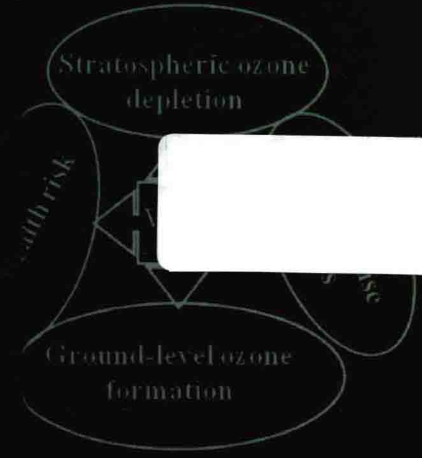
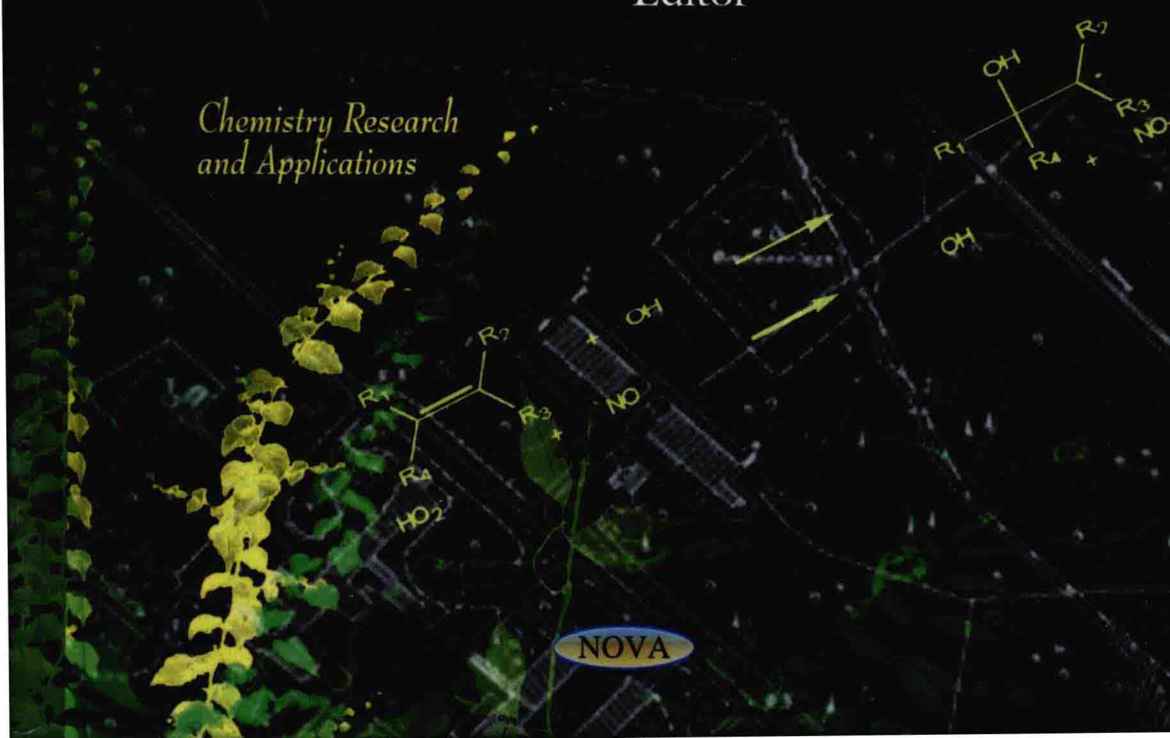


Volatile Organic Compounds

Emission, Pollution and Control

Khaled Chetehouna
Editor

Chemistry Research and Applications



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CHEMISTRY RESEARCH AND APPLICATIONS

VOLATILE ORGANIC COMPOUNDS

EMISSION, POLLUTION AND CONTROL

KHALED CHETEHOUNA
EDITOR

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PREFACE

Volatile Organic Compounds (VOCs) have anthropogenic and biogenic origins. At earth scale, the natural sources represent a great part of the total VOCs present in the atmosphere but in industrialized regions, anthropogenic ones become majority due to the various human activities related mainly to chemical industries (liquid fuels, solvents, thinners, detergents, degreasers, cleaners and lubricants). Almost all VOCs have effects on human health and many of them are even carcinogenic. It is also known that the VOCs can affect the central nervous system and may have mutagenic effects. Apart from human health, they also play an important role towards the environment, especially in the atmospheric pollution processes. Indeed, VOCs emissions lead to the promotion of photochemical reactions in the atmosphere (ozone formation, depletion of the stratospheric ozone layer and formation of photochemical smog). The present book gathers and presents some current research from across the world conducted by scientific experts in their fields. In seven valuable contributions, it deals with the emission and the environmental impact as well as the control of the Volatile Organic Compounds.

Chapter 1 – The turbulent dispersion process responsible of the VOCs transport within and above the canopy is still under study. This issue is of great interest since VOCs contribute to the global chemical reactions encountered into the troposphere. At the forest scale, VOCs are expected to travel within and above the forest, interacting with each other or with other chemical compounds. Some quantitative information can be given about the VOCs transport mechanisms in forest through the physical modeling in wind tunnel. Indeed the forest can be replicated at a reduced scale with an aerodynamical "drag-porosity concept" and the VOCs emissions can be modeled through the emission of a passive tracer through an area source. This approach will be illustrated through the Emission and Chemical transformation of Organic compounds (ECHO) project.

The concept of this project was to combine field experiments, laboratory experiments investigating emission and uptake of trace compounds by the plants, and modelling experiments simulating the chemistry of biogenic trace gases and the dynamics of a forest stand under well-defined conditions. The chosen site was the forest area surrounding the Forschungszentrum Juelich (Juelich Research Centre, Germany). In order to simulate the dynamical properties, the forest area was modelled to a scale of 1:300 and studied in the large boundary layer wind tunnel at the Meteorological Institute of Hamburg University. The model of the forest must reproduce the resistance to the wind generated by this porous environment. Rings of metallic mesh were used to represent the trees following preliminary tests to find an arrangement of these rings that provided the appropriate aerodynamic characteristics of a forest. The turbulence properties of the flow were measured in the wind tunnel within and above the canopy. Subsequently, they were compared with field data obtained at the Juelich Research Centre, in order to test the quality of the modelling concept. The comparison showed a good agreement and results were consistent with previous studies. Tracer-gas experiments were carried out in the field within the canopy, which were then replicated in the wind tunnel. The order of magnitude of the dimensionless concentration downwind of the point source was in agreement with the field experiments.

Wind tunnel footprint experiments gave quantitative information about the VOCs origin and their transit time within the forest before that they were sampled at a specific location.

Chapter 2 – The countries of the Mediterranean basin are particularly affected by fires, which travel several thousand hectares per year. France is particularly vulnerable to wildland fires and mainly Corsica, where 84,000 hectares of maquis and forest have been burnt from 1995 to 2009. This paper present an estimation of Volatile Organic Compounds (VOCs) emitted in Corsica during this period. The authors first deal with the identification and the quantification of the main VOCs found in wildfire smoke. These results were obtained on a combustion chamber of 0.4 m^3 containing fuel submitted to an epiradiator and a sampling pump with an adsorbent tube (Tenax TA). The analysis is carried out with an Automated Thermal Desorption (ATD) coupled with a Gas Chromatography (GC) and with two detectors: Mass Spectrometry (MS) and Flame Ionization Detector (FID). 71 VOCs were identified. These emissions represent 25.4 kg/ha burnt. An extrapolation of these results for fires in Corsica leads to almost 1.92 Gigagrams of VOCs emitted into the atmosphere from 1995 to 2009. Forest fires increase the potential risk for the population long time exposure.

Chapter 3 – The effect of temperature on Biogenic Volatile Organic Compounds (BVOCs) emissions from five vegetal species was studied between 70 and 180 °C, range during which vegetation produces high amount of these gases. Emissions were investigated at small and middle scales. For a given species, if emitted BVOCs content does not change, the relative percentage of each volatile compound varies according to temperature. High amount of terpenoid compounds were emitted, except for Cistus albidus, and emissions are increasing with temperature. The main identified compounds are thymol, l-fenchone, α-pinene, 3-hexen-1-ol and limonene for respectively Thymus vulgaris, Lavandula stœchas, Rosmarinus officinalis, Cistus albidus and Pinus pinea. The results obtained will permit to develop a database of BVOCs emissions at elevated temperature and to include their combustion in physical forest fires models.

Chapter 4 – The Pearl River Delta (PRD) of China— encompasses 0.41% of China's land area but accounts for about 9% of China's national GDP— has been a rapidly developing economic region since 1980s. Like many other megacities in the world, it suffers from serious air pollution problems, particularly ozone (O_3) pollution. O_3, produced from a series of chemical reactions in the presence of nitrogen oxides (NOX), volatile organic compounds (VOCs) and sunlight, is harmful to both human health and environment. As a major precursor of tropospheric O_3, VOCs originate from both anthropogenic and biogenic sources. Biogenic VOCs (BVOCs), primarily composed of isoprene and monoterpenes, are emitted naturally in substantial quantities from certain types of terrestrial vegetation. The atmospheric reactivities of most BVOCs are higher than those of many anthropogenic VOCs (AVOCs), and thus, they are believed to play an important role in the formation of tropospheric O_3. In metropolitan cities, the potential of BVOCs to form O_3 is amplified by high concentrations of NOx. Therefore, characterization of BVOCs is essential for understanding O_3 chemistry in urban areas, and for the regional air quality modelling. The following book chapter will summarize the findings from various air quality studies conducted in the PRD region, and provide a comprehensive review of the contribution of BVOCs to O_3 formation in a wide range of space and time. By thoroughly evaluating the implications of photochemical oxidation of BVOCs, more effective air quality regulations could be developed to control O_3 pollution.

Chapter 5 – Tree species emit oxygen and Biogenic Volatile Organic compounds (BVOCs) which react in the atmosphere generating other chemical species including ozone (O_3). At the same time, trees capture particulate matter and gases (carbon dioxide, nitrogen oxides, and ozone).

Ozone is a secondary pollutant especially abundant in urban atmospheres. Santiago, Chile, is affected by high concentrations of O_3, especially in the northeast of the city and during the austral summer. Due to the aesthetic, climatic, and ecological benefits derived from trees, the Chilean government has been using them in a natural decontamination strategy especially for removing particulate matter and some gases not to mention the potential production of ozone through the emission of BVOCs.

Since BVOCs emissions are species-specific, their contribution to the photochemical reactivity in urban environment is very much related to plant biodiversity in the urban forest.

In this chapter the authors report a reanalysis and summary of the different works made by our group, focus on determining EF of isoprene and monoterpenes from around 33% of the Santiago urban forest. This study also includes the ability of urban forest species to generate O_3 through an index called the Photochemical Ozone Creation Index (POCI).

This report looks at 15 trees, exotic and native, studied at different stages of growth (small, young and adult) and seasons (austral autumn and spring). Standard EF are reported according to normalization proposed by Guenther et al., 1995. A discussion considering the standard and non standard EF is also included. Results show that, in general, exotic trees are more pollutant than native trees because the EF and POCI values of exotic trees are higher than those of native species. Those results are relevant if trees are used for decontamination purposes.

Modifications made to the emission inventory of BVOCs replacing EF, included by default in the model by the experimental EF, demonstrate that the taxonomical approaches of EF overestimate biogenic emissions. The integration of the different parameters contributes to the discussion for selecting the species more beneficial for the Metropolitan Region of Chile from the environmental and human health point of view.

Also some information is given about BVOCs emissions from other Latin American countries.

Chapter 6 – Volatile Organic Compounds (VOCs) are recognized as major responsible for the increase in global air pollution due to their contribution to ozone and photochemical smog. Currently, the most active catalysts for VOCs oxidation are based on noble and transition metals.

Among noble metals, platinum, palladium and rhodium exhibit high activity and selectivity at low temperature, but they are unstable in the presence of chloride compounds.

Systems based on transition metal oxides (such as V_2O_5, MnO_2, Co_3O_4-based oxides) are generally less active than noble metals, some formulations are stable to chlorines and their cost is significantly lower.

Supported ruthenium catalysts have received much attention over the past years, because of their high activity in oxidation as well as reduction reactions. Such catalysts have been proved to be among the best catalytic systems for oxidation of various substrates, such as carbon monoxide, ammonia, hydrogen, alcohols, diesel soot, and even in low temperature oxidation of HCl. However, few studies on VOCs oxidation over supported Ru have been conducted so far, especially in light alkane combustion. The physicochemical properties of Ru catalysts have been found to strongly influence activity and stability. Therefore, the comparison between catalysts prepared by different methods and pre-treated in different conditions is difficult.

In order to give a general overview on the state of art, the present chapter focuses on the latest results on the catalytic performance of Ru catalysts for light alkanes oxidation with special attention to the structure-activity relationship.

Chapter 7 – Volatile Organic Compounds (VOCs) are critical toxic substances that may cause harmful effects on human health when are emitted into the environment. The control of the emissions of VOCs into the atmosphere is one of the major environmental problems nowadays. Many conventional methods have been developed for industrial gaseous waste treatment but adsorption of contaminants onto adsorbents and their subsequent desorption for reuse or destruction has acquired high approval. Adsorption has been shown to be a process cost-effective and environmental friendly compared to other technologies such as absorption, biofiltration, or thermal catalysis.

This chapter summarises the general backgrounds described in the literature related to the control of the emissions of VOCs. Firstly, a state of the art of the sources of emissions of VOCs, and their main effects to human health and environment is presented. Then, the main technologies for VOCs control, their principles, limitations, applications and their remediation costs are briefly reviewed. Finally, the use of natural adsorbents as an economic alternative for the abatement of VOCs is discussed.

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Chapter 1

PHYSICAL MODELLING OF BIOGENIC VOCS EMISSION AND DISPERSION IN A FOREST STAND

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ABSTRACT

The turbulent dispersion process responsible of the VOCs transport within and above the canopy is still under study. This issue is of great interest since VOCs contribute to the global chemical reactions encountered into the troposphere. At the forest scale, VOCs are expected to travel within and above the forest, interacting with each other or with other chemical compounds. Some quantitative information can be given about the VOCs transport mechanisms in forest through the physical modeling in wind tunnel. Indeed the forest can be replicated at a reduced scale with an aerodynamical "drag-porosity concept" and the VOCs emissions can be modeled through the emission of a passive tracer through an area source. This approach will be illustrated through the Emission and Chemical transformation of Organic compounds (ECHO) project.

The concept of this project was to combine field experiments, laboratory experiments investigating emission and uptake of trace

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compounds by the plants, and modelling experiments simulating the chemistry of biogenic trace gases and the dynamics of a forest stand under well-defined conditions. The chosen site was the forest area surrounding the Forschungszentrum Juelich (Juelich Research Centre, Germany). In order to simulate the dynamical properties, the forest area was modelled to a scale of 1:300 and studied in the large boundary layer wind tunnel at the Meteorological Institute of Hamburg University. The model of the forest must reproduce the resistance to the wind generated by this porous environment. Rings of metallic mesh were used to represent the trees following preliminary tests to find an arrangement of these rings that provided the appropriate aerodynamic characteristics for a forest. The turbulence properties of the flow were measured in the wind tunnel within and above the canopy. Subsequently, they were compared with field data obtained at the Juelich Research Centre, in order to test the quality of the modelling concept. The comparison showed a good agreement and results were consistent with previous studies. Tracer-gas experiments were carried out in the field within the canopy, which were then replicated in the wind tunnel. The order of magnitude of the dimensionless concentration downwind of the point source was in agreement with the field experiments.

Wind tunnel footprint experiments gave quantitative information about the VOCs origin and their transit time within the forest before that they were sampled at a specific location.

Keywords: Wind tunnel, turbulence, forest, porous media, shear layer, footprint experiments

INTRODUCTION

In the framework of the ECHO (Emission and Chemical transformation of Organic compounds) project, the transport of the biogenic volatile organic compounds (BVOC) inside and above a forest canopy was investigated. The goal was to determine the net source of reactive trace compounds supplied by a mixed forest stand. The emission rates of BVOC from a mixed forest stand needed to be quantified, the amount of primary emitted VOC, which are transported directly into the planetary boundary layer and the amount of VOC, which are chemically processed within the canopy needed to be determined. Specialists with different competences, as biologists, chemists and meteorologists, were federated in that project to study these different questions. Methods of investigation used all available tools, to include field campaigns, laboratory experiments, numerical and physical modelling. The latter tool consists in measuring in an atmospheric boundary layer wind tunnel the turbulent flow and associated fluxes which develop on a forest area modeled at a reduced geometric scale. In opposition to field experiments, the possibility to control boundary conditions during testing ensures the statistical representativeness of the obtained results. Providing the Reynolds independency, it is straightforward to prove that the results about dispersion process obtained in wind tunnel can be up-scaled at field scale.

The contribution to the ECHO project of the University of Hamburg was to design a model of the finite forest area and to study it in its atmospheric boundary layer wind tunnel WOTAN. The flow properties and the transport of emissions within and above the canopy were studied. The chosen field site was the finite mixed forest area surrounding the Research Centre of Jülich (Germany). In order to reproduce the resistance to the wind generated by the trees while enabling an easy reproducibility of the model, an arrangement of opened rings made from metallic mesh was chosen. A comparable design was used by Beger (1983) to model a forest area but no further publications related to this set-up are available. In this study, a quadratic arrangement of metallic mesh was used. Hall et al. (1999) used some closed rings of metallic mesh to model high vegetation inside courtyards. Their choice was intuitive and the quality of the physical modelling was not tested. The set-up chosen in the present chapter is based on the same geometry but is not designed with respect to shape, drag coefficient or Leaf Area Index (LAI) similarities between field and model. The strategy was to achieve the same aerodynamic properties of the inside and above canopy flow, as measured at the field site.

The description of the model and the validity of the modeling concept against field data will be first detailed, through velocity and concentration measurements. After this validation stage, some footprint experiments will be presented in order to give information about the transit path and time of BVOC within and above the forest stand. Finally, the turbulent fluxes of BVOC above the forest will be quantified and some turbulent patterns responsible of these fluxes will be described.

The present chapter is a synthesis of Aubrun and Leitl (2004), Aubrun et al. (2003, 2005).

THE FOREST SITE AND THE FIELD EXPERIMENTS

The deciduous forest stand in Jülich is representative of a typical European forest area (Figure 1). It covers 350 ha and is located in a farmlandtype region. The inhomogeneity in the distribution of tree species, of tree age and of tree height is significant. As a consequence, a careful tree inventory was carried out. The meteorological conditions are permanently recorded at the meteorological tower at 7 stations located from 10 to 120 meters above ground. In the framework of the research project ECHO, three additional measurement towers were built-up inside the forest in order to measure the meteorological conditions as well as the biogenic VOC concentrations inside and immediately above the forest canopy. The main tower is located in an area planted with oak and beech trees, which are 150 years old. The local average tree height is between 25 and 30 m and the local Leaf-Area-Index is 3.6, which is considered as representative of a dense canopy.

The 10-min-average horizontal velocity and its standard deviation were measured at the main tower with Ultra-Sonic Anemometers-Thermometers during 2 hours on the 13th of September 2000 at 5, 10, 17 and 30 m with a mean wind direction of 281° and a mean wind speed of 4.2 m s^{-1} measured at 30 m above ground. At the meteorological tower, the mean temperature gradient was determined between 20m and 120m as –1.59 °C/100m. According to the terminology of the VDI-guideline 3782/1 (2001), the diffusion class during this experiment was 'C' in terms of Pasquill's classification scheme (Pasquill, 1974), denoted as 'neutral'. The forest fetch of the main tower for a westerly wind direction is 1400 m with the last 370 m covered with 25-30 m trees. These measurements are used to perform the comparison with the wind tunnel data.

In September 2000 and June 2001, several tracer experiments were carried out at the ECHO site. The aim was to provide basic information about the dispersion process inside the forest and to supply a data set, to help design and validate the wind tunnel model of the ECHO site. Westerly winds correspond to one of the most frequent situations at the field site. As a consequence, the experiments were focused on these wind directions.

Sulphur hexafluoride (SF6) was used as tracer. The advantages of SF6 are numerous in that it is inert, non-toxic, has a very low atmospheric background concentration (~ 5ppt), and can be easily detected by an online gas chromatography technique. Furthermore, SF6 is a man-made gas, which is not released through natural processes.

SF6 is released directly from gas cylinders provided by the manufacturer. The cylinders contain SF6 in liquid phase. The vapour pressure above the liquid phase keeps constant at about 13 bars until the cylinder is empty. Constant release rates (~0.2 g s-1) are adjusted by a pressure reduction valve combined with a flow resistor. The achieved accuracy of the source flow rate