

# **GREEN CHEMISTRY**

**Designing Chemistry  
for the Environment**

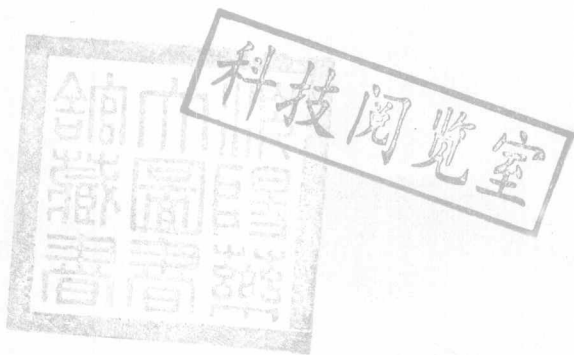


**EDITED BY**

**Paul T. Anastas and Tracy C. Williamson**

**ACS Symposium Series 626**

# Green Chemistry



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# Green Chemistry

## Designing Chemistry for the Environment

**Paul T. Anastas, EDITOR**

**Tracy C. Williamson, EDITOR**

*Office of Pollution Prevention and Toxics  
U.S. Environmental Protection Agency*

Developed from a symposium sponsored  
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## Foreword

THE ACS SYMPOSIUM SERIES was first published in 1974 to provide a mechanism for publishing symposia quickly in book form. The purpose of this series is to publish comprehensive books developed from symposia, which are usually "snapshots in time" of the current research being done on a topic, plus some review material on the topic. For this reason, it is necessary that the papers be published as quickly as possible.

Before a symposium-based book is put under contract, the proposed table of contents is reviewed for appropriateness to the topic and for comprehensiveness of the collection. Some papers are excluded at this point, and others are added to round out the scope of the volume. In addition, a draft of each paper is peer-reviewed prior to final acceptance or rejection. This anonymous review process is supervised by the organizer(s) of the symposium, who become the editor(s) of the book. The authors then revise their papers according to the recommendations of both the reviewers and the editors, prepare camera-ready copy, and submit the final papers to the editors, who check that all necessary revisions have been made.

As a rule, only original research papers and original review papers are included in the volumes. Verbatim reproductions of previously published papers are not accepted.

## Preface

**G**REEN CHEMISTRY focuses on the design, manufacture, and use of chemicals and chemical processes that have little or no pollution potential or environmental risk and are both economically and technologically feasible. The principles of green chemistry can be applied to all areas of chemistry including synthesis, catalysis, reaction conditions, separations, analysis, and monitoring.

The chemical industry in the United States releases more than 3 billion tons of chemical waste each year to the environment. Industry then spends \$150 billion per year in waste treatment, control, and disposal costs. The challenge for chemists involved at all stages of chemical design, manufacture, and use is to make incremental changes that, when summed, will achieve significant accomplishments in the design of new products and processes that are less polluting and hazardous to the environment.

The symposium upon which this book is based was organized by Joseph J. Breen and Allan Ford under the auspices of the Division of Environmental Chemistry, Inc. This book is composed primarily of topics that were presented at sessions of the symposium that were chaired by the editors of this volume. In addition, presentations from another session of the same symposium that focused on environmentally benign chemistry research in the international arena, chaired by Steven Hassur, have also been included.

This book presents the current research efforts and recent results of leaders in the field of green chemical syntheses and processes. The projects described cover a range of topics that are broadly applicable to the chemical industry as well as to chemical education. As such, this book should appeal to chemists from academia, industry, and government who are involved in fundamental research, methods development and application, education, and decision making. Our hope is that this book will provide a wealth of information to chemists involved in chemical synthesis and processing at the research, applied, and management levels and will also act as a catalyst in stimulating many more chemists to become involved in the design and use of chemical syntheses and processes in an environmentally responsible manner.



## **Disclaimer**

We edited this book in our private capacities. No official support or endorsement of the U.S. Environmental Protection Agency is intended or should be inferred.

## **Acknowledgments**

We thank the many people who contributed their time and efforts toward making this volume possible. The dedication of Joseph Breen in furthering the cause of green chemistry through all avenues and specifically for his role in organizing the Design for the Environment Symposium is valued and appreciated. We also recognize the Division of Environmental Chemistry, Inc., and Allan Ford for their contributions to the symposium. The assistance of Margaret Cavanaugh and Maria Burka in identifying individuals for the original symposium sessions is much appreciated. We also thank Steven Hassur for his role in organizing the international session of the symposium.

Chemists who dedicated their time to provide insight and support for this book include: Steven DeVito, Russell Farris, Carol Farris, Daniel Lin, Daniel Bushman, Jenny Tou, Caroline Weeks, Diana Darling, Steven Hassur, Paul Tobin, Paul Bickart, Gregory Fritz, and Fred Metz. Many thanks to Rhonda Bitterli, whose guidance was essential to getting this volume initiated. Thanks to the ACS Books Department Staff, including Barbara Pralle and Charlotte McNaughton. And most of all, thanks to each of the authors whose outstanding efforts have made this volume so valuable.

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December 12, 1995

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## Chapter 1

# Green Chemistry: An Overview

Paul T. Anastas and Tracy C. Williamson

Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, Mail Code 7406, 401 M Street, S.W., Washington, DC 20460

Green Chemistry is an approach to the synthesis, processing and use of chemicals that reduces risks to humans and the environment. Many innovative chemistries have been developed over the past several years that are effective, efficient and more environmentally benign. These approaches include new syntheses and processes as well as new tools for instructing aspiring chemists how to do chemistry in a more environmentally benign manner. The benefits to industry as well as the environment are all a part of the positive impact that Green Chemistry is having in the chemistry community and in society in general.

Over the past few years, the chemistry community has been mobilized to develop new chemistries that are less hazardous to human health and the environment. This new approach has received extensive attention (*1-16*) and goes by many names including Green Chemistry, Environmentally Benign Chemistry, Clean Chemistry, Atom Economy and Benign By Design Chemistry. Under all of these different designations there is a movement toward pursuing chemistry with the knowledge that the consequences of chemistry do not stop with the properties of the target molecule or the efficacy of a particular reagent. The impacts of the chemistry that we design as chemists are felt by the people that come in contact with the substances we make and use and by the environment in which they are contained.

For those of us who have been given the capacity to understand chemistry and practice it as our livelihood, it is and should be expected that we will use this capacity wisely. With knowledge comes the burden of responsibility. Chemists do not have the luxury of ignorance and cannot turn a blind eye to the effects of the science in which we are engaged. Because we are able to develop new chemistries that are more benign, we are obligated to do so.

This volume details how chemists from all over the world are using their creativity and innovation to develop new synthetic methods, reaction conditions, analytical tools, catalysts and processes under the new paradigm of Green Chemistry. It is a challenge for the chemistry community to look at the excellent work that has been and continues to be done and to ask the question, "Is the chemistry *I* am doing the most benign that I can make it?"

One obvious but important point: nothing is benign. All substances and all activity have some impact just by their being. What is being discussed when the term benign by design or environmentally benign chemistry is used is simply an ideal. Striving to make chemistry more benign wherever possible is merely a goal. Much like the goal of "zero defects" that was espoused by the manufacturing sector, benign chemistry is merely a statement of aiming for perfection.

Chemists working toward this goal have made dramatic advances in technologies that not only address issues of environmental and health impacts but do so in a manner that satisfies the efficacy, efficiency and economic criteria that are crucial to having these technologies incorporated into widespread use. It is exactly because many of these new approaches are economically beneficial that they become market catalyzed. While most approaches to environmental protection historically have been economically costly, the Green Chemistry approach is a way of alleviating industry and society of those costs.

### What is Green Chemistry?

While it has already been mentioned that nothing is truly environmentally benign, there are substances that are known to be more toxic to humans and more harmful to the environment than others. By using the extensive data available on human health effects and ecological impacts for a wide variety of individual chemicals and chemical classes, chemists can make informed choices as to which chemicals would be more favorable to use in a particular synthesis or process. Simply stated, Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc., that are hazardous to human health or the environment.

Green Chemistry is a fundamental and important tool in accomplishing pollution prevention. Pollution prevention is an approach to addressing environmental issues that involves preventing waste from being formed so that it does not have to be dealt with later by treatment or disposal. The Pollution Prevention Act of 1990 (17) established this approach as the national policy of United States and the nation's "central ethic" (18) in dealing with environmental problems.

There is no doubt that over the past 20 years, the chemistry community, and in particular, the chemical industry, has made extensive efforts to reduce the risk associated with the manufacture and use of various chemicals. There have been innovative chemistries developed to treat chemical wastes and remediate hazardous waste sites. New monitoring and analytical tools have been developed for detecting contamination in air, water and soils. New handling procedures and containment technologies have been developed to minimize exposure. While these areas are laudable efforts in the reduction of risk, they are not pollution prevention or Green

Chemistry, but rather are approaches to pollutant control. Many different ways to accomplish pollution prevention have been demonstrated and include engineering solutions, inventory control and "housekeeping" changes. Approaches such as these are necessary and have been successful in preventing pollution, but they also are not Green Chemistry. There is excellent chemistry that is not pollution prevention and there are pollution prevention technologies that are not chemistry. Green Chemistry is using chemistry for pollution prevention.

No one who understands chemistry, risk assessment and pollution prevention would claim that assessing which substances or processes are more environmentally benign is an easy task. To the contrary, the implications of changing from one substance to another are often felt throughout the life-cycle of the product or process. This difficulty for obtaining a quantifiable measurement of environmental impact has been, however, too often used historically as a rationale for doing nothing. The fact is that for many products and for many processes, clear determinations can be made. Many synthetic transformations have clear advantages over others, and certain target molecules are able to achieve the same level of efficacy of function while being significantly less toxic.

It is important that chemists develop new Green Chemistry options even on an incremental basis. While all elements of the lifecycle of a new chemical or process may not be environmentally benign, it is nonetheless important to improve those stages where improvements can be made. The next phase of an investigation can then focus on the elements of the lifecycle that are still in need of improvement. Even though a new Green Chemistry methodology does not solve at once every problem associated with the lifecycle of a particular chemical or process, the advances that it does make are nonetheless very important.

This volume highlights some of the many advances currently being made in Green Chemistry that are everything from incremental to universal in their impact on the problems that they are addressing. The work described is pioneering and highly innovative, and will provide an information data set of proven Green Chemistry methods and techniques that chemists in the future will need in order to be able to design entire synthetic pathways and processes that are more environmentally benign.

### **Why is Green Chemistry Important?**

In 1993, 30 billion pounds of chemicals were released to air, land and water as tracked by the Toxic Release Inventory of the U.S. Environmental Protection Agency (see Figure 1). While this data covers releases from a variety of industrial sectors, it includes only 365 of the approximately 70,000 chemicals available in commerce today. Of the industrial sectors that are covered by the toxic release inventory, the chemical manufacturing sector is understandably the largest releaser of chemicals to the environment, releasing more than 4 times as many pounds to the environment as the next highest sector (see Figure 2).

The current status of environmental protection in the United States is constructed from a generation of statutes and regulations. The vast majority of these regulations were written at a time where command and control approaches to environmental protection was the order of the day. Many of these laws require

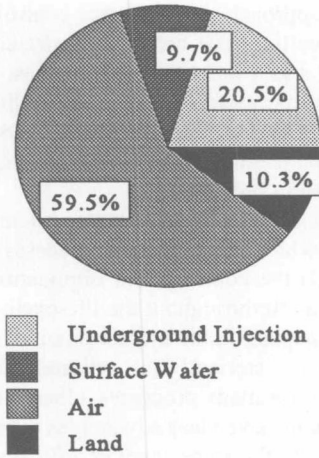


Figure 1. Distribution of Chemical Releases to the Environment

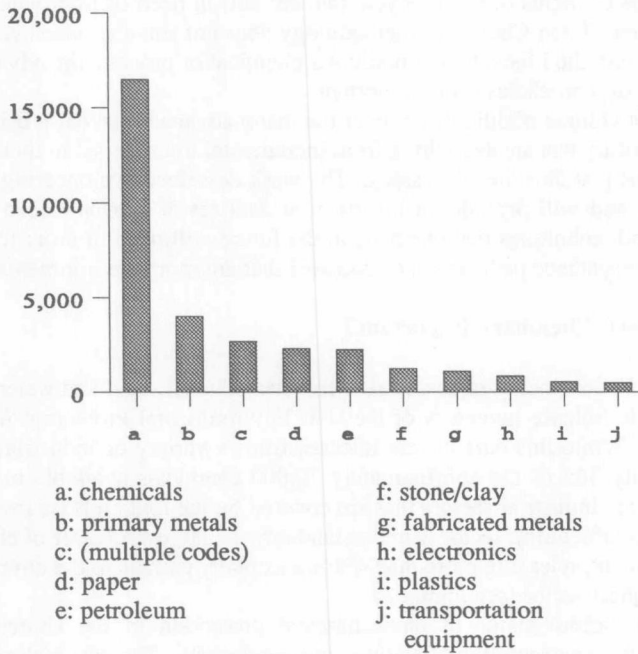


Figure 2. Chemical Releases by Industry Sector (in millions of pounds)



companies either explicitly through methodology-based regulations or implicitly through performance-based regulations to have a variety of waste handling, treatment, control and disposal processes in place to meet environmental mandates. Often these process include equipment with fairly high capital costs.

On a societal level, it is clear that the true costs of the environmental impacts due to the manufacture, processing, use and disposal of all products have not been fully incorporated into the price of the goods. These costs are contained in site remediation, health care expenditures and ecosystem destruction. Therefore, from an economic standpoint, it is clear that we not only want to have sustainable technology but we want it to be cost neutral at a minimum and profitable when at all possible.

The challenge facing industry and society at large is extending technological innovation in a way that is sustainable both economically and environmentally. Certainly the chemical industry has met this challenge economically. In the United States, the chemical industry accounts for the second largest trade surplus of all industrial sectors. With respect to environmental protection, many industrial sectors have made significant progress in reducing emissions over the past decade (see Figure 3). Yet, even with these improvements, the impact of the manufacture, processing, use and disposal of chemicals is staggering.

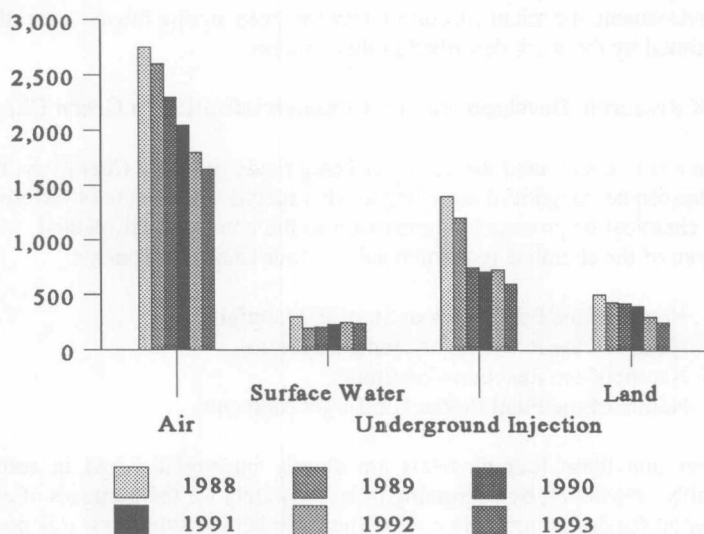


Figure 3. Change in Total Chemical Releases

Green Chemistry provides the best opportunity for manufacturers, processors and users of chemicals to carry out their work in the most economically and environmentally beneficial way. With the challenges facing industry including