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Toward Sustainable Chemistry

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Chemistry has an important role to play in achieving a sustainable civilization on Earth. The present economy remains utterly dependent on a massive inward flow of natural resources that includes vast amounts of nonrenewables. This is followed by a reverse flow of economically spent matter back to the ecosphere. Chemical sustainability problems are determined largely by these economy-ecosphere material flows (see the figure, below), which current chemistry education essentially ignores. It has become an imperative* that chemists lead in developing the technological dimension of a sustainable civilization.



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Ecospherical responsibility of chemists. Diagram based on ideas of Herman E. Daly.

When chemists teach their students about the compositions, outcomes, mechanisms, controlling forces, and economic value of chemical processes, the attendant dangers to human health and to the ecosphere must be emphasized across all courses. In dedicated advanced courses, we must challenge students to conceive of sustainable processes and orient them by emphasizing through concept and example how safe processes can be developed that are also profitable.

Green or sustainable chemistry[†] can contribute to achieving sustainability in three key areas. First, renewable energy technologies will be the central pillar of a sustainable high-technology civilization. Chemists can contribute to the development of the economically feasible conversion of solar into chemical energy and the improvement of solar to electrical energy conversion. Second, the reagents used by the chemical industry, today mostly derived from oil, must increasingly be obtained from renewable sources to reduce our dependence on fossilized carbon. This important area is beginning to flourish, but is not the subject of this essay. Third, polluting technologies must be replaced by benign alternatives. This field is receiving considerable attention, but the dedicated research community is small and is merely scratching the surface of an immense problem that I will now sketch.

Many forces give rise to chemical pollution, but there is one overarching scientific reason why chemical technology pollutes. Chemists developing new processes strive principally to achieve reactions that only produce the desired product. This selectivity is achieved by using relatively simple reagent designs and employing almost the entire periodic table to attain diverse reactivity. In contrast, nature accomplishes a huge range of selective biochemical processes mostly with just a handful of environmentally common elements. Selectivity is achieved through a reagent design that is much more elaborate than the synthetic one. For example, electric eels can store charge via concentration gradients of biochemically common alkali metal ions across the membranes of electroplaques. In contrast, most batteries used for storing charge require biochemically foreign, toxic elements, such as lead and cadmium. Because of this strategic difference, manmade technologies often distribute throughout the environment persistent pollutants that are toxic because they contain elements that are used sparingly or not at all in biochemistry.

Persistent bioaccumulative pollutants pose the greatest chemical threat to sustainability. They can be grouped into two classes. Toxic elements are the prototypical persistent pollutants; long-lived radioactive elements are especially dangerous examples. New toxicities continue to be discovered for biologically uncommon elements. The second class consists of degradation-resistant molecules. Many characterized examples originate from the chlorine industry[‡] and are also potently bioaccumulative. For example, polychlorinated dibenzo-dioxins and -furans (PCDDs and PCDFs) are deadly, persistent organic pollutants. They can form in the bleaching of wood pulp with chlorine-based oxidants, the incineration of chlorine-containing compounds and organic matter, and the recycling of metals. The United Nations Environmental Program (UNEP) International Agreement on persistent organic pollutants lists 12 "priority" pollutant compounds and classes of compounds for global phaseout. All are organochlorines.

Imagine all of Earth's chemistry as a mail sorter's wall of letter slots in a post office, with the network of compartments extending toward infinity (see the figure, below). Each compartment represents a separate chemistry so that, for example, thousands of compartments are associated with stratospheric chemistry or with a human cell. An environmentally mobile persistent pollutant can move from compartment to compartment, sampling a large number and finding those compartments that it can

perturb. Many perturbations may be inconsequential, but others can cause unforeseen catastrophes, such as the ozone hole or some of the manifestations of endocrine disruption.[§] Most compartments remain unidentified and even for known compartments, the interactions of the pollutant with the compartment's contents can usually not be foreseen, giving ample reason for scientific humility when considering the safety of persistent mobile compounds. We should heed the historical lesson that persistent pollutants are capable of environmental mayhem, and treat them with extreme caution. In cases where the use of a persistent pollutant is based on a compelling benefit, as with DDT (dichlorodiphenyltrichloroethane) in malaria-infested regions, chemists must face the challenge of finding safe alternatives.



The chemistry of the ecosphere viewed as a mail sorter's network.

Consider, for instance, the alarming reproductive damage that can be inflicted by minute quantities of endocrine-disrupting chemicals (EDCs), such as PCDDs, polychlorobiphenyls (PCBs), and the pesticides endosulfan and atrazine.[‡] EDCs disrupt the body's natural control over the reproductive system by mimicking or blocking the regulatory functions of the steroid hormones or altering the amounts of hormones in the body. Uncertainty still clouds our understanding of their full impact, but mass sterilization is one limiting conceivable outcome of ignoring the demonstrated dangers of EDCs. Our present knowledge strongly suggests that anthropogenic EDCs should be identified and eliminated altogether.

Stringent regulations based on the precautionary principle and the principle of "reversed onus"[‡] should be developed to guard against the release of new environmentally mobile persistent compounds; a precise definition of persistence also needs to be developed. This would provide a regulatory foundation for weeding persistent bioaccumulative compounds out of all technology, and highlight where research is needed to find safe alternatives. Groundbreaking legislative proposals toward this goal are about to be considered in the Swedish Parliament.

In their current formal training, all chemistry students will learn that the chlorination of phenol proceeds by a mechanism known as electrophilic aromatic substitution. But very few will learn of EDCs and their dangers or come to know that prime examples of EDCs, namely PCDDs, are produced in trace quantities whenever phenol is chlorinated. This hazardous omission illustrates one important type of content that is simply missing from the conventional curriculum.

Green chemistry can dramatically reduce environmental burdens of both classes of persistent pollutants by moving the elemental balance of technology closer to that of biochemistry. Significant reductions in the dispersal of many persistent pollutants have already been achieved. By the late 17th century, the use of lead oxide as a correcting agent for acidic wine was banned on pain of death in

Ulm in the duchy of Wurtemberg.[‡] More recently, large reductions in lead pollution have been achieved in what are recognizable examples of green chemistry, for instance, by replacement of lead additives in paint with safe alternatives, by the development of cleaner batteries, and by the as yet unfinished and sometimes flawed progression away from tetraethyl lead toward safer combustion promoters in fuels. PCDDs and PCDFs have been greatly reduced in the pulp and paper industry by the replacement of chlorine with chlorine dioxide as the principal bleaching agent.

Nevertheless, much more can and must be done. For example, chlorine-based oxidations such as pulp bleaching, water disinfection, household and institutional cleaning, and clothing care continue to produce huge volumes of organochlorine-containing effluent. Despite industry efforts to reduce pollutant concentrations, some of the inescapable trace contaminants are persistent, bioaccumulative carcinogens and/or EDCs. Chlorine-based oxidation technologies could be replaced with alternatives based on catalytic activation of nature's principal oxidizing agents, oxygen or hydrogen peroxide. My research group has patented TAML activators, which are potent but selective peroxide-activating catalysts comprised of biochemically common elements for these and other fields of use. Environmental considerations also underpin the worldwide investigation and development of supercritical and near-critical carbon dioxide as a clean solvent. The present search for safer solvents in the green chemistry community is distinguished by a remarkable burst of creativity that perhaps reaches its zenith in ionic liquids. These solvents have unique properties such as the absence of any vapor pressure under standard conditions.

Pollutant production can also be reduced by improving process selectivity, reducing energy intensity, and minimizing the flow of matter to and from the ecosphere via atom economic processes, that is, processes optimized to reduce per unit of product the quantities of chemicals employed in the reactions as solvents and reagents or produced as by-products.

To achieve such sustainable chemistry requires a sea change in the chemical community. The principles of green or sustainable chemistry must become an integral part of chemical education and practice. However, there are several obstacles to overcome. First, chemists need to comprehensively incorporate environmental considerations into their decisions concerning the reactions and technologies to be developed in the laboratory. These questions need to become as important as those associated with the selectivity of the technology and how it works. Principles upon which to base these decisions have already been developed.[†] Second, it is critical that chemistry that is not really green does not get sold as such, and that the public is not misled with false or insufficient safety information. For example, certain chlorine industry companies have sought to protect their profits by distorting scientific data to make dioxins appear to be less harmful to humans than they actually are.[‡] The general trust that chemical risk is treated in a fair and reasonable manner must be strengthened. Third, since many chemical sustainability goals such as those associated with solar energy conversion call for ambitious, highly creative research approaches, short-term and myopic thinking must be avoided. Government, universities, and industry must learn to value and support research programs that do not rapidly produce publications, but instead present reasonable promise of promoting sustainability. Fourth, chemistry exerts a near boundless influence on human action and is thus inextricably intertwined with ethics. An understanding of sustainability ethics* is therefore an essential component of a healthy chemical education.

The all-encompassing challenge lying before green chemists is to understand the ethical forces, chemical-ecosphere relations, educational needs, and research imperatives that sustainability brings center stage and to reconcile this understanding as much as possible with economic maxims. If chemists increasingly direct their strengths to contributing to a sustainable civilization, chemistry will

become more interesting and compelling to people, and may lose its "toxic" image. It will become more worthy of public support and spawn exciting economic enterprises that nurture sustainability.

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