

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

## AQUATIC ORGANIC MATTER FLUORESCENCE

This is the first comprehensive text on the theory and practice of aquatic organic matter fluorescence analysis, written by the experts who pioneered the research area. This book covers the topic in the broadest possible terms, providing a common reference for making measurements that are comparable across disciplines, and allowing consistent interpretation of data and results. The book includes the fundamental physics and chemistry of organic matter fluorescence, as well as the effects of environmental factors. All aspects of sample handling, data processing, and the operation of both field and laboratory instrumentation are included, providing the practical advice required for successful fluorescence analyses. Advanced methods for data interpretation and modeling, including parallel factor analysis, are also discussed. The book will be of interest to those establishing field, laboratory, or industrial applications of fluorescence, including advanced students and researchers in environmental chemistry, marine science, environmental geosciences, environmental engineering, soil science, and physical geography.

PAULA G. COBLE is Professor in the College of Marine Science at the University of South Florida and has been involved in research on the fluorescence of natural organic matter for twenty years.

JAMIE LEAD is Professor of Environmental Nanoscience and Risk and Director of the Environmental Nanoscience and Risk SmartState Center at the University of South Carolina and Adjunct Professor of Environmental Nanoscience and Director of the Facility for Environmental Nanoscience Analysis and Characterisation at the University of Birmingham, UK.

ANDY BAKER is Director of the Connected Waters Initiative Research Centre at the University of New South Wales and Research Program Leader in the National Centre for Groundwater Research and Training, Australia.

DARREN M. REYNOLDS leads a research group within the Centre for Research in Biosciences and sits on the Scientific Advisory Board for the Institute of Bio-Sensing Technology at the University of the West of England, Bristol.

ROBERT G. M. SPENCER is Assistant Scientist at the Woods Hole Research Center, Falmouth, Massachusetts. He is an Earth system scientist whose research encompasses both aquatic geochemistry and biogeochemistry, focused predominantly on the carbon and nitrogen cycles.

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

---

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

CAMBRIDGE ENVIRONMENTAL  
CHEMISTRY SERIES

*Series editors:*

P. G. C. Campbell, Institut National de la Recherche Scientifique, Université de Québec, Canada

R. M. Harrison, School of Chemistry, University of Birmingham, UK

S. J. de Mora, Plymouth Marine Laboratory, Plymouth, UK

This wide-ranging series aims to cover all areas of environmental chemistry, placing emphasis on both basic scientific and pollution-oriented aspects. A central core of textbooks, suitable for those taking courses in environmental sciences, ecology, and chemistry, provides comprehensive coverage at the undergraduate and first-year postgraduate level of atmospheric science, chemical sedimentology, freshwater chemistry, marine chemistry, and soil chemistry. At a more advanced level, the series contains topical accounts of current research interest.

*All books available in the series:*

P. Brimblecombe *Air Composition and Chemistry, Second Edition*

A. C. Chamberlain *Radioactive Aerosols*

M. Cresser, K. Killham, and A. Edwards *Soil Chemistry and its Applications*

A. Edwards and M. Cresser *Acidification of Freshwaters*

R. M. Harrison and S. J. de Mora *Introductory Chemistry for the Environmental Sciences, Second Edition*

T. D. Jickells and J. E. Rae *Biogeochemistry of Intertidal Sediments*

S. J. de Mora *Tributyltin: Case Study of an Environmental Contaminant*

S. J. de Mora, S. Demers, and M. Vernet *The Effect of UV Radiation in the Marine Environment*

S. Roy, E. S. Egeland, G. Johnsen, and C. A. Llewellyn *Phytoplankton Pigments:*

*Characterization, Chemotaxonomy and Applications in Oceanography*

E. Tipping *Cation Binding by Humic Substances*

D. A. Wright and P. Welbourn *Environmental Toxicology*

S. Roy, C. A. Llewellyn, E. S. Egeland, and G. Johnson *Phytoplankton Pigments*

P. G. Coble, J. Lead, A. Baker, D. M. Reynolds, and R. G. M. Spencer *Aquatic Organic Matter Fluorescence*

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

---

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

# AQUATIC ORGANIC MATTER FLUORESCENCE

*Edited by*

PAULA G. COBLE

*University of South Florida*

JAMIE LEAD

*University of South Carolina*

ANDY BAKER

*University of New South Wales, Sydney*

DARREN M. REYNOLDS

*University of the West of England, Bristol*

ROBERT G. M. SPENCER

*Woods Hole Research Center*



**CAMBRIDGE**  
UNIVERSITY PRESS

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

## CAMBRIDGE UNIVERSITY PRESS

32 Avenue of the Americas, New York, NY 10013-2473, USA

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning, and research at the highest international levels of excellence.

[www.cambridge.org](http://www.cambridge.org)

Information on this title: [www.cambridge.org/9780521764612](http://www.cambridge.org/9780521764612)

© Cambridge University Press 2014

This publication is in copyright. Subject to statutory exception and to the provisions of relevant collective licensing agreements, no reproduction of any part may take place without the written permission of Cambridge University Press.

First published 2014

Printed in the United States of America

*A catalog record for this publication is available from the British Library.*

*Library of Congress Cataloging in Publication data*

Aquatic organic matter fluorescence / [edited by] Paula Coble, Jamie Lead, Andy Baker.

pages cm. – (Cambridge environmental chemistry series)

Includes bibliographical references and index.

ISBN 978-0-521-76461-2 (hardback)

1. Chemical oceanography. 2. Water chemistry. 3. Biogeochemistry. 4. Seawater – Organic compound content. 5. Bioluminescence. I. Coble, Paula.

GC116.A78 2014

572'.435809162–dc23 2013038167

ISBN 978-0-521-76461-2 Hardback

Cambridge University Press has no responsibility for the persistence or accuracy of URLs for external or third-party Internet Web sites referred to in this publication and does not guarantee that any content on such Web sites is, or will remain, accurate or appropriate.

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

## Contents

<i>List of Contributors</i>	<i>page</i> ix
<i>About the Editors</i>	xi
<i>Preface</i>	xiii
<b>Part I Introduction</b>	
1 The Principles of Fluorescence	3
DARREN M. REYNOLDS	
2 Fluorescence and Dissolved Organic Matter: A Chemist's Perspective	35
GEORGE AIKEN	
3 Aquatic Organic Matter Fluorescence	75
PAULA G. COBLE, ROBERT G. M. SPENCER, ANDY BAKER, AND DARREN M. REYNOLDS	
<b>Part II Instrumentation and Sampling</b>	
4 Sampling Design for Organic Matter Fluorescence Analysis	125
ROBERT G. M. SPENCER AND PAULA G. COBLE	
5 Optical Spectroscopy Instrumentation Design, Quality Assurance, and Control: Bench-Top Fluorimetry	147
JOHN R. GILCHRIST AND DARREN M. REYNOLDS	
6 Experimental Design and Quality Assurance: In Situ Fluorescence Instrumentation	190
ROBYN N. CONMY, CARLOS E. DEL CASTILLO, BRYAN D. DOWNING, AND ROBERT F. CHEN	
<b>Part III Environmental Effects</b>	
7 Physicochemical Effects on Dissolved Organic Matter Fluorescence in Natural Waters	233
CHRISTOPHER L. OSBURN, ROSSANA DEL VECCHIO, AND THOMAS J. BOYD	

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

viii

*Contents*

- 8 Biological Origins and Fate of Fluorescent Dissolved Organic Matter in Aquatic Environments 278  
COLIN A. STEDMON AND ROSE M. CORY

**Part IV Interpretation and Classification**

- 9 Fluorescence Indices and Their Interpretation 303  
RACHEL S. GABOR, ANDY BAKER, DIANE M. MCKNIGHT,  
AND MATTHEW P. MILLER
- 10 Chemometric Analysis of Organic Matter Fluorescence 339  
KATHLEEN R. MURPHY, RASMUS BRO, AND COLIN A. STEDMON

*The color plate section follows page 178*



Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

## Contributors

**George Aiken**

U.S. Geological Survey, Water Resources Discipline, National Research Program,  
Boulder, Colorado, US

**Andy Baker**

Connected Waters Initiative Research Centre, University of New South Wales,  
Sydney, Australia

**Thomas J. Boyd**

Chemistry Division, U.S. Naval Research Laboratory, Washington, DC, US

**Rasmus Bro**

University of Copenhagen, Faculty of Life Sciences, Department  
of Food Science, Frederiksberg C, Denmark

**Robert F. Chen**

University of Massachusetts, Boston, US

**Paula G. Coble**

College of Marine Science, University of South Florida, St. Petersburg, US

**Robyn N. Conmy**

U.S. Environmental Protection Agency, National Risk Management Research  
Laboratory, Cincinnati, Ohio, US

**Rose M. Cory**

Department of Earth & Environmental Sciences, University of Michigan, US

**Carlos E. Del Castillo**

Johns Hopkins University, Baltimore, Maryland, US

**Rossana Del Vecchio**

Earth System Science Interdisciplinary Center, University of Maryland, College Park, US

**Bryan D. Downing**

U.S. Geological Survey, Sacramento, California, US

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

x

*Contributors*

**Rachel S. Gabor**

Environmental Studies and Institute of Arctic and Alpine Research,  
University of Colorado, Boulder, US

**John R. Gilchrist**

Gilden Photonics Ltd., Clydebank, UK

**Diane M. McKnight**

Department of Civil, Environmental, and Architectural Engineering and Institute  
of Arctic and Alpine Research, University of Colorado, Boulder, US

**Matthew P. Miller**

U.S. Geological Survey, Utah Water Science Center, Moab, US

**Kathleen R. Murphy**

Water Environment Technology, Department of Civil and Environmental Engineering,  
Chalmers University of Technology, Gothenburg, Sweden

**Christopher L. Osburn**

Department of Marine, Earth, and Atmospheric Sciences, North Carolina State  
University, Raleigh, US

**Darren M. Reynolds**

Centre for Research in Biosciences, University of the West of England,  
Bristol, UK

**Robert G. M. Spencer**

Woods Hole Research Center, Falmouth, Massachusetts, US

**Colin A. Stedmon**

National Institute for Aquatic Resources, Technical University of Denmark,  
Kavalergården, Denmark

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

## About the Editors

PAULA G. COBLE is Professor in the College of Marine Science at the University of South Florida and has been involved in research on the fluorescence of natural organic matter for twenty years. She is one of the original researchers to use excitation–emission matrix spectroscopy (EEMS) for characterization of aquatic colored dissolved organic matter (CDOM) and has published several reviews on the topic. Coble’s research interests have focused on cycling of CDOM in marine and estuarine systems, development and deployment of in situ fluorometers, and using fluorescence to trace organic matter cycling and water mass mixing. Most recently, Coble has been advancing application of the EEMS technique to the study of oil spills in the marine environment, including distinguishing between the effects of physical and chemical dispersion.

JAMIE LEAD is Professor of Environmental Nanoscience and Risk and Director of the Environmental Nanoscience and Risk SmartState Center at the University of South Carolina and Adjunct Professor of Environmental Nanoscience and Director of the Facility for Environmental Nanoscience Analysis and Characterisation, University of Birmingham, United Kingdom. His research aims to understand both natural and manufactured nanoparticles and their interactions, as well as their fate and impact in the environment, and encompasses work from synthesis and characterization to risk and regulation.

ANDY BAKER is Director of the Connected Waters Initiative Research Centre at the University of New South Wales and Research Program Leader in the National Centre for Groundwater Research and Training, Australia. He is a researcher in the contrasting fields of past climate change, hydrogeology, organic matter characterization, and isotope geochemistry. Common themes include an interdisciplinary scientific approach between the subject areas of geography, Earth science, environmental science, and engineering. Baker has published more than one hundred fifty internationally refereed papers, including papers in high-citation-rate journals such as *Nature* and *Science*, and has been awarded and successfully managed more than sixty research grant applications. He was awarded a Phillip Leverhulme Prize in 2003 and a Durham University Institute for Advanced Studies Fellowship in 2009. Baker’s role in aquatic organic matter fluorescence commenced in the 1990s with his investigation of organic matter preserved in cave stalagmites. This led to

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

research on organic matter fluorescence properties of karst groundwaters, UK rivers, and, finally, engineered systems such as drinking and waste water treatment systems.

DARREN M. REYNOLDS leads a research group within the Centre for Research in Biosciences and sits on the Scientific Advisory Board for the Institute of Bio-Sensing Technology at the University of the West of England, Bristol. He is a multidisciplinary scientist concerned with the development of technology platforms for applications in the fields of environment/agri-food and health. Reynolds's research interests include the development of optical technologies and techniques for environmental and biological sensing and bio-prospecting applications. He is currently involved in the development and use of synthetic biology (bioluminescent reporter bacteria) for the discovery and characterization of bacteriophage and to assess their potential use as a bio-control/antimicrobial in the health and agri-food sectors. He is developing, in collaboration with industrial partners, in situ fluorescence sensors to help further understand the role of dissolved organic matter in underpinning the microbial processes in aquatic systems through time.

ROBERT G. M. SPENCER is Assistant Scientist at the Woods Hole Research Center, Falmouth, Massachusetts. He is an Earth system scientist whose research encompasses both aquatic geochemistry and biogeochemistry, focused predominantly on the carbon and nitrogen cycles. The majority of his research centers on the interface between the hydrosphere and biosphere over environmental time scales within natural systems. Spencer is a highly interdisciplinary scientist and uses a suite of analytical techniques to examine the influence of physical, chemical, and biological processes – especially watershed hydrology, ecosystem processing, global climate change, and land use change – on the carbon and nitrogen cycles within aquatic and terrestrial environments. A major focus of Spencer's current research is examining controls on the export, processing, and fate of organic matter in the critical zone from the tropics to the Arctic, from soils and glaciers through rivers and estuaries and into the ocean. Spencer has utilized organic matter fluorescence extensively in this research for delineating sources and degradation histories of organic matter, as well as to improve resolution of components of the organic matter pool (e.g., dissolved organic carbon and biomarkers).

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

## Preface

This volume is a response to the explosion of interest in the use of fluorescence spectroscopy to analyze organic matter in the aquatic environment and the realization that a book was needed that combined relevant information on fluorescence principles, laboratory and field methodologies, and data handling and interpretation. The editorial and author teams are drawn from a wide range of disciplines, which reflects the multidisciplinary interest in aquatic organic matter fluorescence. Despite more than thirty years of interest in the topics, until recently, research was undertaken primarily within disciplines, without the benefits of a genuine interdisciplinary approach. We hope that this volume goes some way to address this. It is intended as a core text for anyone starting to undertake research into aquatic organic matter fluorescence, with a potential readership in the fields of environmental chemistry, marine science, environmental geosciences, environmental engineering, soil science, and physical geography. The first three chapters provide an overview to the field of aquatic organic matter fluorescence: Chapter 1 outlines the principles of fluorescence, Chapter 2 synthesizes the relationship between fluorescence and dissolved organic matter chemistry, and Chapter 3 provides a multidisciplinary overview of the history and current understanding of aquatic organic matter fluorescence. As such, we anticipate that these chapters will be of broad interest to students and researchers interested in optical methods in environmental science and the environmental chemistry of organic matter. The next three chapters focus on instrumentation and sampling: Chapter 4 details sampling protocols essential for successful fluorescence analyses, and Chapters 5 and 6 provide insights into laboratory (bench) and field (in situ) methodologies. These chapters will be of particular interest to anyone intending to establish field, laboratory, or industrial applications of fluorescence, including undergraduate project students, PhD and postdoctoral researchers, and research and development officers. Chapters 7 and 8 investigate environmental effects on aquatic organic matter fluorescence, detailing the chemical and biological reprocessing of organic matter in natural and engineered systems. These chapters are relevant to anyone interested in the nature of organic matter transformations in the natural and engineered environments, from transformations within river systems through to chemical properties relevant to water treatment processes. Finally, Chapters 9 and 10 summarize methods used in the analysis and interpretation of fluorescence data, focusing on the use of indices and multivariate statistical and modeling approaches.

Cambridge University Press

978-0-521-76461-2 - Aquatic Organic Matter Fluorescence

Edited by Paula G. Coble, Jamie Lead, Andy Baker, Darren M. Reynolds and Robert G. M. Spencer

Frontmatter

[More information](#)

As with all research textbooks published in a rapidly moving field, our challenge is to produce a volume that is relevant both today and in the years to come. The future for research into aquatic organic matter fluorescence is exciting, as research opportunities develop with improvements in technology. At the time of writing, routine fluorescence analyses are still three-way analyses (excitation, emission, intensity), with the use of xenon light sources, diffraction gratings, and photomultiplier tubes. However, the use of ultraviolet light-emitting diodes (LEDs) as light sources, and charge-coupled devices (CCDs) as detectors, is increasing. The former permit a decrease in instrument power output and size, leading to increased portability and more diverse in situ applications. The latter increases analysis speed and the possibility of four-way analyses (excitation, emission, intensity, time) and novel experimentation. The recent development of turnkey instrumentation, with integrated absorbance measurements and multivariate modeling software, makes aquatic organic matter fluorescence measurements easier for the non-expert than they have ever been before. We feel this latter development makes the need for this book more relevant than ever.

This volume is an outcome of a series of research initiatives led by the editors over the last decade. In part, it is a result of the UK initiative Fluoronet, a knowledge transfer network funded by the Natural Environment Research Council between 2006 and 2009 and led by Andy Baker and Jamie Lead when they both worked at the University of Birmingham, United Kingdom. Numerous training courses and workshops run by Fluoronet members, including Darren M. Reynolds and Robert G. M. Spencer, have helped guide the requirements of the contents of this book. At the same time, scientific sessions on organic matter characterization at the American Geophysical Union Fall Meetings in 2006 and 2007 started to bring together research teams from diverse disciplines. Informal gatherings, and then formal meetings, occurred around these sessions. These led to the idea of the need for both a specialist conference, to compare methodologies and establish protocols between different disciplinary groups, as well as for a multidisciplinary research textbook. The resulting meeting was an American Geophysical Union Chapman Conference on Organic Matter Fluorescence, proposed and convened by Paula G. Coble and Andy Baker at the University of Birmingham, United Kingdom, in 2008. Several years later, we are proud that this edited volume has been produced by Cambridge University Press.