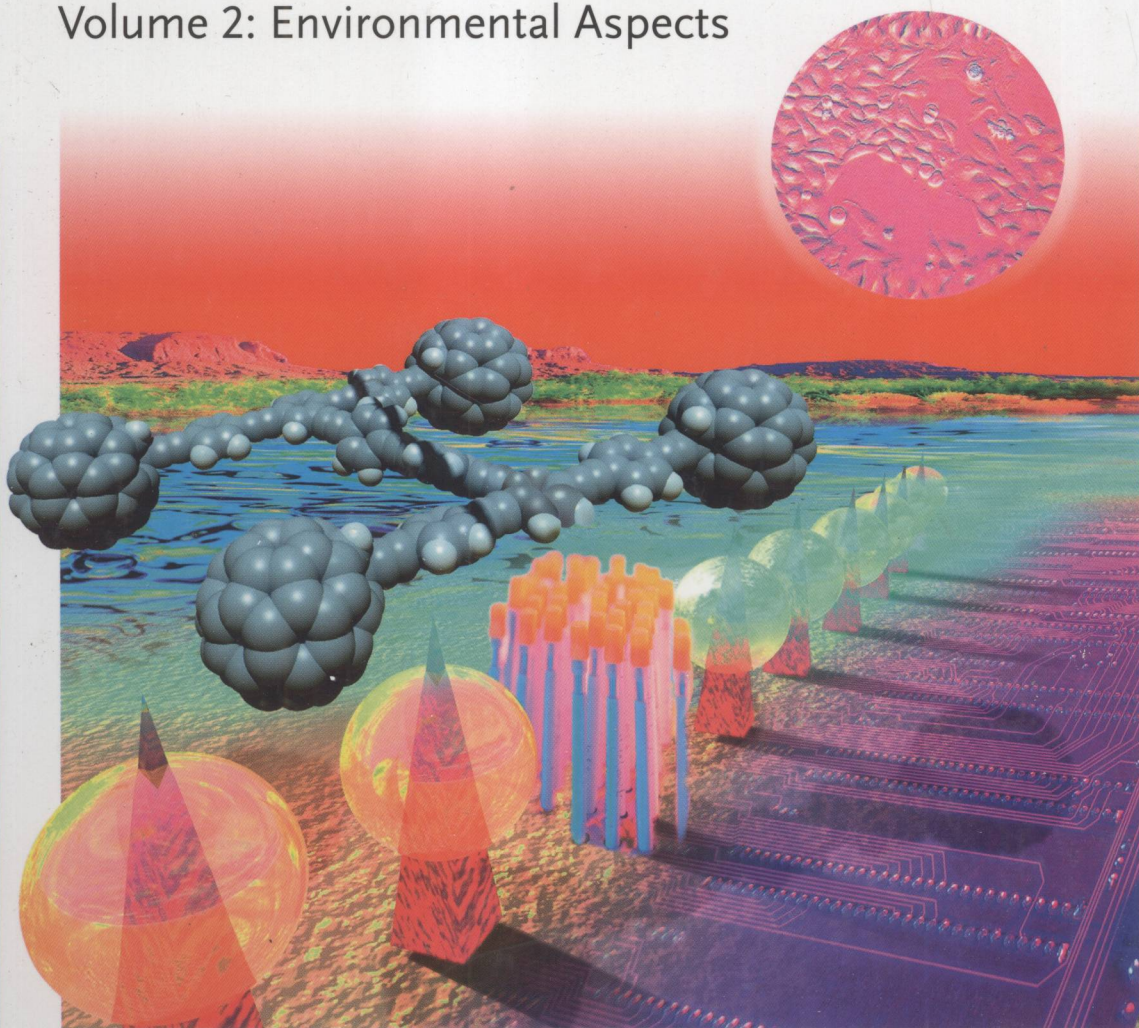


Edited by Harald F. Krug

 WILEY-VCH

# Nanotechnology

Volume 2: Environmental Aspects



TB 383  
N186.18  
✓.2

G. Schmid, H. Krug, R. Waser, V. Vogel, H. Fuchs,  
M. Grätzel, K. Kalyanasundaram, L. Chi (Eds.)

# Nanotechnology

Volume 2: Environmental Aspects

*Edited by Harald Krug*



WILEY-VCH Verlag GmbH & Co. KGaA



#### **The Editor**

**Prof. Dr. Harald F. Krug**

EMPA - Materials Science & Technology  
Lerchenfeldstr. 5  
9014 St. Gallen  
Switzerland

**Cover:** Nanocar reproduced with kind permission  
of Y. Shirai/Rice University

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

**Library of Congress Card No.:** applied for

#### **British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

#### **Bibliographic information published by the Deutsche Nationalbibliothek**

Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA,  
Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

**Typesetting** Thomson Digital, Noida, India

**Printing** betz-druck GmbH, Darmstadt

**Binding** Litges & Dopf Buchbinderei GmbH,  
Heppenheim

Printed in the Federal Republic of Germany  
Printed on acid-free paper

**ISBN:** 978-3-527-31735-6

**Nanotechnology**

Volume 2: Environmental Aspects

*Edited by Harald Krug*

## ***Related Titles***

### **Nanotechnologies for the Life Sciences**

Challa S. S. R. Kumar (ed.)

#### **Volume 1: Biofunctionalization of Nanomaterials**

2005

978-3-527-31381-5

#### **Volume 2: Biological and Pharmaceutical Nanomaterials**

2005

978-3-427-31382

#### **Volume 3: Nanosystem Characterization Tools in the Life Sciences**

2005

978-3-527-31383-9

#### **Volume 4: Nanodevices for the Life Sciences**

2006

978-3-527-31384-6

#### **Volume 5: Nanomaterials - Toxicity, Health and Environmental Issues**

2006

978-3-527-31385-3

#### **Volume 6: Nanomaterials for Cancer Therapy**

2006

978-3-527-31386-0

#### **Volume 7: Nanomaterials for Cancer Diagnosis**

2006

978-3-527-31387-7

#### **Volume 8: Nanomaterials for Biosensors**

2006

978-3-527-31388-4

#### **Volume 9: Tissue, Cell and Organ Engineering**

2006

978-3-527-31389-1

#### **Volume 10: Nanomaterials for Medical Diagnosis and Therapy**

2007

978-3-527-31390-7

### **Nanotechnology**

Günter Schmid (ed.)

#### **Volume 1: Principles and Fundamentals**

2008

978-3-527-31732-5

Harald Krug (ed.)

#### **Volume 2: Environmental Aspects**

2008

978-3-527-31735-6

Rainer Waser (ed.)

#### **Volume 3: Information Technology I**

2008

978-3-527-31738-7

Rainer Waser (ed.)

#### **Volume 3: Information Technology II**

2008

978-3-527-31737-0

Viola Vogel (ed.)

#### **Volume 5: Nanomedicine and Nanobiotechnology**

2009

978-3-527-31736-3

Harald Fuchs (ed.)

#### **Volume 6: Nanoprobes**

2009

978-3-527-31733-2

Michael Grätzel, Kuppaswamy Kalyanasundaram (eds.)

#### **Volume 7: Light and Energy**

2009

978-3-527-31734-9

Lifeng Chi (ed.)

#### **Volume 8: Nanostructured Surfaces**

2009

978-3-527-31739-4

[www.wiley.com/go/nanotechnology](http://www.wiley.com/go/nanotechnology)

## Preface

“Nowhere the Nature of things is greater than in the smallest things,” stated Pliny the Elder almost 2000 years ago. With these few words, he combined the special properties of small things with the “environment”.

This combination – which forms the central aspect of this book – demonstrates the multifaceted correlation between *Nanotechnology* and environmental problems. The many promises made during the past two decades on the one hand, and the demand for higher safety and the regulation of new technologies on the other hand, highlight the fact that today the use of nanomaterials within the environment is a very sensitive issue. The first chemical revolution bestowed on us some critical environmental problems which still have not been satisfactorily resolved today. An example is the relationship between the distribution of pollutants and their control, with many organizations and societal groups demanding a better control of chemicals and their associated technological difficulties. The questions that arise from these considerations are addressed in the second volume of this series on *Nanotechnology*. In this respect, *Environmental Aspects* covers both sides of the coin, from the use of nanomaterials as catalysts to reduce or prevent pollution or identify the situation both early and accurately, to solving energy-related problems by applying nanotechnology or addressing environmental difficulties arising during the production and use of nanoparticles. The aging of nanoparticles in the atmosphere, and the related problems of their presence in the environment, have also been addressed in this book.

The initial planning of this book proved difficult when some of the selected authors were forced to cancel their collaboration for reasons of ill health, and I extend my sympathy to these colleagues. However, I was extremely pleased to find in all cases not only substitutes but true experts in these fields who proved capable of presenting an outstanding summary on all topics relating to *Nanotechnology* and the *Environment*.

Clearly, I would like to express my sincere thanks to all authors of the chapters, for their dedication and patience during the preparation of this book. My special thanks go to Günther Schmid, the editor of the series *Nanotechnology*, who invited and motivated me to edit this volume on *Environmental Aspects*, and of course to the staff

of Wiley-VCH – and in particular Gudrun Walter, Steffen Pauly and Axel Eberhard – who supported me in every possible way. My thanks also go to Waltraud Wüst, without whom even this preface would not have been written. Last, but not least, I thank my wife for her great patience, as she spent many hours alone while I was working at my desk.

St. Gallen, March 2008

*Harald F. Krug*

## List of Contributors

### **Billie L. Abrams**

Danish Technical University  
Department of Physics  
Nano DTU  
Center for Integrated Nanoparticle  
Functionality (CINF)  
2800 Kongens Lyngby  
Denmark

### **Norman S. Allen**

Manchester Metropolitan University  
Biology, Chemistry and Health Sciences  
Chester Street  
Manchester M1 5GD  
United Kingdom

### **Christof Asbach**

Institute of Energy and Environmental  
Technology (IUTA) e.V.  
Air Quality & Sustainable  
Nanotechnology  
Bliersheimer Strasse 60  
47229 Duisburg  
Germany

### **Irene Bröske-Hohfeld**

Helmholtz Zentrum München  
Institut für Epidemiologie  
Ingolstädter Landstrasse 1  
85764 Neuherberg  
Germany

### **Claire Bygott**

Millennium Chemicals (Lyondell  
Group)  
P.O. Box 26  
Grimsby  
Lincolnshire DN41 8DP  
United Kingdom

### **Joydeep Dutta**

Asian Institute of Technology  
School of Engineering and Technology  
P.O. Box 4, Klong Luang  
Pathumthani 12 120  
Thailand

### **Michele Edge**

Manchester Metropolitan University  
Biology, Chemistry and Health Sciences  
Chester Street  
Manchester M1 5GD  
United Kingdom

### **Heinz Fissan**

Institute of Energy and Environmental  
Technology (IUTA) e.V.  
Air Quality & Sustainable  
Nanotechnology  
Bliersheimer Strasse 60  
47229 Duisburg  
Germany



**Petra Klug**

Forschungszentrum Karlsruhe GmbH  
Molecular & Environmental Toxicology  
Laboratory  
Hermann-von-Helmholtz-Platz 1  
76344 Egg.-Leopoldshafen  
Germany

**Harald F. Krug**

Empa – Materials Science & Technology  
Lerchenfeldstrasse 5  
9014 St. Gallen  
Switzerland

**Thomas A. J. Kuhlbusch**

Institute of Energy and Environmental  
Technology (IUTA) e.V.  
Air Quality & Sustainable  
Nanotechnology  
Bliersheimer Strasse 60  
47229 Duisburg  
Germany

**Deanna N. Leka**

The Woodrow Wilson International  
Center for Scholars  
Washington  
DC  
USA

**Shannon M. Lloyd**

Concurrent Technologies Corporation  
100 CTC Drive  
Johnstown  
PA, 15904  
USA

**Julie Maltby**

Millennium Chemicals (Lyondell  
Group)  
P.O. Box 26  
Grimsby  
Lincolnshire DN41 8DP  
United Kingdom

**Bernd Nowack**

Empa – Materials Science & Technology  
Technology and Society Laboratory  
Lerchenfeldstrasse 5  
9014 St. Gallen  
Switzerland

**Annette Peters**

Helmholtz Zentrum München  
Institut für Epidemiologie  
Ingolstädter Landstrasse 1  
85764 Neuherberg  
Germany

**Ulrich Pöschl**

Max Planck Institute for Chemistry  
Biogeochemistry Department  
Becherweg 27/29  
55128 Mainz  
Germany

**Ketra A. Schmitt**

Battelle Memorial Institute  
505 King Avenue  
Columbus  
OH, 43201  
USA

**John Stratton**

Millennium Chemicals (Lyondell  
Group)  
P.O. Box 26  
Grimsby  
Lincolnshire DN41 8DP  
United Kingdom

**Abhilash Sugunan**

Asian Institute of Technology  
School of Engineering and Technology  
P.O. Box 4, Klong Luang  
Pathumthani 12 120  
Thailand

**Ian Ivar Suni**

Clarkson University  
Department of Chemical and  
Biomolecular Engineering  
Potsdam  
NY 13699-5705  
USA

**Jess P. Wilcoxon**

University of Birmingham  
Nanophysics Research Laboratory  
Edgbaston Road  
Birmingham B15 2TT  
United Kingdom

**Joanne Verran**

Manchester Metropolitan University  
Biology, Chemistry and Health Sciences  
Chester Street  
Manchester M1 5GD  
United Kingdom

## Contents

**Preface** *XI*

**List of Contributors** *XIII*

<b>1</b>	<b>Pollution Prevention and Treatment Using Nanotechnology</b>	<b>1</b>
	<i>Bernd Nowack</i>	
1.1	Introduction	1
1.2	More Efficient Resource and Energy Consumption	3
1.3	Pollution Detection and Sensing	4
1.4	Water Treatment	4
1.4.1	Adsorption of Pollutants	4
1.4.2	Magnetic Nanoparticles	6
1.4.3	Nanofiltration	6
1.4.4	Degradation of Pollutants	6
1.4.5	Zerovalent Iron	7
1.5	Soil and Groundwater Remediation	9
1.6	Environmental Risks	10
1.6.1	Behavior in the Environment	10
1.6.2	Ecotoxicology	11
1.7	Conclusions	11
	References	12
<b>2</b>	<b>Photocatalytic Surfaces: Antipollution and Antimicrobial Effects</b>	<b>17</b>
	<i>Norman S. Allen, Michele Edge, Joanne Verran, John Stratton, Julie Maltby, and Claire Bygott</i>	
2.1	Introduction to Photocatalysis: Titanium Dioxide Chemistry and Structure–Activity	17
2.2	Applications	26
2.3	Photocatalytic Chemistry	26
2.4	Photoactivity Tests for 2-Propanol Oxidation and Hydroxyl Content	31

2.5	Self-Cleaning Effects: Paints/Cementitious Materials	33
2.5.1	Antibacterial Effect	38
2.5.2	Depollution: NO <sub>x</sub> /VOC Removal	42
2.6	Conclusions	48
	References	49

### **3 Nanosized Photocatalysts in Environmental Remediation 51**

*Jess P. Wilcoxon and Billie L. Abrams*

3.1	Introduction	51
3.1.1	Global Issues	51
3.1.2	Scope	53
3.2	General Field of Environmental Remediation	54
3.3	Photocatalysis	57
3.3.1	History and Background	57
3.3.2	Definitions	58
3.3.3	Well-Known Example – Water Splitting Reaction	59
3.4	Design Issues for Environmental Remediation Photocatalysts	60
3.4.1	Introduction	60
3.4.2	Charge Separation	61
3.4.3	pH of Solution	62
3.4.4	Charge Transfer	62
3.4.5	Presence of Simple and Complex Salts	62
3.4.6	Effect of Surfactants	64
3.4.7	Effect of Solvent and Dissolved Oxygen	65
3.4.8	Light Intensity	66
3.5	Potential for Nanomaterials in Environmental Remediation	66
3.5.1	Introduction	66
3.5.2	Nanomaterials and Advantages in Photocatalysis	68
3.5.2.1	Semiconductor Nanoclusters	68
3.5.2.2	Quantum Confinement	68
3.5.2.3	Surface Chemistry	71
3.5.2.4	Other Unique Materials Properties	71
3.5.2.5	Importance of Nanocluster Photostability	72
3.6	Nanoparticle Synthesis and Characterization	73
3.6.1	Introduction	73
3.6.2	Characterization	74
3.6.3	Detailed Examples of Nanocluster Synthesis and Photocatalysis	77
3.6.3.1	Semiconductor Nanoclusters	77
3.6.3.2	TiO <sub>2</sub>	78
3.6.3.3	Alternative Photocatalytic Materials	83
3.6.3.4	MoS <sub>2</sub> and Other Metal Dichalcogenides	86
3.7	Current and Future Technological Applications of Photocatalysts for Environmental Remediation	112
3.7.1	Indoor Air Purification	113
3.7.2	Outdoor Air Purification	115

3.8	Conclusion	117
	References	119
<b>4</b>	<b>Pollution Treatment, Remediation and Sensing</b>	<b>125</b>
	<i>Abhilash Sugunan and Joydeep Dutta</i>	
4.1	Introduction	125
4.2	Treatment Technologies to Remove Environmental Pollutants	127
4.3	Remediation Technologies to Clean Up Environmental Pollutants Effectively	131
4.4	Sensors	133
4.4.1	Biosensors	134
4.4.2	Electrochemical Sensors	134
4.4.3	Mass Sensors	135
4.4.4	Optical Sensors	137
4.4.5	Gas Sensors	138
4.4.6	Novel Sensing Technologies and Devices for Pollutant and Microbial Detection	140
4.4.6.1	Real-Time Chemical Composition Measurements of Fine and Ultrafine Airborne Particles	140
4.4.6.2	Ultrasensitive Detection of Pathogens in Water	140
4.4.6.3	Detection of Heavy Metals in Water	141
4.5	Conclusions	143
	References	143
<b>5</b>	<b>Benefits in Energy Budget</b>	<b>147</b>
	<i>Ian Ivar Suni</i>	
5.1	Introduction	147
5.2	Nanomaterials in Fuel Cells	148
5.2.1	Low-Temperature Fuel Cell Technology	148
5.2.2	Nanoparticle Catalysts in Low-Temperature Fuel Cells	150
5.2.3	Fuel Cell Catalyst Support Materials	151
5.2.4	Carbon Nanotubes: Science and Technology	152
5.2.5	Carbon Nanotubes within Operating PEMFCs	153
5.3	Hydrogen Storage	157
5.3.1	Hydrogen Storage Using Carbon Nanomaterials	158
5.4	Solar Cells	159
5.4.1	Solar Energy Basics, Including Quantum Confinement	159
5.4.2	Nanocrystalline Dye-Sensitized Solar Cells	161
5.4.3	Nanomaterials in Solar Cell Counter Electrodes	164
5.5	Lithium Ion Battery Anode Materials	165
5.5.1	Lithium Ion Batteries	165
5.5.2	Nanomaterials for Lithium Ion Storage: Sn Nanoparticles	166
5.5.3	Nanomaterials for Lithium Ion Storage: Si Nanocomposites	169
5.5.4	Nanomaterials for Lithium Ion Storage: Carbon Nanotubes and Carbon Nanotube-Based Composites	170

- 5.5.5 Lithium Ion Storage: Further Considerations 171
- References 172

## **6 An Industrial Ecology Perspective 177**

*Shannon M. Lloyd, Deanna N. Lekas, and Ketra A. Schmitt*

- 6.1 Introduction 177
- 6.1.1 Industrial Ecology 177
- 6.1.2 Applying Industrial Ecology to Nanotechnology 178
- 6.2 Life Cycle Assessment 179
- 6.2.1 Background on Life Cycle Assessment 179
- 6.2.2 Life Cycle Implications for Nanotechnology 180
- 6.2.3 Life Cycle Studies Conducted to Date 181
- 6.3 Substance Flow Analysis 184
- 6.3.1 Background on Substance Flow Analysis 184
- 6.3.2 Substance Flow Analysis Implications for Nanotechnology 185
- 6.3.3 Summary of Substance Flow Analysis Work Conducted to Date 185
- 6.4 Corporate Social Responsibility 186
- 6.4.1 Background on Corporate Social Responsibility 186
- 6.4.2 Corporate Social Responsibility Implications for Nanotechnology 187
- 6.4.3 Summary of Work Conducted to Understand Nanofirm EHS Concerns and Actions 188
- 6.5 Conclusions 189
- References 190

## **7 Composition, Transformation and Effects of Nanoparticles in the Atmosphere 195**

*Ulrich Pöschl*

- 7.1 Introduction 195
- 7.2 Composition 199
- 7.2.1 Carbonaceous Components 199
- 7.2.2 Primary and Secondary Organic Components 202
- 7.3 Transformation 205
- 7.3.1 Chemical Transformation of Carbonaceous Aerosol Components 208
- 7.3.2 Restructuring, Phase Transitions, Hygroscopic Growth and CCN/IN Activation of Aerosol Particles upon Interaction with Water Vapor 212
- 7.4 Climate and Health Effects 216
- 7.5 Summary and Outlook 219
- References 221

## **8 Measurement and Detection of Nanoparticles Within the Environment 229**

*Thomas A.J. Kuhlbusch, Heinz Fissan, and Christof Asbach*

- 8.1 Introduction 229
- 8.2 Occurrence of Nanoparticles in Environmental Media 233

8.2.1	Ambient Environment	233
8.2.1.1	Water and Soils	233
8.2.1.2	Air	234
8.2.2	Workplace Environment	234
8.3	Nanoparticle Detection and Measurement Techniques	235
8.3.1	Soil	235
8.3.2	Water and Liquids	235
8.3.2.1	Coulter Counter	235
8.3.2.2	Light Scattering	236
8.3.3	Air	238
8.3.3.1	Basics	238
8.3.3.2	Online Physical Characterization	243
8.3.3.3	Online Physical–Chemical Characterization	256
8.3.3.4	Offline Physical Characterization	258
8.4	Nanoparticle Detection and Measurement Strategies	259
	References	262
<b>9</b>	<b>Epidemiological Studies on Particulate Air Pollution</b>	<b>267</b>
	<i>Irene Bröske-Hohlfeld and Annette Peters</i>	
9.1	Introduction	267
9.1.1	Outline of the Chapter	267
9.1.2	A Short Definition of Particle Sizes	268
9.1.3	A Brief Comment on Epidemiological Study Design	269
9.2	Potential Entry Routes for Nanoparticles into the Human Body	270
9.2.1	Inhalation and Metabolism of Airborne Particles	270
9.3	Studies of Environmental Air Pollution in the USA and Europe	271
9.3.1	PM <sub>10</sub> and PM <sub>2.5</sub>	271
9.3.1.1	Short-Term Studies	272
9.3.1.2	Long-Term Studies	272
9.3.2	Ultrafine Particles (UFP)	273
9.4	Cardiovascular Disease	275
9.5	Respiratory Disease	276
9.5.1	Deterioration of Lung Function and Respiratory Symptoms	276
9.5.2	Asthma and Allergies	277
9.5.3	Lung Cancer	278
9.6	Diseases of the Central Nervous System	279
9.7	Particulate Air Pollution at the Workplace	281
	References	286
<b>10</b>	<b>Impact of Nanotechnological Developments on the Environment</b>	<b>291</b>
	<i>Harald F. Krug and Petra Klug</i>	
10.1	Problem	291
10.2	Risk Management	292
10.3	Sources of Nanoparticles: New Products	294
10.4	Production and Use of Nanomaterials	296

10.5	Workplace and the Environment: Effects and Aspects of Nanomaterials	297
10.6	Distribution of Nanoparticles in Ambient Air	298
10.7	Distribution of Nanoparticles in Water	299
10.8	Conclusions	302
	References	303
	<b>Index</b>	<b>307</b>



## 1

**Pollution Prevention and Treatment Using Nanotechnology***Bernd Nowack***1.1****Introduction**

Environmental nanotechnology is considered to play a key role in the shaping of current environmental engineering and science. Looking at the nanoscale has stimulated the development and use of novel and cost-effective technologies for remediation, pollution detection, catalysis and others [1]. However, there is also a wide debate about the safety of nanoparticles and their potential impact on environment and biota [2, 3], not only among scientists but also the public [4, 5]. Especially the new field of nanotoxicology has received a lot of attention in recent years [6, 7]. Nanotechnology and the environment – is it therefore a Janus-faced relationship? There is the huge hope that nanotechnological applications and products will lead to a cleaner and healthier environment [8]. Maintaining and re-improving the quality of water, air and soil, so that the Earth will be able to support human and other life sustainably, are one of the great challenges of our time. The scarcity of water, in terms of both quantity and quality, poses a significant threat to the well-being of people, especially in developing countries. Great hope is placed on the role that nanotechnology can play in providing clean water to these countries in an efficient and cheap way [9]. On the other hand, the discussion about the potential adverse effects of nanoparticles has increased steadily in recent years and is a top priority in agencies all over the world [10, 11]. Figure 1.1 shows the hits for a search for “risk” related to nanotechnology in the Web of Science. Publications that deal in one way or other with “risk” have skyrocketed in the last few years since 2002.

The same properties that can be deleterious for the environment can be advantageous for technical applications and are exploited for treatment and remediation. Figure 1.2 shows a few examples of this Janus face of nanotechnology: engineered particles with high mobility are needed for efficient groundwater remediation, but at the same time this property will render a particle more difficult to remove during water treatment. The toxicity of some nanoparticles can be used for water disinfection where killing of microorganisms is intended, whereas the same property is unwanted