



Issues in Environmental Science and Technology  
EDITORS: R.E. HESTER AND R.M. HARRISON

4

# Volatile Organic Compounds in the Atmosphere





## Volatile Organic Compounds in the Atmosphere

# ISSUES IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY

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# Preface

Whilst volatile organic compounds (VOCs) have never had the high profile of some other pollutants which have attracted attention from pressure groups and the media, collectively they represent one of the most important groups of trace atmospheric constituents. They are important in all parts of the globe and over a wide range of altitudes. Some are appreciably toxic in their own right and the UK Expert Panel on Air Quality Standards has recommended guidelines for benzene and 1,3-butadiene in the atmosphere which have been accepted by the British government; some other countries have also set air quality standards for benzene. Other VOCs are important primarily because of their atmospheric reactivity and consequent influence on the concentrations of tropospheric photochemical ozone, both in pollution episodes and in the background atmosphere. The photochemical ozone creation potential concept seeks to quantify this influence. Moving to higher altitudes, the impact of chlorofluorocarbons (CFCs) on stratospheric ozone has been a crucial one and, thanks to the Montreal Protocol, the ozone layer should be protected from this influence. However, CFCs play an important role both as industrial chemicals and within consumer products and it has proved difficult to find replacements which offer the same benefits of non-inflammability, high stability, and low toxicity, but which have a benign influence on the atmosphere.

Within this Issue we seek to explore many of the scientific aspects relating to volatile organic compounds in the atmosphere. In the first article, Dick Derwent of the Meteorological Office provides a broadly-based introduction to the atmospheric cycle of VOCs by considering their sources, distribution, and fates. This sets the scene for more specialized subsequent articles. Recent years have seen a growing appreciation of the importance of naturally generated VOCs in the atmosphere. In some areas with warm climates, VOCs from vegetation can play an equal or greater role than anthropogenic sources in contributing to low-level ozone formation. Much still needs to be learned about the chemistry and fluxes of these natural VOCs and Nick Hewitt and Xu-Liang Cao of Lancaster University provide a state of the art review of current knowledge. The recent availability of automated instrumentation for monitoring VOCs in urban air has led to a rapid expansion of our database and knowledge. Geoff Dollard and colleagues from the National Environmental Technology Centre explain the UK hydrocarbon monitoring network, one of the most advanced networks in the world, and discuss some of the early data from it.

## *Preface*

Many countries are now signatories to international agreements to limit and ultimately reduce emissions of VOCs to the atmosphere. Such controls can only be effective in the context of high quality source inventory information and Neil Passant of the National Environmental Technology Centre reviews information on source inventories and their development and considers control strategy options for VOCs. The atmospheric chemistry of VOCs is crucial to a full appreciation of their behaviour and two articles deal, respectively, with the tropospheric and stratospheric behaviour of important VOC compounds. Roger Atkinson of the University of California reviews the gas phase tropospheric chemistry of organic compounds whilst Pauline Midgley, an independent consultant, considers the impact of CFCs and their alternatives on the chemistry and physics of the stratosphere and troposphere.

Recent work has shown that construction materials and furnishings can act as a major source of VOCs in indoor air, and concentrations of some compounds indoors may greatly exceed outdoor concentrations. Derrick Crump of the Building Research Establishment has led a major programme of research on this topic and presents data from his and other studies in an article on VOCs in indoor air. In the final article, John Murlis describes the policy implications of VOCs and the development of policy in the UK.

We believe that this Issue has assembled some of the most up-to-date and relevant material from the large body of information now currently available on atmospheric VOCs. Each of the authors is a recognized expert in his or her particular area and we feel confident that this Issue will prove extremely valuable to our widely-based readership.

Ronald E. Hester  
Roy M. Harrison



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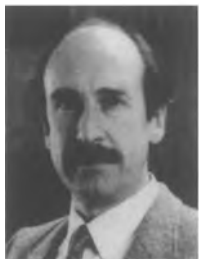
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## Editors



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Ronald E. Hester is Professor of Chemistry in the University of York. He was for short periods a research fellow in Cambridge and an assistant professor at Cornell before being appointed to a lectureship in chemistry in York in 1965. He has been a full professor in York since 1983. His more than 250 publications are mainly in the area of vibrational spectroscopy, latterly focusing on time-resolved studies of photoreaction intermediates and on biomolecular systems in solution. He is active in environmental chemistry and is a founder member and former chairman of the Environment Group of The Royal Society of Chemistry and editor of 'Industry and the Environment in Perspective' (RSC, 1983) and 'Understanding Our Environment' (RSC, 1986). As a member of the Council of the UK Science and Engineering Research Council and several of its sub-committees, panels, and boards, he has been heavily involved in national science policy and administration. He was, from 1991–93, a member of the UK Department of the Environment Advisory Committee on Hazardous Substances and is currently a member of the Publications and Information Board of The Royal Society of Chemistry.



**Roy M. Harrison, BSc, PhD, DSc(Birmingham), FRSC, CChem, FRMetS, FRSH**

Roy M. Harrison is Queen Elizabeth II Birmingham Centenary Professor of Environmental Health in the University of Birmingham. He was previously Lecturer in Environmental Sciences at the University of Lancaster and Reader and Director of the Institute of Aerosol Science at the University of Essex. His more than 200 publications are mainly in the field of environmental chemistry, although his current work includes studies of human health impacts of atmospheric pollutants as well as research into the chemistry of pollution phenomena. He is a former member and past Chairman of the Environment Group of The Royal Society of Chemistry for whom he has edited 'Pollution: Causes, Effects and Control', (RSC, 1983; Second Edition, 1990) and 'Understanding our Environment: An Introduction to Environmental Chemistry and Pollution' (RSC, Second Edition, 1992). He has a close interest in scientific and policy aspects of air pollution, currently being Chairman of the Department of Environment Quality of Urban Air Review Group as well as a member of the DoE Expert Panel on Air Quality Standards and Photochemical Oxidants Review Group and the Department of Health Committee on the Medical Effects of Air Pollutants.

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# Sources, Distributions, and Fates of VOCs in the Atmosphere

RICHARD G. DERWENT

## 1 Introduction

### *Historical Background*

The role and importance in atmospheric chemistry of organic compounds produced by human activity was established about fifty years ago by Haagen-Smit in his pioneering studies of Los Angeles smog.<sup>1</sup> He identified the key importance of hydrocarbon oxidation, in the presence of sunlight and oxides of nitrogen, as a photochemical source of ozone and other oxidants. Detailed understanding of the mechanism of photochemical smog formation has developed since then through the combination of smog chamber, laboratory chemical kinetics, field experiment, air quality monitoring, and computer modelling studies.

An understanding of the importance of the organic compounds emitted from the natural biosphere developed somewhat later with the recognition of the importance of the isoprene and terpene emissions from plants and trees.<sup>2</sup> The oxidation of these organic compounds leads to the production of carbon monoxide<sup>3</sup> and aerosol particles, the latter being responsible for the haze associated with forested regions.

Since these early pioneering studies, photochemical smog has subsequently been detected in almost all of the world's major urban and industrial centres, at levels which exceed internationally agreed criteria values set to protect human health.<sup>4</sup> Chlorinated organic compounds from human activities now reach the stratosphere, where processing by solar radiation yields active odd-chlorine species which are potent depleting agents of the stratospheric ozone layer.<sup>5</sup>

Despite the importance given now to organic compounds, their routine measurement in the atmosphere has only recently become commonplace. Furthermore, there are few detailed emission inventories for the major urban and industrial centres for which man-made emissions are fully resolved by species.

<sup>1</sup> A. J. Haagen-Smit, C. E. Bradley, and M. M. Fox, *Ind. Eng. Chem.*, 1953, **45**, 2086.

<sup>2</sup> R. A. Rasmussen and F. W. Went, *Proc. Natl. Acad. Sci. USA*, 1965, **53**, 215.

<sup>3</sup> E. Robinson and R. C. Robbins, SRI Project PR 6755, Stanford Research Institute, California, 1968.

<sup>4</sup> World Health Organisation, 'Air quality guidelines for Europe', European Series no. 23, WHO Regional Publications, Copenhagen, 1987.

<sup>5</sup> World Meteorological Office, 'Scientific Assessment of Ozone Depletion: 1991', Global Ozone Research and Monitoring Project Report no. 25, Geneva, Switzerland, 1992.