ANTHROPOGENIC AND BIOGENIC INFLUENCES ON THE OXIDIZING CAPACITY OF THE ATMOSPHERE

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Project summary

The oxidizing capacity of the atmosphere consists in its own ability to cleanse itself from a number of pollutants. It determines the fate and lifetime of a large number of chemical compounds, including greenhouse gases. For example, the abundance of methane (one of the major greenhouse gases) is largely controlled by its chemical reaction with the hydroxyl radical (OH). It follows that any perturbation affecting the concentration of this OH radical will also influence the abundance of methane as well as of many other gases. In fact, many other chemical compounds present in the atmosphere influence the oxidizing capacity of the atmosphere. These include hydrocarbons, carbon monoxide and the nitrogen oxides. All these compounds have both biogenic and anthropogenic sources. In other terms, human activities have a very large impact on the concentration of these gases. Industrial activities, the burning of fossil fuels, deforestation, the burning of savannas and forests and the use of fertilizers in agriculture are among the most prominent processes responsible for the emissions of these pollutants, causing their atmospheric concentration to increase significantly. It is therefore of great importance to understand the budget (sources and sinks) of these chemical species, and also to quantify how human activities might have influenced them.

The biosphere (vegetation, soils, and oceans) has also a large influence on the chemical composition of the troposphere. For example, the emissions of very reactive non-methane hydrocarbons (NMHCs) by vegetation are believed to have a significant impact on the budget of species like carbon monoxide, ozone, the hydroxyl radical, and aerosols. The emissions as well as the complex oxidation mechanisms of these hydrocarbons are still not well understood and quantified, however. Additional investigations aiming at the elucidation of these processes are therefore required in order to better characterize the natural environment in which the human perturbation takes places.

In this project, the impact of anthropogenic and biogenic emissions on the formation of tropospheric ozone and other oxidants has been investigated through a combination of modelling activities and laboratory studies. Atmospheric models are the best tools available in order to estimate the impact of anthropogenic emissions on harmful pollutants (like ozone) and radiatively important compounds (like methane, ozone, and aerosols). These models are a simplified representation of the real atmosphere. They take into account most of the physical and chemical processes influencing the tropospheric composition at the global scale. The confrontation of the model results with observations and the continuous improvement of the model parameterizations are important aspects of this project. Another very important aspect of this project is the development and application of new measurement techniques appropriate to the elucidation of key chemical reactions of biogenic non-methane hydrocarbons. The studies conducted using these techniques are crucial in order to narrow the uncertainties related to the chemistry of biogenic hydrocarbons.

Objectives

The major objectives of our project are the following:

- To narrow the uncertainties in the processes influencing the global composition of the troposphere; more specifically, to quantify the impact of biogenic volatile organic compounds; even more specifically, determine the products and yields of the reaction of important biogenic hydrocarbons (the monoterpenes α- and β-pinene) with the hydroxyl radical (OH)

- to quantify the influence of human activities on the composition of the global troposphere (in particular, oxidants) and on its oxidizing capacity

Results

Our results are in line with the objectives stated above:

A. Narrowing the uncertainties

We contributed to the elucidation of the chemical degradation of two important biogenic non-methane hydrocarbons (α-pinene and β-pinene) in their reactions with hydroxyl radicals. Several reaction products not known before have been identified, and reaction schemes explaining their formation have been proposed.

The following results were obtained:

1. In the case of α-pinene, carbon dioxide, carbon monoxide, and acetone were identified and quantified via on line mass spectrometric analysis. The product yields were found to be strongly pressure dependent, indicating that the fate of the initially formed α-pinene-OH adduct is determined by its stabilisation rate.
2. The more important products are the semi-volatile compounds, for which new analytical detection methods have been developed. These products were first collected on a liquid nitrogen trap and subsequently identified by mass spectrometry. The analysis showed that campholenealdehyde and pinonaldehyde were formed as oxidation products for the α-pinene reaction, with pinonaldehyde being the main product. In the case of the β-pinene reaction, the measurements showed nopinone as the main oxidation product.
3. A new sampling method has been applied for the detection of light carbonyl compounds. In this way, formaldehyde, acetaldehyde and acetone could be determined for the α-pinene system. For the β-pinene system, the following products have been detected: nopinone, acetone, acetaldehyde, formaldehyde and for the first time trans-3-hydroxynopinone, perillaldehyde, perilla alcohol and myrtanal. The latter four compounds are possibly good sensors for unravelling the degradation mechanisms of β-pinene.
4. Mechanisms have been proposed explaining the formation of these products. We concluded that the current Master Chemical Mechanism (MCM) describing the degradation of terpenes is unable to explain the observed product yields and will have to be adjusted accordingly.

In addition, and in collaboration with international research teams, we completed the development and validation of two comprehensive chemical-transport models of the global troposphere, the IMAGES and MOZART models. Both models are valuable tools, which have been used by several international teams in order to quantify the processes controlling the composition of the troposphere, and in particular ozone and its precursors. For example, these models were used to determine the influence of various emission processes (biomass burning, lightning, etc.) on the distribution of chemical compounds. The budget of ozone and the respective contributions of various chemical processes to its formation and loss have been quantified.

New techniques have been proposed and applied in order to understand how the observations of chemical compounds can be used in order to provide useful constraints on the emissions of ozone precursors. In future studies, these developments will be the basis for the exploitation of satellite measurements of tropospheric compounds.

B. Quantify the influence of human activities

Both the IMAGES and MOZART models have been used in order to provide quantitative assessments of the anthropogenic impact on the tropospheric composition. These results were obtained in part in the framework of international assessments (IPCC).

- The impact of the subsonic aircraft emissions on tropospheric ozone and on the oxidizing capacity of the atmosphere has been evaluated. These emissions are found to enhance ozone concentrations by about 6% during the summer in our latitudes. The impact of aviation is expected to increase in the future according to the models.
- The future impact of industrialisation and of increased energy demand and population has been estimated, based on scenarios for the anthropogenic emissions of ozone precursors in the 21st century. The possible impact of climatic changes on tropospheric chemistry has also been estimated. The calculated increases in surface level ozone concentrations are found to be very large in the heavily populated areas in the Tropics. These ozone levels will represent a major threat to public health and agriculture in these areas. Important differences between the predictions by different models have been noted, however.

Valorisation

- Our results have been made available by communications in international conferences and publications in international journals, as well as e.g. via an EUROTRAC programme website.
- The laboratory results of our project has been incorporated in the European Environmental Research Programme EUROTRAC 2, within the project "Chemical Mechanism Development" (CMD).
- The model results on the future impact of aviation and industrialisation on the tropospheric composition are contribution to two assessment reports of the Intergovernmental Panel for Climate Change (IPCC).

Recommendations

- Given the widely accepted importance of tropospheric chemistry in outstanding issues such as climate change and air quality, and because of the large remaining uncertainties in the processes involved, we strongly recommend that the Belgian and European research efforts be sustained and possibly enhanced in this area.

- More specifically, noting the importance of the biosphere in the climate system as well as the very large remaining uncertainties in the quantification of biospheric emissions and impacts, we recommend that research efforts be sustained in this area.

- Because the emissions of non-greenhouse gases like carbon monoxide, nitrogen oxides, and non-methane hydrocarbons are known to enhance the abundance of ozone (a greenhouse gas) in the troposphere, we believe that these emissions should be considered in future efforts to mitigate climate change.

- Noting that tropospheric ozone levels are expected to increase to very high values in many heavily populated areas of the world, thereby representing a considerable threat to human health and agricultural yields in these areas, we recommend that strategies be elaborated in order to reduce the emissions of ozone precursors (carbon monoxide, nitrogen oxides and hydrocarbons), not only in our countries, but also in the rest of the world.