Feature: Persistence – Book Review

Atmospheric Degradation of Organic Substances

Data for Persistence and Long-range Transport Potential

Handbook/Reference Book

With a Foreword by K.-G. Steinhäuser

Authors: Walter Klöpffer and Burkhard Wagner
Publisher: Wiley-VCH, Weinheim, 1st Ed. February 2007. XV, 243 Pages, Hardcover. 149.00 Euro. ISBN-10: 3-527-31606-X; ISBN-13: 978-3-527-31606-9
Reviewer: PD Dr. Martin Scheringer, Institute for Chemical and Bioengineering, ETH Zürich, 8093 Zürich, Switzerland (scheringer@chem.ethz.ch)

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This book is an important publication at the right time. It provides a valuable compilation of existing data and, at the same time, points out the need for more and innovative research in the field of atmospheric reactivity of organic chemicals. The book also provides an interesting discussion of the context in which experimental research into atmospheric reactivity of organic chemicals has to be seen. The success of methods for estimating reaction rate constants from the molecular structure (quantitative structure-reactivity relationships, QSRRs) created the impression that experimental research in this field was no longer a research priority – although important aspects of the atmospheric degradation of organic compounds have not been understood yet.

To provide this broader perspective is the aim of **Chapter 1**, a historical overview of experimental methods, estimation methods (QSRRs), and the legislative context of these different methods. The chapter tells the story of an interesting development, reaching from Rachel Carson's Silent Spring to the phase of extensive experimental research in the 1970s and 1980s, the development and increasing acceptance of QSRRs in the 1990s, the political and scientific interest in POPs in the 1990s, the increasing importance of multimedia models in risk assessment, and to the current situation with reliable QSRR methods for volatile chemicals but a severe lack of knowledge and research activity in the field of semivolatile organic chemicals (SOCs).

Chapter 2 presents a very useful introduction into atmospheric degradation reactions of organic chemicals, including 240 references leading to more specific information. It covers the theory of indirect and direct photochemical reactions and of heterogeneous reactions on aerosol surfaces and in water droplets, gives an overview of experimental methods for these different types of reactions and draws conclusions about the calculation of atmospheric lifetimes. Indirect degradation reactions are extensively discussed for the OH and NO_3 radicals and for ozone. In all sections of this chapter, the material is illustrated with many examples, which considerably facilitates the understanding by readers who are not yet familiar with the topic. This chapter provides the background that is needed to use the data given in Chapter 3 but it also contains useful material for an introductory course in environmental chemistry.

A topic that could additionally have been included in Chapter 2 is the temperature dependence of indirect photochemical reactions, in particular because in Chapter 3 data about temperature dependence of reaction rate constants are provided for many chemicals.

Chapter 3, comprising about 100 pages, contains a wealth of empirical data on gas-phase reactions of organic chemicals with OH, NO_3, and ozone and on direct photolysis. In total, 1081 chemicals are covered, and virtually all data that were published before July 2006 have been included (536 references). The chemicals are listed alphabetically; every entry consists of the chemical name, the CAS number, values for the second-order rate constants k_{OH}, $k_{nitrate}$, k_{ozone} and $k_{h\nu}$ at 298 K, along with a quality index and references for each of these four rate constants. For more than 90% of the chemicals, k_{OH} is available; $k_{nitrate}$ and k_{ozone} are given for about 30% of the chemicals. Data on direct photolysis are scarce (less than 5% of the chemicals). The quality index is given as R ('recommended', sound empirical basis with several measurements at different temperatures), A ('average' of several values in the original literature), S ('single', only a single value available or sufficiently reliable), or E ('extrapolated' for rate constants not measured at 298 K or not measured in the gas phase).

An extremely valuable part of Chapter 3 is the footnotes (which are actually endnotes) assigned to many of the references in the list of chemicals. These 336 endnotes provide additional information about the conditions of measurement for many of the data entries; often, the temperature dependence of the rate constant and the corresponding activation energy are given. This makes it possible to put the numerical values of the rate constants into perspective and to see if there are uncertainties that make it advisable to consult the original literature. Unfortunately, this list of reaction rate constants is not available in electronic format, which impedes an efficient analysis of the complete dataset. Hopefully, the publisher will consider a second edition of the book provided on CD-ROM, similar to other compilations of chemical property data.

In addition to the valuable data compilation the book provides, **it points out the need for more measurements of atmospheric degradation reactions**. This need mainly concerns semivolatile compounds such as current-use pesticides, polybrominated (and other) flame retardants, but also additional measurements for acknowledged POPs (DDT, PCBs, etc.) because also for these chemicals, a broader data basis is desirable. As described in the book, measurements for SOCs are difficult to perform because of the low vapor pressure of these compounds. On the other hand, this implies that measurements for SOCs are not at all routine work but will require original scientific research, which would make this kind of investigation innovative and rewarding. But also for volatile compounds a data set including more than the about 1000 chemicals presented in this book is highly desirable. More measurements for volatile (and semivolatile) compounds will have two advantages: they directly lead to data about individual chemicals of high concern or interest and, in addition, they provide a broader basis for the improvement of existing QSRRs.

Conclusion. Today, the need for reliable chemical property data is higher than ever, in particular in the context of REACh, the new chemicals legislation of the EU. At the same time, however, it has become very difficult or even impossible to identify reliable numerical values for a given chemical property because the scientific literature often provides an non-transparent mixture of measurements, estimates, and guesses of property data. The body of scientific literature has become so broad that it requires large efforts to evaluate all values that may be available for a given property and to identify the most reliable ones. This situation has been illustrated with the example of DDT (Pontolillo and Eganhouse 2001) and this example stands for many more chemicals and chemical properties. In this situation, a data compilation providing access to the original literature along with comments and interpretation of the data reported is of great importance.

I recommend this valuable book to all users in academia, government, and industry who need information about the atmospheric fate of organic chemicals, also as teachers or students, who are looking for input data for multimedia models, or are in other ways involved in the hazard and risk assessment of chemicals. The atmospheric fate of organic chemicals is an essential part of the risk assessment of chemicals, and this book is an excellent foundation for a more systematic and comprehensive treatment of this part.

Pontolillo J, Eganhouse RP (2001): The Search for Reliable Aqueous Solubility and Octanol-Water Partition Coefficient Data for Hydrophobic Organic Compounds: DDT and DDE as a Case Study. U.S. Geological Survey, Water-Resources Investigations Report 01-4201, Reston, Virginia, 2001 <http://pubs.water.usgs.gov/wri014201/>

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By the Reviewer

Persistence and Spatial Range of Environmental Chemicals

New Ethical and Scientific Concepts for Risk Assessment

Autor: Martin Scheringer
Verlag: Wiley-VCH, Weinheim, Oktober 2002 (1st ed.); 119.00 Euro, XIV, 294 Pages; Hardcover – Monograph – ISBN-10: 3-527-30527-0; ISBN-13: 978-3-527-30527-8

Short description. Chemical risk assessment for the thousands of chemicals currently in use is a near-impossible task with the methodology used so far. This book provides the first coherent introduction to a new concept based on the criteria of persistence and spatial range. The concept makes chemical risk assessment manageable while still providing a meaningful evaluation of each chemical. Essential reading for everybody needing to stay in touch with the progress in scientific research on environmental chemicals or the current debate on chemicals regulation.

From the contents

Related literature

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