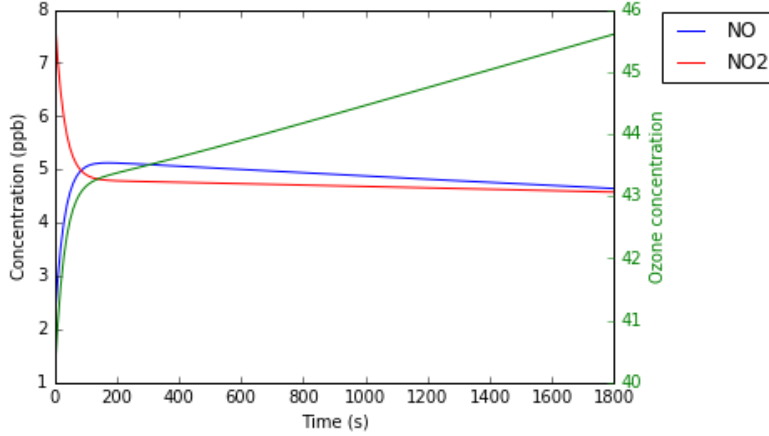| Species	Chemical formula	Mixing ratio (ppb)
Ozone	O_3	40
Nitric oxide	NO	2
Nitrogen dioxide	NO_2	8
Carbon monoxide	CO	200
Nitric acid	HNO_3	2
Absolute water vapor	H_2O	2%
VOCs		
Methane	CH_4	1800
Ethene	C_2H_4	0.91
Propene	C_3H_6	0.29
Formaldehyde	HCHO	3.14
Acetaldehyde	CH_3CHO	2.98
Isoprene	C_5H_8	0.28
Methanol	CH_3OH	7.38
Ethanol	C_2H_5OH	2.37
Peroxyacetyl nitrate	PAN	0.46

Figure 4: The base case with the initial values from Table 1 showing concentrations of ozone, NO and NO_2 versus time.

3.2 Temperature

In most reactions temperature helps to accelerate the speed. How much the temperature helps is different from reaction to reaction. Therefore the temperature has been studied from extreme minimum (-40 °C) to extreme maximum (60 °C) for surface temperatures. When temperature was not the parameter in focus it was set to 10 °C. This because it is a good mean value for the temperature in London.

3.3 Humidity

As water vapor is important for the production of OH radicals it is hence a worthy parameter to study, due to that OH is one of the keystones in the tropospheric chemistry as seen in Figure 1. How the humidity influences the process of ozone and NO_x was tested by setting it to absolute humidity, in the model described by Equation 3, and then changing the temperature as in Section 3.1.1. Then setting the humidity to relative humidity, in the model described by Equation 4, and doing the same process with the temperature.

$$\text{Absolute humidity} = 0.02 * \text{M} \tag{3}$$

$$\text{M} = \frac{pN_a}{10^6 R_g T}$$

where 0.02 comes from the 2% water vapor in Table 1, p is the average surface pressure of 1000 hPa, $N_a = 6.022 \cdot 10^{23}$ mol^{-1} is Avogadro's constant, $R_g = 8.3145$ kg m^2 s^{-2} K^{-1} mol^{-1} is the universal gas constant [5] and T is the temperature. M is a variant of the ideal gas law:

$$pV = nR_g T = Nk_b T$$

where V is volume, n is the amount of substance of gas, $N = nN_a$ is the total number of molecules and $k_b = R_g/N_a$ is Boltzmann constant. [5]

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$$\frac{10(\text{RH} \cdot 100)}{1.38 \cdot 10^{-16} \cdot T} \cdot 6.1078 \cdot \exp((-(597.3 - 0.57(T - 273.15)) \cdot \frac{18}{1.986} \cdot (T^{-1} - \frac{1}{273.15})) \quad (4)$$

where RH was set to 0.70 (70%) as a mean value suited for London. When humidity was not the parameter that was studied it was set to relative humidity.

3.4 Solar radiation

As mentioned in Section 2.1.1 the solar radiation is noted as the energy of a photon, $E = h\nu$. Since h is a constant the energy is dependent on the frequency of the photon ν. As these photons is emitted from the sun an energy flux is created. This flux is described by the Stefan-Boltzmanns law seen in Equation 5.

$$J = \sigma T^4 \quad (5)$$

where J is the energy, $\sigma = 5.67 \cdot 10^{-8}$ W m^{-2} K^{-4} is the Stefan-Boltzmann constant and T is the temperature of the body that is emitting the energy flux. As seen in Equation 5 the radiation is strongly dependent on the temperature and as the sun's temperature is about 5900 K its radiation is also very high. However, since the Earth is at a great distance from the sun the average solar radiation to the surface is 1367 W m^{-2}. [13]

As can be seen in Figure 1, the cycle in Reaction C4 and in the Reactions C5 to C11 the solar radiation plays a very important role for the tropospheric chemistry. In Section 2.1.1 it was mentioned that with no solar radiation the ozone concentration would decrease while with sunlight it would be a source. So this correlation of ozone and NO$_x$ concentration due to solar radiation was studied with model runs with different percentage of a regular day of actinic flux (sunlight). Also the breaking point of how much of the actinic flux is needed for the process to turn into to a source was studied.

The actinic flux has the unit photons cm^{-2} s^{-1} nm^{-1} sr^{-1} and how 100% actinic flux vary with the wavelength of the photon is shown in Figure 5. In comparison to real values, the values in Figure 5 is well-established [6]. In the result solar radiation is given in percentage of actinic flux. For the other runs when solar radiation was set constant it was at 100% actinic flux. This as it is a suited value that corresponds to a midday during summer in southern Sweden which has about the same climate as London.

3.5 Background concentrations and emission rates

In the tropospheric chemistry all species depend somehow on each other, as seen in Figure 1. Furthermore, as seen in Figure 2 the ozone highly depends on both NO$_x$ and VOC. Because of this, runs with different ratios of NO$_x$ and VOCs was performed. Here mostly to see how their ratios effect the process of ozone concentration, but also to see the effect on the process of NO$_x$. Since the start up case shown i Table 1 has 2 ppb of NO and 8 ppb of NO$_2$ the ratios was made so that the total start up concentration of NO$_x$ was 10 ppb. Studies with the relation 10/10, 8/10, 6/10, 5/10, 4/10, 2/10 and 0/10 between NO and NO$_2$ with the ratio NO$_2$/NO$_x$ were performed. Runs with a case of especially high concentration of NO$_x$ were also preformed, here with the values 1000 ppb of NO and 120 ppb NO$_2$. To keep the same ratio the runs was with the NO$_2$/NO$_x$ relation of 1120/1120,
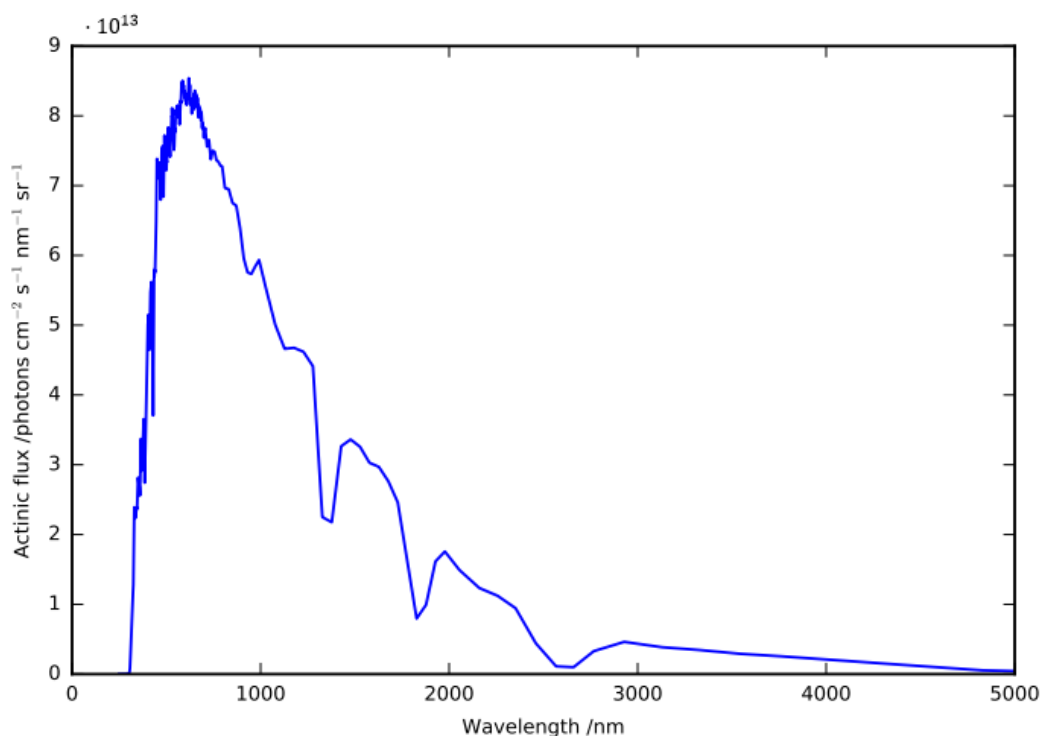
Figure 5: 100% actinic flux as a function of the wavelength of the photon. This corresponds to the sunlight on midday during summer. (Adopted from Magnus Joelsson, personal communications, 2018)

896/1120, 672/1120, 560/1120, 448/1120, 224/1120, 0/1120. This extra study was preformed to see how high concentration of NO_x influence the tropospheric chemistry. This case corresponds to a scenario of large pollution from combustion emission from carriage.

In the results the NO_x is presented as both the total concentration of NO_x and in the relation NO_2/NO_x. The reason is that because the NO and NO_2 goes from one to another they can be seen as one species which is NO_x. This also makes the relation relevant since it shows the interplay between NO and NO_2 in the total amount of NO_x. Why it is NO_2/NO_x instead of NO/NO_x is because it is the standard way to present them in other work. Also because when real measurements are preformed they measures the concentration of NO_2 and NO_x.

The study for the effect of different VOC ratio was a little different. As a VOC enters the cycle in Figure 1 it will go through chemical processes and loose, among others, a carbon atom. Ones it does it will be a new kind of hydrocarbon, CO or CO_2. If it still is a hydrocarbon it can enter the cycle again. Thus it is the amount of carbon in the VOC that determine how many times it can go through the cycle in Figure 1. Therefore will the amount of carbon be used to quantify the VOC. Since the VOCs contains of several species the relation was made so that every initial value in Table 1 of the VOCs and CO concentrations (all the carbon compounds in Table 1) was multiplied with 0, 0.25, 0.5, 0.75, 1, 1.25, 1.5 in different runs. However, since the initial value of methane (and CO) was vastly larger than the other VOCs a second test with all the non-methane volatile organic compounds (NMVOC) was preformed, here also excluding CO. The NMVOCs was multiplied with the same factors as for all the carbon compounds.

4 Results and discussion

4.1 Temperature and humidity

How ozone and NO_x change with temperature is shown in Figures 6 and 7. These figures shows the concentration after 30 minute simulation plotted against the different temperatures. Also the relation in NO_x with NO_2/NO_x is shown.
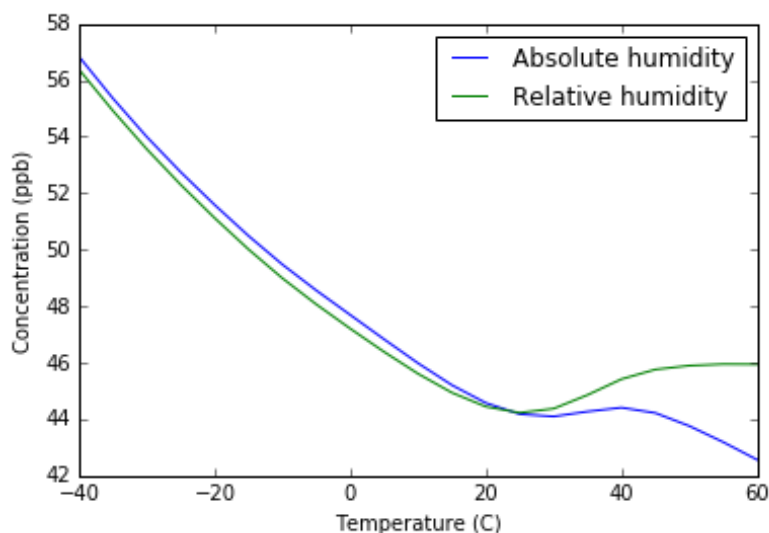

Figure 6: Ozone concentration after 30 min versus different temperature

As the concentration of ozone has the initial value of 40 ppb it can be seen in Figure 6 that the end value of ozone concentration at 30 min has always increased. However, the increase is substantial larger for low temperatures. For both absolute and relative humidity the concentration of ozone decreases with the increase of temperature until the temperature is around 20 - 25 °C where the ozone concentration starts to increase. It is also here a clear difference for relative and absolute humidity appear. For absolute humidity the ozone concentration has a small increase until 40 °C and then it decreases again. Though, for the relative humidity there is a larger increase until around 40 - 45 °C where the concentration levels out to appear constant.

To explain why the ozone concentration changes like this several factors have to be looked at. First off, the NO_x in the system is either NO_2 on the left side in Reaction C4 or as NO on the right hand side. In Figure 7 it can be seen that at low temperatures there are more NO than NO_2 in the system and hence there is an overlay at the right hand side. This give that the cycle produce more ozone and NO than Reaction C1 reduce it, which can be seen in Figures 6 and 7. As the temperature increases the rate of the reaction C1 increases with it and both the concentration of ozone and NO decreases. Then to explain why the ozone concentration increases again at 20 - 25 °C the VOCs have to be considered. As can be seen in Figure 1 and the Reactions C5 to C11, VOCs can produce ozone without disturbing the balance of NO_x. This is also discussed in Section 4.3.2 below. The rate at which OH is produced increases with the temperature and as seen in Figure 1 more OH give more VOCs. In Figure 12 in Section 4.3.2 below there is showed that more VOCs result in more ozone. This can explain why there is a sudden increase of ozone concentration at 20 - 25 °C, the increased temperature produce more VOC.
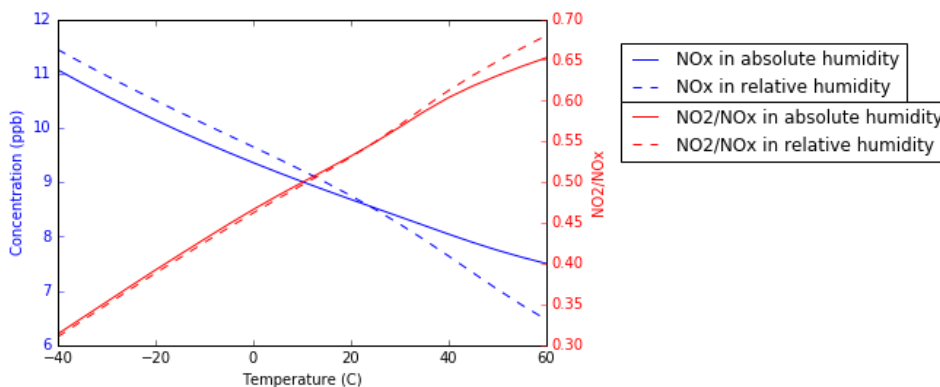
14

Figure 7: NO_x concentration and NO_2 / NO_x after 30 min versus different temperature

The difference in absolute and relative humidity is mostly the amount of water vapor. In absolute humidity the concentration of water can be seen as constant. However, in relative humidity the amount of water vapor is highly dependent on temperature, where it increases with it. This result in that at low temperatures there is more water vapor in absolute humidity, but as the temperature increases this change and the relative humidity then contains of more. Figure 6 show how the different humidities result in different increases of ozone concentration. This is due to when there is more water molecules the production of OH radicals increase. As already discussed the OH helps to produce more peroxy radicals which produce more ozone. This is why the increase is higher for the relative humidity, the higher concentrations of water that give further OH. This can also explain why the concentration of ozone starts to decrease again in the absolute humidity at 40 - 45 °C. There is less water and therefore less OH which result in that the produce of VOC does not get so high and cannot help to produce more ozone. Hence the Reaction C1 has its overtake again and consumes the ozone and NO. This can also be seen in Figure 7 where there is a small change in the NO_2/NO_x relation in favor of NO at around 20 - 25 ° and then the concentration of NO decreases again. The increase of OH for higher temperatures and especially for the relative humidity can also be seen in Figure 7, as OH is a sink for NO_x when OH reacts with NO_2 and produce HNO_3. This is seen as the concentration of NO_x has a more rapid decrease as the temperature increases in relative humidity compared to in absolute humidity as seen in Figure 7.

4.2 Solar radiation

How ozone and NO_x change with solar radiation is shown in Figures 8 and 9. These figures show the concentration after 30 minute simulation plotted against the percentage of actinic flux. Also the relation in NO_x with NO_2/NO_x is shown.

As the concentration of ozone has the initial value of 40 ppb it can be seen that with no photons acting on the chemistry the ozone concentration has decreased. When the actinic flux proceeds beyond 18% - 20% the ozone concentration becomes unchanged and then starts to increase. This corresponds to what was mentioned in Section 2.1.1 that with no solar radiation the photolysis in Reaction C2 cannot occur and hence no ozone is produced since there is no production of NO and O. It is worth to point out that this breaking point at 18% - 20% has no significant quantitative value. However, it shows that sunlight does not have to be so bright to turn into a source, already the light at
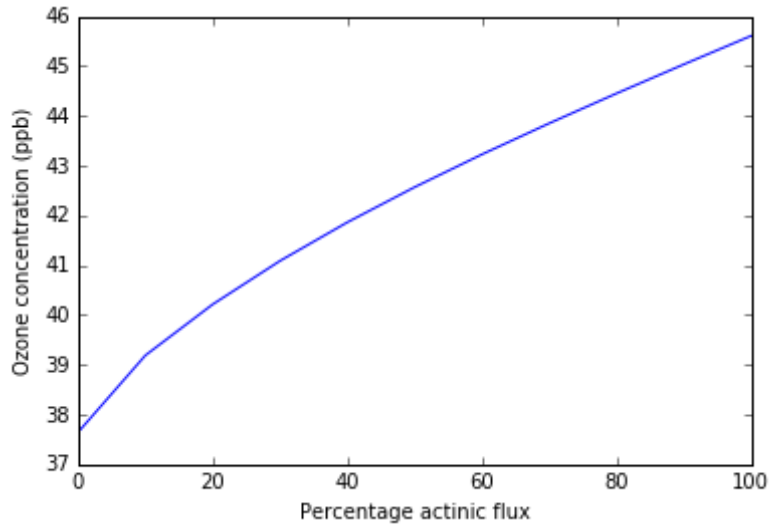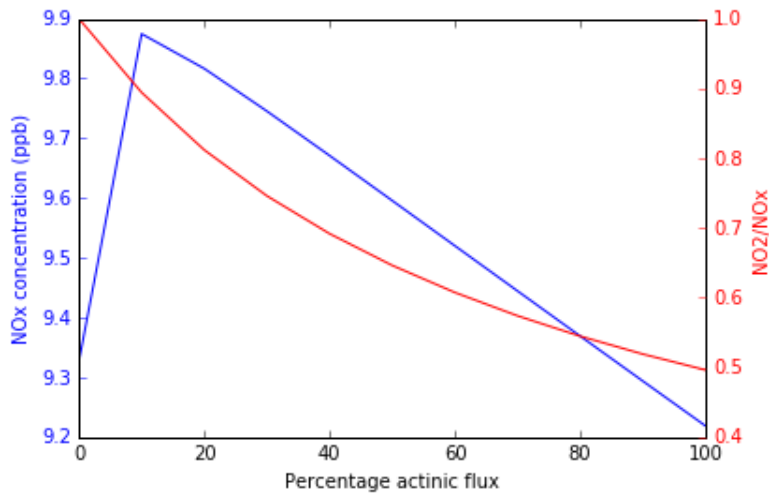
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Figure 8: Ozone concentration versus actinic flux

Figure 9: NO_x concentration and NO_2 / NO_x versus actinic flux

sunrise and sunset will start the process.

For the concentration of NO_x it turns out that the sunlight always is a sink as its initially concentration is 10 ppb. However, as the decrease is so small it might be seen as negligible. Here it is more interesting to see that it is just below the breaking point at 18% - 20% that the $[NO_x]$ is mostly conserved and at low and high actinic flux it can act as a sink. This is as NO_2 and ozone can react and produce NO_3 and O_2, but since NO_3 easily photolysis this is only essential at no or low solar radiation. The NO_3 then reacts with NO_2 and produce N_2O_5. This is hence a sink for NO_x and can explain the lower concentration of NO_x at no and low actinic flux.

Even though the $[NO_x]$ is almost conserved the amount of NO and NO_2 change drastically. With no sunlight the concentration of NO is zero and then the relation change virtually exponentially to become $[NO] = [NO_2]$ at 100% actinic flux. The reason for the low concentration of NO at no sunlight can be due to that there is still ozone all around

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so Reaction C1 can still happen and react all NO to NO_2. Though, with no sunlight the photolysis of NO_2 in Reaction C2 will not happen so all the NO_x stays as NO_2. This can also explain the loss of ozone seen in Figure 8.

4.3 Background concentrations and emission rates

4.3.1 NO_2/NO_x ratio

How ozone and NO_x change with the NO_2/NO_x ratio is shown in Figures 10 and 11. Both with the regular case in Table 1 and with a high NO_x case with $[NO] = 1000$ ppb and $[NO_2] = 120$ ppb. The figures show the concentration after 30 minute simulation plotted against the ratio NO_2/NO_x. Also the relation in NO_x with NO_2/NO_x is shown.
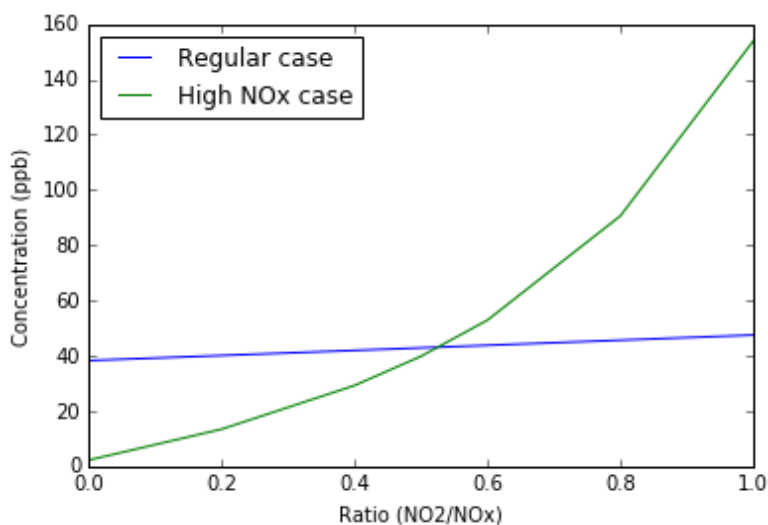

Figure 10: Ozone concentration versus NO_x (NO_2 / NO_x) ratio for regular and high NO_x case

It can be seen in Figure 10 that for the regular case the ozone increases linearly as the ratio increases (i.e. $[NO_2]$ increases). When the relation of NO_2/NO_x is 0/10 the concentration of ozone has decreased. This can again be explained with Reaction C1 and Equation 1. Though as the ratio change and the $[NO_2]$ increase the cycle in Reaction C4 is frequently producing ozone and hence the linear increase of ozone. In the high NO_x case there is also an increase of ozone as the ratio increases. However, this is a way more drastic increase and can be seen as virtually exponential. When the ratio is 0/1120 almost all ozone is consumed and the ozone concentration is near zero. Here again explained with Reaction 1 and Equation 1. Furthermore, when the ratio increase so does the concentration of NO_2 and with that high concentrations there is no stop in the cycle in Reaction C4 so the ozone increase into extreme high values.

It can be seen in Figure 11 that the concentration of NO_x is in both the regular and high NO_x case preserved. So it does not matter which ratio or which initial value it is, the $[NO_x]$ stay approximately the same for respective case. However, as in Section 4.2 the end value of the ratio NO_2/NO_x changed with the parameter. This is though more drastic for the high NO_x case. In the regular case the end values of NO_2/NO_x only changes by 0.05 with the ratio, but for the high NO_x case the relation changes from around 0.05 to
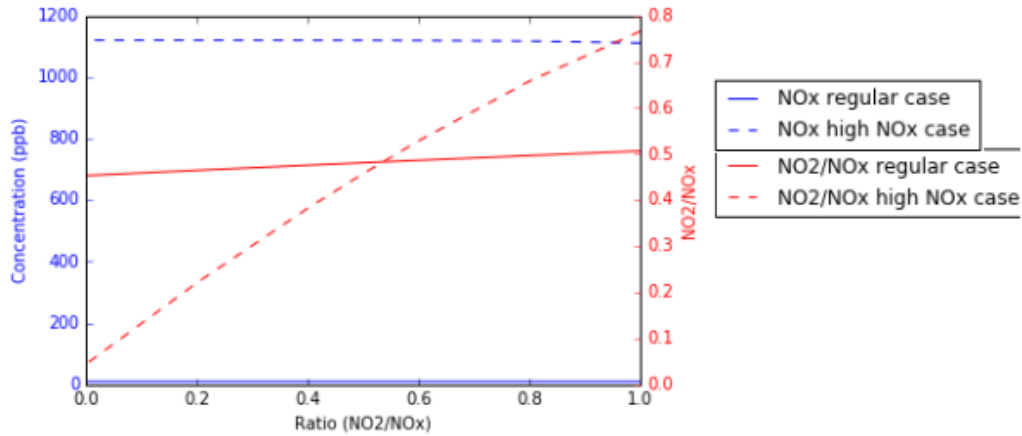
Figure 11: NO_x concentration and 30 min values of NO_2 / NO_x versus initial NO_x (NO_2 / NO_x) ratio for regular and high NO_x case

0.75 with the ratio. This can be explain that with so high initial values of $[NO_x]$ the $[NO]$ and $[NO_2]$ does not have time to be consumed and convect to some sort of equilibrium at 0.5 for the end value of NO_2/NO_x, as seen for the regular case. This is why the end values for relation NO_2/NO_x in the high NO_x case follows more strictly along the initial values for ratio on the x-axis in Figure 11.

4.3.2 VOC ratio

How ozone and NO_x change with the change of VOC and CO is shown in Figures 12, 13, 14, 15, 16 and 17. Here with both the regular case in Table 1 and the high NO_x case as in Section 4.3.1. The figures again show the concentration after 30 minute plotted against the amount of carbon from the VOC and CO the runs started with. The use of only carbons is to quantify the number of VOC and CO. The relation in NO_x with NO_2/NO_x is also shown.
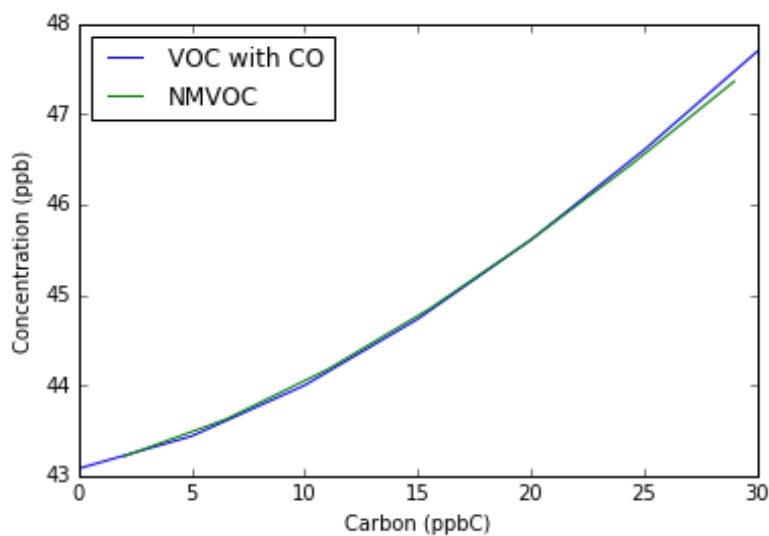

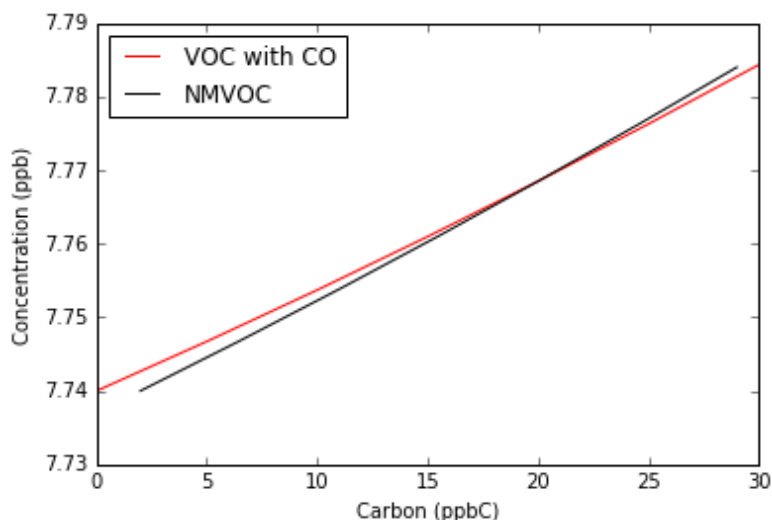Figure 12: Ozone concentration versus VOC with CO and NMVOC ratio for regular case

Figure 13: Ozone concentration versus VOC with CO and NMVOC ratio for high NO_x case
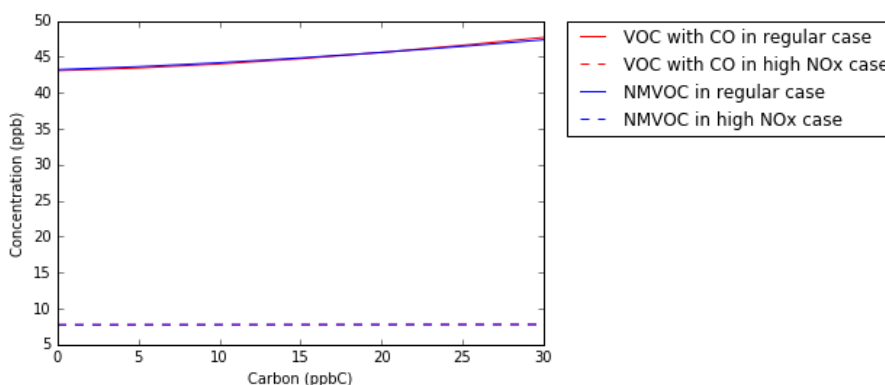

Figure 14: Ozone concentration versus VOC with CO and NMVOC ratio for regular and high NO_x case

In Figures 12 and 13 it can be seen how ozone concentration increases with the carbons and that both runs with all the carbon compounds and only the NMVOC give almost the same result. How little the differences are is easier to see in the high NO_x case in Figure 13 as the increase of ozone there is so small. This give that even though there is a lot more of methane and CO than the NMVOCs there is no difference in the production of ozone. For the regular case there is a virtually exponential increase of ozone concentration with the increase of carbon. In the high NO_x case the increase of ozone is more linear with the increase of carbon. So the increase of carbon give, as expected from Section 2.1.3, more increase in ozone concentration. In Figure 14 the huge difference in ozone concentration can be seen for the two cases. This is due to the high concentration of NO (1000 ppb) in the high NO_x case.

A theory why the huge increase of methane, when all the VOC with CO is increased is not making the production of ozone yield to so high concentrations as it could from the Reactions C5 to C11 is that there is too much methane. An initial value of 1800 ppb is already a high concentration and when it is increased to 2700 ppb there is an abundance

that cannot react in the chains. Another, more significant, reason is that CH_4 is more stable and less reactive with OH than the other VOC. This makes the NMVOC to be more substantial in the reactions.
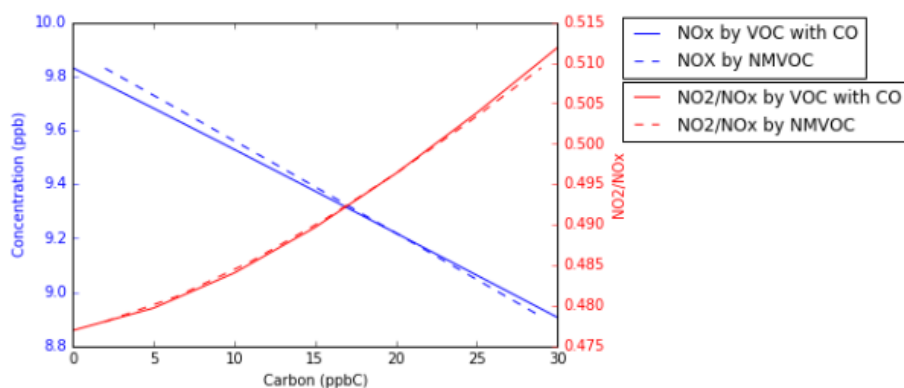

Figure 15: NO_x concentration and NO_2 / NO_x versus VOC with CO and NMVOC in regular case
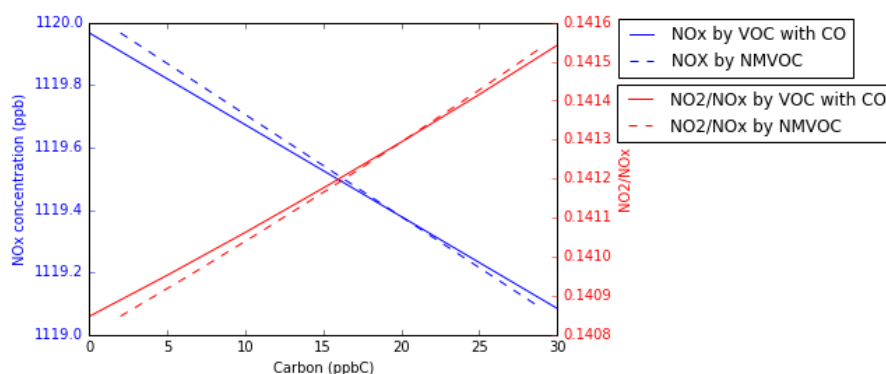

Figure 16: NO_x concentration and NO_2 / NO_x versus VOC with CO and NMVOC ratio for high NO_x case

For the regular case in Figure 15 it can be seen that NO_x behave the same for both the carbon ratios. The $[NO_x]$ decreases from and to the same values, just above 9.8 ppb down to around 8.9 ppb. Also the relation NO_2/NO_x is virtually the same for the ratios. What can be seen here is that when the concentrations of hydrocarbons and CO increases so does the concentration of NO_2 (in relation to NO). This can be connected to the tropospheric chemistry in Figure 1. As the amount of the different hydrocarbons increase the cycle gets a refill of components to go around. As the initial amount of NO_x does not change in the different runs the balance of the reactions in the cycle is only dependent on the hydrocarbons. Then as the cycle continues with more hydrocarbons a result is that NO becomes NO_2 which is what can be seen in the results. Also as the $[NO_x]$ starts to contain more and more NO_2 additional ozone can be produce. This is also an explanation for the virtually exponential increase of ozone seen above in Figure 12.
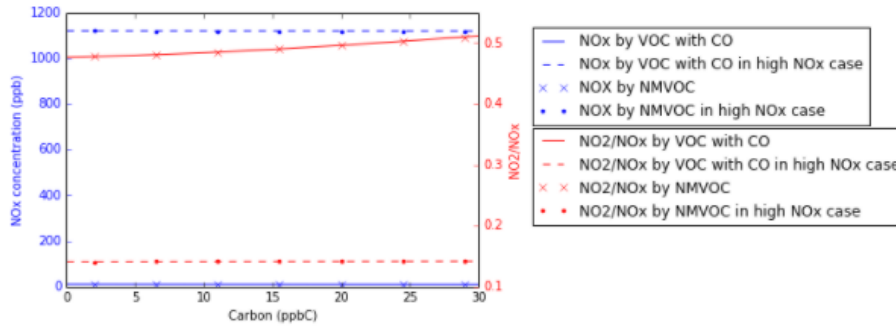
Figure 17: NO_x concentration and NO_2 / NO_x versus VOC with CO and NMVOC ratio for regular and high NO_x case

In the high NO_x case in Figure 16 it can be seen that the $[NO_x]$ decreases as the regular case for both the carbon ratios. However, the relation NO_2/NO_x is increasing in favor of NO_2 but since the concentration of NO is so high from the start the chemistry does not have time to consume it to equilibrium so there is no significant difference. In Figure 17 the huge difference in NO_x can be seen for the two cases.

5 Conclusion

It was seen that all the different parameters had each an effect on how the concentration of ozone and NO_x change with time in an urban environment. When the temperature increased, so did the rate of when NO react with ozone and when OH radicals is produce. This led to a decrease of NO and ozone with temperature, but it also led to an increase of VOC which then increased the ozone concentration again. The humidity played a role in how large this increase was as in relative humidity there is more water and hence larger capacity to produce OH. The solar radiation acted just as expected in that with the ozone concentration increases with the sunlight. Furthermore, it was found that with no sunlight the concentration of ozone decreased. It was also found that with no sunlight all the NO_x consisted of only NO_2 and when the sunlight increased the photolysis on NO_2 started. With 100% actinic flux the NO_x consisted of equal amount of NO and NO_2.

When the initial values of the ratio NO_2/NO_x was changed it resulted in that with more NO the ozone concentration decreased but as the NO_x consisted of more and more NO_2 the ozone increased. In the regular case this increase was linear and for the high NO_x case it was more exponential. The end values of the concentration of NO_x was almost unchanged with the initial values from the ratio. However, the end values of the relation NO_2/NO_x changed with the initial values of the ratio. Though for the regular case this change was minimal. When the amount of VOC and CO was changed the ozone concentration increased with the carbons, both for the regular and high NO_x cases. It was found that the change of ozone was the same for both when the VOC with CO and when only the NMVOC was changed. So the small change in the NMVOC was more essential for the produce of ozone than the large change of methane and CO. The changes of NO_x was the same for both of the cases of carbons.

If a study would be done with a complex time consuming model such as mentioned in Section 2.2 all of these effects would occur at the same time. So all the different parameters would affect the chemistry as seen in the results though in different amounts and at the same time effect each other. This would also be seen if real measurements would be taken.

6   Outlook

Further research could be to do all of the runs again but for both shorter and longer simulation time. As all the species have different lifetimes and all reaction have different rate of speed this could also expand the knowledge of how the parameters studied here effect the pollutants in urban environments.

Besides changing the simulation time one could also run new cases that combines the different parameters to see if and where any synergy effect could occur. Secondly, one could try to model specific places, times or emission scenarios and investigate which combination of parameters that give the most pollutants. This could be interesting for further understanding of the parameters effect and interaction. Furthermore, to specify the models and also to see how the model simulate a real event. Both for more understanding of the model, but also to see which factors that was responsible for a specific event. This could lead to better insight in that event and could also increase the capacity of other models to predict such events.

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