GREEN CHEMISTRY

THEORY AND PRACTICE

Paul T. Anastas
John C. Warner

Green Chemistry: Theory and Practice

Paul T. Anastas

*Office of Pollution Prevention and Toxics,
US Environmental Protection Agency, Washington, DC, USA*

John C. Warner

*Department of Chemistry,
University of Massachusetts, Boston, USA*

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Preface

Green chemistry is not different from traditional chemistry inasmuch as it embraces the same creativity, and innovation that has always been central to classical chemistry. Green chemistry merely pursues those same ideals with additional considerations to those incorporated into the design and implementation of chemistry historically. These considerations, described in this book, reflect the power that the chemist holds not only over the disposition of the chemistry that is created, but also over all of the implications of the chemistry, from its creation, to its use, until its destruction and beyond. Beyond, because a chemist can not only design a substance to have certain characteristics during its useful life, but can also design what that substance will become (or break down into) after its useful life is over.

This book is not a moral judgment on chemistry but it does elucidate the obligations that chemists, as scientists, have in making choices when designing chemical methodologies. Chemistry itself can be neither 'good' nor 'bad' in a moral sense, as it is merely a natural phenomenon following physical laws. Chemists, however, possess the knowledge and skills to make decisions in the practice of their trade that can result in immense benefit to society or cause harm to life and living systems and they therefore have responsibility for the character of the decisions made. So, while the science of chemistry can be neither holy nor evil, people of either amoral, ignorant, or irresponsible character have misused chemistry and have created a popular disdain for the 'central science' and those who make it their trade.

Basic research in green chemistry is needed. The discovery and development of fundamental chemical transformations that are not harmful to the environment will be the driving force that moves this area forward. Applications of these discoveries will be and have been utilized both for economic and scientific reasons. These methodologies have the potential to affect every aspect of life, just as the field of chemistry has done in the past. Because a synthetic methodology is not sentient, it does not know if it is going to wind up making a pharmaceutical, a paint, or a food additive and thus have a positive impact on all of those chemical products.

It is the chemist who makes these discoveries. It is the chemist who creates the tools, the synthetic methods, that are used throughout industry. Ultimately, because of this role, it is the chemist who has the responsibility for the character of the tools that are in the toolbox. Fortunately for society, it is these same chemists who are solely, uniquely qualified to make those decisions and those discoveries. Green chemistry utilizes the same skills that chemists have always used throughout the history of the science. This book strives to provide a basis and a framework for pursuing the science in the most creative, innovative, and responsible manner possible.

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1 *Introduction*

1.1 The current status of chemistry and the environment

The status of chemistry in society is a profound dichotomy of perceptions, and neither of these perceptions are in consistent agreement with the facts. While those engaged in the science and industry of chemistry hail the accomplishments that have come from the central science, there are a large number of people who view chemicals and chemistry as something to be afraid of, curtailed, and avoided wherever possible. Neither of these perspectives can possibly capture the full vision of chemistry because it encompasses the characterization, interaction, and manipulation of all matter. The true nature of chemistry, therefore, is complex and vast, as is its effect.

Chemistry has resulted in the medical revolution of the past century in which drugs such as antibiotics have been used to cure diseases that have ravaged mankind for millennia. These advances, brought about by chemistry, have resulted in the average life expectancy rising from 47 in 1900, to 75 years in the 1990s.[1] The world's food supply has seen an explosive expansion in this century because of the development of chemicals that protect crops and enhance growth. In virtually every arena and every aspect of material life – transportation, communication, clothing, shelter, etc. – chemistry has resulted in an improvement, not merely in the trappings of life, but also in the quality of the lives of the billions of individuals who now inhabit the planet.

These almost unbelievable achievements have come at a price. That price is the toll that the manufacture, use, and disposal of synthetic chemicals have taken on human health and the environment. The United States keeps a record of releases of toxic chemicals to the environment by industry, called the Toxics Release Inventory (TRI). The TRI,[2] established under the Emergency Planning and Community Right-to-Know Act, tracks the release of chemicals and classes of chemicals by a variety of sectors of industry on a facility-by-facility basis. While this process provides extremely useful information that was not known prior to its inception in 1986, the chemicals that it covers are only a small fraction of the approximately 75 000 substances in commercial use today and so the amounts of chemicals released to the environment are staggering.

For the 1994 reporting year, there were 2.26 billion pounds of the approximately 300+ hazardous substances released to the environment. At that rate, in the time that it would take you to read one page of this book, over one ton of hazardous waste will have been released to the air, water, and land by industry. The greatest release of hazardous waste to the environment is the chemical industry (Fig. 1.1). Of the top ten industrial sectors whose releases are tracked by the TRI, the chemical industry, including metals, releases more pounds of waste to the environment than the other nine industrial sectors combined.

1.2 Evolution of the environmental movement

1.2.1 Public awareness

It is only fairly recently that the issue of the 'environmental impact' of chemical substances has come into the public dialogue and been fully recognized as a problem. In the years following World War II, there were little or no environmental regulations to speak of that effected the manner in which chemical substances could be manufactured, used, or disposed of. It wasn't until the late 1950s and early 1960s that concern developed over how chemical substances may cause harm to human health and the environment.

In 1962, Rachael Carson wrote the book *Silent Spring*, which detailed the effects of certain pesticides on the eggs of various birds.[3] It illustrated how the use of DDT and other pesticides could spread throughout the food chain, causing irreparable and unanticipated harm. It was the unanticipated nature of the harm that caused a public outcry and resulted in regulatory controls on pesticides which are manufactured and used in the United States.

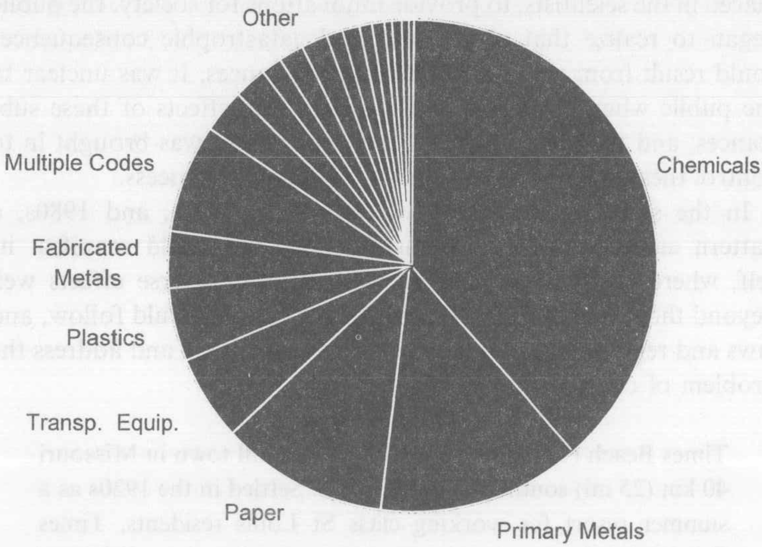

Fig. 1.1. Proportion of hazardous waste released to the environment by the major industrial sectors.[4]

In 1961, there was a scare in Europe about a substance called thalidomide, which was used by pregnant women to lessen the effects of nausea and vomiting during pregnancy ('morning sickness'). As a result of using this drug, the children of the women taking the drug suffered acute birth defects, in many cases in the form of missing or grossly deformed limbs. About 10 000 such children were born world-wide, with 5000 in Germany alone. (Doubts concerning the drug's safety had prevented its sale in the United States.) The tragedy led to stringent governmental regulations for testing new drugs for teratogenic (malformation-inducing) hazards. These 'thalidomide babies', as they are sometimes referred to, caused a great deal of fear in the general public about the effects of synthetic chemicals and the unintended effects that they could have on humans.

In both of the above cases, the public was well aware that the substances in question were designed by scientists, people that the public felt had a great deal more knowledge than they about the chemicals that were being made. Despite the confidence that they had placed in the scientists, to provide innovations for society, the public began to realize that unintended and catastrophic consequences could result from the use of chemical substances. It was unclear to the public whether anyone could control the effects of these substances, and the result was that the government was brought in to control these substances through the regulatory process.

In the subsequent decades of the 1960s, 1970s, and 1980s, a pattern emerged: an environmental problem would manifest itself, where chemical substances were having adverse effects well beyond their intended use, a vocal public outcry would follow, and laws and regulations would be generated to govern and address the problem of chemicals in the environment.

> Times Beach (1983 est. pop. 2000) is a small town in Missouri 40 km (25 mi) south-west of St Louis. Settled in the 1920s as a summer resort for working class St Louis residents, Times Beach soon became a permanent community of small homes and trailer parks. In 1982 the soil along the roads in Times Beach was found to be contaminated with the toxic chemical dioxin. [The town was one of at least 26 and perhaps as many as 100 sites in Missouri that may have been contaminated when dioxin-tainted waste oil was sprayed on the roads a decade ago. The level of dioxin in the soil at these sites varied from around 300 to 740 parts per billion. The federal Center for Disease Control (CDC) rates soil with dioxin readings of over one part per billion as unsafe for long-term contact.] The problems of Times Beach residents were compounded by a flood in late 1982, which forced about 700 families to leave their homes. Government officials urged residents not to attempt to clean up the contaminated mud and debris that had been deposited in their homes by the flood. The federal government provided temporary shelter and, in an unprecedented decision, arranged to buy the entire town, using $33 million from the special fund for toxic waste clean-up.

In addition to the Times Beach situation there were other environmental disaters occurring in the same time-frame. One that caught the public's attention was Love Canal.

> Long-term contamination was involved in the disastrous events at the Love Canal in Niagara Falls, NY. A chemical and plastics company had used an old canal bed in this area as a chemical dump from the 1930s to the early 1950s. The land was given to the city of Niagara Falls in 1953, and a new school and a housing tract were built on it. In 1971, the chemical substances that had been dumped there years before began leaking through the clay cap that sealed the dump, and the area was contaminated by at least 82 chemicals, including a number of suspected carcinogens: benzene, some chlorinated hydrocarbons, and dioxin. Health effects that were linked to the chemical exposure at Love Canal included high birth defect and miscarriage rates, as well as liver cancer and a high incidence of seizure-inducing nervous disease among the neighborhood children. The region was declared an official disaster area. The state paid $10 million to buy some of the homes and another $10 million to try to stop the leakage. About 1000 families had to be relocated. Portions of the site were cleaned up sufficiently by 1990 for houses located there to be put up for sale.

Both the Times Beach and Love Canal events caused sufficient public dismay to prompt the United States Congress to pass new laws to deal with the particular problems that were of the highest visibility. Congress passed the law that became known as Superfund, which would require the clean-up of designated toxic waste sites throughout the country.

Environmental disasters have often resulted in new, and specific, laws being enacted. In the early 1970s, the Cuyahoga River in Ohio was so acutely polluted that it caught fire. The sight of a major river in flames because of chemical pollution prompted calls for legislation to ensure clean water controls through regulation. Nightly news reports showing the brown haze of the Los Angeles or Pittsburgh skylines of the 1960s and 1970s resulted in a variety of Clean Air legislation, including the Clean Air Act. In the 1980s, as the nature of the impact of chlorofluorocarbons (CFCs) on the stratospheric ozone layer became clearer through the use of satellite photographs and the work of Nobel laureate chemists Rowland and Molina, the Montreal Protocol which first called for CFCs to be phased out was adopted. Accidental chemical disasters such as the tragedy at Bhopal, India, where hundreds of people were killed as a result of an accident at a Union Carbide plant that generated the extremely toxic methyl isocyanate, generated the Emergency Planning and Community Right-to-Know Act of 1986.

All of these examples are of unforeseen chemical consequences resulting in tragedy, and the tragedy resulting in public outrage, and the public outrage resulting in legislation to control the manufacture, use, or disposal of chemical substances. But the question should be asked, what has been the nature of these new laws to control chemical substances and are they the only way or the most effective way of protecting human health and the environment from unanticipated outcomes?

1.2.2 'Dilution is the solution to pollution'

During the period prior to the advent of laws that control the release of chemical substances to the environment and significant exposure to people, it was not uncommon for substances to be released directly to the air, water, and land for final disposal. At the time, it was thought that mere decrease of concentration of a substance in a particular medium would be sufficient to mitigate its ultimate impact. This practice and the underlying thinking was sometimes summarized as 'dilution is the solution to pollution'. As absurd as this philosophy is now known to be, it was espoused at a time when factors such as chronic toxicity, bioaccumulation, and even carcinogenicity were not nearly as well understood as they are now.

1.2.3 Waste treatment and abatement through command and control

As toxicity end-points and environmental effects became better known, environmental laws reflected this knowledge by strictly controlling the amounts of a substance that could be released into any particular receiving stream. This first approach to the 'command and control' method of environmental regulation often uses standards or guideline concentrations, e.g. maximum concentration guideline levels (mcgls), to dictate what levels of a particular chemical can be present in the water without adversely affecting humans or the environment.

One of the major shortcomings of this regulatory approach is that it does not usually consider the synergistic effects of other substances present in the water with that of the regulated substance. If a substance that was regulated at a certain concentration resulted in deleterious effects when present in the water with a second, unregulated, substance at a certain concentration level, the public may not be adequately protected from harmful exposures to these substances. The shortcoming of not being able to regulate synergistic effects adequately is widespread throughout current environmental regulations and is not exclusively a problem with regulating concentrations of a substance through command and control.

As environmental regulations progressed, there was an increased emphasis on either treatment of wastes prior to their release, or abatement of the wastes subsequent to their release, in order to mitigate the risks to human health and the environment. Through the use of treatment technologies ranging from neutralization of acids, to scrubbers for air stack emissions, to incineration, environmental statutes required that wastes be transformed into more innocuous forms in order to minimize the impacts of chemical substances.

1.2.4 Pollution prevention

In 1990, the Pollution Prevention Act (PPA), which evolved from the traditional approach of command and control and treatment and abatement, was passed by the United States Congress.[5] The PPA sets a national environmental policy that states that the option of first choice is to prevent the formation of waste at the source. By utilizing a variety of methodologies and techniques, pollution can be prevented, thereby obviating the need for any further treatment or control of chemical substances (Fig. 1.2).