Teaching and Learning about Sustainability

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Teaching and Learning about Sustainability

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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 the series is to publish timely, comprehensive books developed from the ACS sponsored symposia based on current scientific research. Occasionally, books are developed from symposia sponsored by other organizations when the topic is of keen interest to the chemistry audience.

Before agreeing to publish a book, the proposed table of contents is reviewed for appropriate and comprehensive coverage and for interest to the audience. Some papers may be excluded to better focus the book; others may be added to provide comprehensiveness. When appropriate, overview or introductory chapters are added. Drafts of chapters are peer-reviewed prior to final acceptance or rejection, and manuscripts are prepared in camera-ready format.

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

ACS Books Department

Preface

> *"For the goals to be reached, everyone needs to do their part: Governments, the private sector, civil society and people like you."*
>
> Sustainable Development Goals
> United Nations, 2015

Yes, we each need to do our part. People like you.

We need to do our part in technical divisions, like those to which you belong. And we need to do our part in our professional society, the American Chemical Society.

This book in the ACS Symposium Series involved many who did their part setting and achieving goals related to sustainability. The idea for this symposium originated with a brainstorming session hosted by CEI, the ACS Committee on Environmental Improvement. At this session, we championed the idea of hosting a symposium that would feature approaches to sustainability from the perspective of those in different technical divisions. We envisioned a symposium that would be an oral version of the popular Sci-Mix poster session at national meetings. We called this symposium **Sustain-Mix!**

With generous support of an Innovative Programming Grant from the ACS Divisional Activities Committee, we offered hospitality to those who spoke and who attended. The Division of Chemical Education (CHED) hosted the symposium, and we charged each speaker with the task of discussing ways in which chemists in that division were working toward the goal of sustainability.

The goals of **Sustain-Mix** were two-fold. First, we aimed to provide a forum in which examples of sustainability in a wide variety of chemical contexts will be discussed, all of potential use in our classrooms or laboratories. Second, we hoped to seed ideas about cross-divisional work that we might be able to do in the future.

In the end, we were delighted to host speakers from 26 technical divisions of the 32 divisions currently in the ACS. Additionally we heard from three outstanding keynote speakers, Matthew Fisher, Catherine Hunt, and Mary Kirchhoff, who opened each of the three half-day sessions.

This book is a glimpse into that program, showcasing the work of many of the presenters who assembled in San Francisco in the summer of 2014.

We gratefully acknowledge these students from Gordon College: Caitlyn Alekshun, Jasmine Johnson, Joshua McLaughlin, Emily Ryan, and John Sexton. They assisted in the preparation of this book by transcribing the lectures for the benefit of the authors.

We hope that the narratives shared by each of our authors will inspire educators to tell stories that in turn will inspire action by their students – the chemists and citizens of tomorrow. All of us need to do our part, seeking paths to a chemical enterprise that meets the needs of the present without compromising the ability of future generations to meet their own needs.

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Editors' Biographies

Irvin J. Levy

Irv Levy is Professor of Chemistry and Chair of the Department of Chemistry at Gordon College in Wenham, MA, where he has served on the faculty since 1985. His professional interests in chemistry are primarily related to the development of educational resources for green chemistry. Current projects involve the creation of green organic chemistry laboratory experiments, the introduction of toxicology into the chemistry curriculum, and community outreach via green chemistry. With his students' help, he has introduced thousands of people to the principles of green chemistry through the development of his *Greener Organic Literacy forum* program. He is a fellow of the Royal Society of Chemistry, Program Chair of the ACS Division of Chemical Education, and a board member for the Beyond Benign Foundation.

Catherine H. Middlecamp

Cathy Middlecamp is a professor in the Nelson Institute for Environmental Studies at the University of Wisconsin-Madison. Her scholarship lies at the intersection of science, people, and the planet. Sustainability education, especially in the context of using the campus as a living-learning laboratory, is the focal point of her graduate student team. She was the editor-in-chief for the 7th and 8th editions of *Chemistry in Context*, a 25-year national curriculum project of the American Chemical Society that engages undergraduates in learning chemistry in the context of real-world issues. Working on the project since 1996, she has served as the lead author for the chapters on air quality, acid rain, ozone depletion, polymers, food, nuclear energy, and sustainability. Middlecamp is a fellow of the AAAS (2004), a fellow of the ACS (2009), and the chair of the ACS Division of Chemical Education (2016).

Chapter 1

Hearing the Cries of the World

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“Improving people’s lives through the transforming power of chemistry” is the vision statement of the American Chemical Society (ACS). One of the great challenges of the 21st century is that of sustainability. Several definitions of sustainability, including the widely quoted one from the Brundtland Commission report as well as the National Research Council report *Our Common Planet,* highlight the importance of meeting the needs of the world’s poor. Meeting needs, protecting the environment, reducing hunger, and ending poverty are actions that respond to the cries of people living in the world at this moment and by doing so, fulfill the ACS vision. This chapter looks both at the questions chemistry is asking right now related to sustainability as well as the questions chemistry SHOULD be asking about sustainability in order to better understand how chemists might “hear the cries of the world.”

Introduction

When I first was asked to contribute to this volume, the image that immediately came to my mind was that of the prominent figure Guanyin from Chinese Buddhism. The reason is because the word “guanyin” literally translates as “Perceiving the Sounds (or Cries) of the World” (*1*). In the context of chemistry and sustainability, I see the challenge presented to the chemistry community as one that involves not only hearing the cries of the world but also responding to them with the particular set of skills that we bring from our discipline.

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How Sustainability Has Been Defined

My starting point is both the vision and the mission of the ACS. The vision of ACS is "improving people's lives through the transforming power of chemistry" (*2*); whereas, the mission of ACS is described as "advancing the broader chemistry enterprise and its practitioners for the benefit of Earth and its people." Within those two statements, there is a very clear recognition of our responsibility to others by making a difference in and improving their lives through the use and products of chemistry.

How is that related to the challenge of sustainability? Probably the most widely used definition of sustainability is "development that meets the needs of the present without compromising the ability of future generations to meet their own needs." This quotes comes from *Our Common Future: The World Commission on Environment and Development*, often referred to as the Brundtland report (*3*), and has been used for years by hundreds and thousands of people. But when talking about "meeting the needs of the present," what exactly are those needs? A 1999 report from the National Research Council entitled *Our Common Journey: Towards a Transition to Sustainability* (*4*) answers this question with language that includes the explicit goal of substantially reducing hunger and poverty as well as reducing the challenge of increasing global population.

Several years after first reading *Our Common Journey*, I went back and read the Brundtland report for the first time. Only then did I realize that the text from *Our Common Future* so widely used to define sustainability did not fully reflect the report's perspective. Below is the sentence and the text that immediately follows it:

> "Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs. This text contains two key concepts:
>
> - the concept of needs, in particular the essential needs of the world's poor, to which overriding priority should be given; and
> - the idea of limitations imposed by the state of technology and social organization on the environment's ability to meet present and future needs."

The first point is the concept of needs, in particular the essential needs of the world's poor, to which overriding priority should be given. What characterizes poverty? The economist Jeffrey Sachs provides a useful answer is his distinction between extreme (absolute) poverty, moderate poverty, and relative poverty (*5*). Extreme poverty is characterized by the inability to meet basic needs for survival – food, health care, safe drinking water, sanitation, education for children, rudimentary shelter, and basic articles of clothing. Moderate poverty is characterized by conditions where the basic needs of life are met, but just barely. The Brundtland description of sustainability clearly sees extreme poverty and, to some extent, moderate poverty, as relevant to the questions of needs. The second point is the idea of limitations. In many symposia on sustainability at

ACS meetings and discussions about sustainability, we have addressed limitations (particularly environmental limitations) and how we can either respect them or find ways to appropriately transcend them. But as far as I can tell, we do not talk nearly as much about the concept of needs, especially the essential needs of the world's poor and the priority that should be given to them.

In 2005, a workshop was organized under the auspices of the Board on Chemical Sciences at the National Academy of Sciences that led to the publication of the report *Sustainability in the Chemical Enterprise* (*6*). The workshop and report focused attention on areas posing the greatest scientific and technical challenges regarding sustainability in the chemical enterprise (both academic and industrial). The report:

> "…is not inclusive of every research topic of relevance to sustainability…the report is meant as a starting point for further analysis, with a focus on those areas that present unique challenges and opportunities where the chemical industry and government research and development funding efforts can help address larger sustainability goals."

Neither the workshop nor the report attempted to describe sustainability in broad terms. Furthermore, neither attempted to encompass all of the dimensions of sustainability from the perspective of chemistry. Rather, they focussed attention on areas in which the greatest scientific and technical challenges remain. The areas included green and sustainable chemistry and engineering, life cycle analysis; toxicology, renewable chemical feedstocks, renewable fuels, energy intensity of chemical processing, separation, sequestration, and utilization of carbon dioxide, and sustainability education.

Many of these areas should come as no surprise to attendees of ACS meetings over the last 10 years, as there has been significant discussion within the Society about them, particularly a growing discussion about sustainability education. That same study laid out a hundred-year time frame that ranked three of those challenges – reduced energy intensity, sustainability education, and carbon management – as critical in the first 20 years, a period that was described as involving continued use of fossil fuels. That same 20-year period also would involve preparing ourselves to phase out the use of fossil fuels. The other challenges would come in the next 80 years after the initial period and would include the actual phasing out of fossil fuel use.

The Triple Bottom Line

At the spring 2007 ACS National Meeting, the Division of Chemical Education sponsored a symposium titled "Sustainability and Chemical Education: Industry's Perspective." As one of the organizers, I noted the words of several speakers. These included statements about how research is not linear, how "it takes a village" to address sustainability issues in chemistry, the challenges with which industry saw itself being faced, and a reference to the "triple bottom line" of people, planet, and profit (*7*).

Over the past 15 years, green chemistry has been a major theme at ACS meetings, and much important work has been done using the 12 Principles of Green Chemistry first articulated by Anastas and Warner (*8*). It took me a number of years to recognize an unstated limitation of the 12 Principles in their application to the challenge of sustainability. That limitation is best described as the absence of "context." To use an admittedly extreme example, the 12 Principles of Green Chemistry can be validly applied to developing a better synthesis of Viagra. I would argue *this* particular application of green chemistry misses the point of sustainability, whereas the application of green chemistry principles to developing new insectides for mosquitos, the deadliest animal in terms of annual human deaths (*9*), is clearly consistent with the definitions of sustainability in both the Bruntdland report and *Our Common Journey*.

My intent here is not to criticize green chemistry. Green chemistry is absolutely essential to the chemical enterprise (academic and industrial) in the 21st century. In the eyes of many chemists, there is *no* 21st century chemistry without green chemistry. So while green chemistry is absolutely essential and necessary, my point is that it is not sufficient. Context matters. The bigger picture matters. The needs and the cries of the world matter.

When we raise the question of how we should take into account the larger context and the cries of the world, we are moving into what is often referred to as the "triple bottom line," the three elements of environment, profit, and community. If we think of these elements in terms of a Venn diagram, then we can have overlap of either two areas or all three. Sustainability is directly in the middle, equally grounded in all three spheres—the environmental, economic, and social aspects. The environmental and economic aspects are ones with which we are most familiar and that most often are part of the exchanges at ACS meetings. The social aspect includes standard of living, state of the community, education, health, well-being, and reduction of poverty. Sustainability is ultimately a challenge of balancing those three aspects in a way that, in the words of *Science for All Americans*, "can provide humanity with the knowledge…needed to develop effective solutions to its global and local problems; without that knowledge, progress toward a safe world will be unnecessarily handicapped" (*10*).

Chemistry and Sustainability

Alex Johnstone famously described the perspectives that make up modern chemistry as the macroscopic, the microscopic, and the symbolic (*11*). Johnstone provides a very powerful way of thinking about the different aspects of chemistry as the discipline is practiced today. Building on Johnstone's thought, Peter Mahaffy has written several recent articles (*12*, *13*) where he has addressed the need to bring the human/social dimension more clearly into chemistry. Mahaffy has argued that we need to add a fourth point, the human element, and turn what Johnstone presented as a triangle into a tetrahedron. With the addition of the human element, we return once again to the planet.

So what things has the chemistry community been talking about recently? We can start with a 2003 report from the National Research Council, *Beyond the Molecular Frontier: Challenges for the Chemical Sciences* (*14*). The chapter headings include Energy, Atmospheric and Environmental Chemistry, Materials by Design, Interface with Biology and Medicine, and Measuring Substances and Structures. In many cases, the connection of the heading to the question of sustainability is crystal clear. One of the things I appreciate about this report is that green chemistry was not identified as a separate chapter. Instead, green chemistry was viewed as a set of strategies, a way of thinking about doing chemistry that ran throughout all of the challenges.

In 2009, ACS produced a wonderful series titled "Global Challenges/ Chemistry Solutions" (*15*) that highlighted chemistry's role in meeting challenges related to water (purification, desalination), climate change (reducing greenhouse gases, permanent solutions), safety and security, fighting disease, new fuels, and food (safety, nutrition). Both this series as well as the earlier report "Beyond the Molecular Frontier" that I described in the preceding paragraph focused on real needs of the world – climate change, water quality, combatting disease, energy – and the contributions that chemistry could make in meeting those needs.

Two years before "Global Challenges/Chemistry Solutions," George Whitesides and George Crabtree published an article in *Science* that focused on the challenge of meeting the world's energy needs and the importance of fundamental research in meeting those needs (*16*). Whitesides and Crabtree stated that the separation between basic and applied research is, in many ways, artificial. They saw many fundamental research questions, such as the oxygen electrode problem and catalysis by design, as being absolutely critical in terms of grappling with the challenge of sustainability and energy. The article was not the only time that Whitesides has argued for the importance of clearly connecting chemistry to real-world problems. In a Comment in *Nature* co-authored with John Deutch and published in 2011 (*17*), the authors argued for an overhaul of the way that chemistry is practiced. Whitesides and Deutch recommended that chemists should rewrite the social contract by reorganizing:

> "to try to solve problems that are important and recognizable to the society that is paying for the research, especially those to do with water, food, health, energy and the environment. To make fundamental discoveries, an approach that starts with practical problems, and uses them to reveal unsolved fundamental problems, will work at least as well as (and arguably better than) one that starts with the familiar questions of familiar disciplines."

More recently Whitesides has published an essay (*18*) in which he explores possible futures for chemistry in the context of new problems, many of them central to the challenge of sustainability.

Many chemists are developing new ways to meet the challenges of sustainability. For example, inorganic chemists are working on new metal catalysts that carry out important reactions in a more energy efficient way; analytical chemists are developing chromatographic methods that utilize highly selective separation devices to minimize solvent waste; colloid chemists are tackling the challenge of characterizing interactions between nanoparticles and structures such as cell surfaces; and atmospheric chemists are faced with the challenge of understanding aerosol formation and material absorption onto an aerosol's surface. It is clear that chemists are talking about many different issues profoundly and deeply related to sustainability, as well as the contributions chemistry can make towards addressing those issues.

What Is Missing for Chemists To Hear the Cries of the World

Is there anything missing? From a technical perspective, I don't see any glaring holes. Some specific questions or challenges possibly are being overlooked, but when considering the major challenges that need to be grappled with to hear and respond to the cries of the world, I don't see massive gaps. For example I have noticed in recent ACS meetings that there has been more and more discussion about what we as chemists can do about the growing issue of water as a limited resource. Certainly, there are things we can do better. In a later chapter, John Fowle will discuss how toxicology is changing based on what we have learned about chemicals, the environment, and how they interact with living systems. This does not mean we have overlooked toxicology; rather, we need to change the way we think based on what we have learned.

We need to talk about sustainability and our discipline's contribution to that challenge; in some ways this conversation has been part of the technical program at ACS meetings for close to a decade. What I see missing, however, is the overriding priority that should be given to the essential needs of the world's poor. Something unique that chemistry contributes to meeting the challenge of sustainability is the way in which we think about, design, and manipulate materials at the molecular scale. That contribution opens up possibilities to make real differences in the lives of others. Green chemistry is one critically important way we think about things on the molecular scale. Fundamentally, we as chemists contribute our thought processes regarding atoms and molecules, as well as their transformations, how to detect and manipulate them, and how to put them together to make things with certain desired characteristics. But we need to ensure that the discussion includes the use of those skills and how to use that perspective to meet the essential needs of the world's poor.

This, in fact, is not a new challenge. In a essay published in 2002, Ismail Serageldin, the director of the library of Alexandria, wrote (*19*):

> "For science to realize its full promise and become the primary force for change in the world, it requires that scientists work to
>
> - *engage scientific research in the pressing issues of our time*
> - *abolish hunger and reduce poverty*
> - *promote a scientific outlook and the values of science*
> - *build real partnerships with the scientists in the South.*

...Implementing this agenda will mean

- *not just new science and technology, but also relevant science and technology*
- *not just communications, but also content*
- *not just technology transfer, but also real collaborations that promote the values of science and the scientific outlook.*"

Serageldin's words were written as the global community was starting to work on the Millennium Development Goals (*20*), which were first proposed at the UN Millennium Summit in 2000 and focused on challenges such as eradicating extreme hunger, reducing child mortality, improving maternal health, combatting diseases such as HIV/AIDS and malaria, and ensuring environmental sustainability. The Millennium Development Goals, intended to be accomplished by 2015, have guided much of the global effort to reduce extreme poverty since that time. As this chapter is being written, the United Nations is poised to adopt a set of Sustainable Development Goals (*21*) that will serve as successors to the Millennium Development Goals. The Sustainable Development Goals target a wider range of challenges to be met, including ones that are clearly in the environmental or economic areas, and so are more explicitly aligned with the triple bottom line.

Clearly chemistry has something to contribute to the achievement of the Sustainable Development Goals. What I am suggesting has been missing from chemistry's current practice is something that we have been stumbling over for a while. Earlier in this chapter I described the "triple bottom line" of sustainability as a Venn diagram with three overlapping circles representing the elements of environment, economy, and community; sustainability was the area where all three circles overlapped equally. But those three elements of the triple bottom line can also be thought of as balls that we have to juggle as we seek to meet global challenges and improve the well being of people around the world. The problem is that we need to find a way to juggle not just the balls of economic and environmental sustainability but to juggle ALL THREE balls of economic AND environmental AND social sustainability. As anyone who has tried juggling knows, the only way to juggle effectively is to give equal and appropriate attention to each ball at the appropriate point in time. One cannot privilege two out of the three without significantly increasing the risk of dropping some or all of the balls.

As we move forward and try to use the unique perspective and skills of chemistry, we want to make sure that the discussion juggles the third ball of the social aspect *equally* with the environmental and economic aspects. Having been involved with the ACS Committee on Environmental Improvement and having attended ACS meetings for over a decade, I find myself at times thinking that the environmental and economic spheres get the lion's share of the attention, and so the change has to involve giving more attention to the social sphere without doing so at the expense of either of the other two. There have been some efforts to give more attention to the social sphere – CHEMRAWN (*22*) and ICOD (*23*) are two that are worth noting – but there is still work to be done before equal attention to all three spheres is clearly an important part of the mainstream of chemistry.

The adoption of the UN Sustainable Development Goals provides the chemistry community with a unique opportunity to accomplish this.

I will close with words written over forty years ago by Jacob Bronowski, the mathematician/mathematical biologist and profound humanist. In his essay "The Disestablishment of Science" (*24*) Bronowski wrote:

> "There is no judgment of a field or line of research that can be confined to its scientific potential. Every judgment in life contains a silent estimate of human and social values too, and the representatives of science will not be able to shirk that. There is no guarantee that scientists will make a better job of fitting science to humanity than has been done before, but it is time that they faced their moral obligations and tried."

My hope is that, as we move forward, the discussions that we hear at ACS meetings acknowledge the wisdom of Bronowski's words and bring those dimensions of human and social values more into the conversation.

References

1. Guanyin. https://en.wikipedia.org/wiki/Guanyin (accessed June 20, 2015).
2. ACS Strategic Plan for 2015 and Beyond Home Page. http://strategy.acs.org (accessed June 20, 2015).
3. World Commission on Environment and Development. *Our Common Future*; Oxford University Press: New York, 1987.
4. National Research Council. *Our Common Journey: A Transition Toward Sustainability*; National Academy Press: Washington, DC, 1999.
5. Sachs, J. D. *The End of Poverty*; Penguin Books: New York, NY, 2005.
6. National Research Council. *Sustainability in the Chemical Industry*; National Academy Press: Washington, DC, 2006.
7. Slaper, T. F.; Hall, T. J. *Indiana Business Review* **2011**, *86*, 4–8.
8. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University: New York, NY, 1998; p 11.
9. Liu, N. *Annu. Rev. Entomol.* **2015**, *60*, 537–559; doi: 10.1146/annurev-ento-010814-020828.
10. American Association for the Advancement of Science (AAAS). *Science for all Americans*; New York: Oxford University Press, 1990.
11. Johnstone, A. H. *J. Chem. Educ.* **2010**, *87*, 22–29; doi: 10.1021/ed800026d.
12. Mahaffy, P. *J. Chem. Educ.* **2006**, *83*, 49–55; doi: 10.1021/ed083p49.
13. Mahaffy, P. In *The Chemical Element: Chemistry's Contribution to Our Global Future*; Garcia-Martinez, J., Serrano-Torregrosa, E., Eds.; Wiley-VCH Verlag GmbH & Co.: Weinheim, Germany, 2011; pp 131−157.
14. National Research Council. *Beyond the Molecular Frontier: Challenges for Chemistry and Chemical Engineering*; National Academies Press: Washington, DC, 2003.
15. American Chemical Society. Global Challenges/Chemistry Solutions. http://www.cendigital.org/acsgccs/2009 (accessed October 1, 2010).

16. Whitesides, G. M.; Crabtree, G. W. *Science* **2007**, *315*, 796–798.
17. Whitesides, G. M.; Deutch, J. *Nature* **2011**, *469*, 21–22.
18. Whitesides, G. M. *Angew. Chem.* **2015**, *54*, 3196–3209.
19. Serageldin, I. *Science* **2002**, *296*, 54–58.
20. http://www.un.org/millenniumgoals/ (accessed September 2015).
21. http://www.un.org/sustainabledevelopment/sustainable-development-goals/ (accessed September 2015).
22. Malin, J. M. *Chem. Int.* **2009**, *29*, 4–7; doi: 10.1515/ci.2007.29.2.4.
23. Matlin, S. *Chem. Int.* **2013**, *35*, 8–11; doi: 10.1515/ci.2007.29.2.4.
24. Bronowski, J. *A Sense of the Future*; MIT Press: Cambridge, MA, 1977; pp 235−248.

Chapter 2

Bridging the Gap, Transforming the Future: Education, Collaboration, Innovation!

Catherine T. Hunt*

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We are facing interrelated global challenges of energy, food, water, and human health. Solving these daunting challenges will require global systems thinking and proactive local action. To understand the intricacies and work through potential solutions will require not only a basic understanding but also a fundamental working knowledge of science, technology, engineering and math (STEM). To this end, science literacy for all must be addressed. We will put a spotlight on two exemplary efforts, the newly-formed American Association of Chemistry Teachers (AACT) and the model RetroFIT Philly "Coolest Block" Competition. I firmly believe that working together as a science literate populous, thinking globally and acting locally, that we can make good decisions and set a sustainable path forward.

Introduction

"Scientific Literacy is the knowledge and understanding of *scientific* concepts and pro-cesses required for personal decision making, participation in civic and cultural affairs, and economic productivity." (*1*)
-U.S. National Center for Education Statistics

We are facing interrelated global challenges of energy, food, water, and human health. Solving these daunting challenges will require global systems

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thinking and proactive local action. To understand the intricacies and work through potential solutions will require not only a basic understanding but also a fundamental working knowledge of science, technology, engineering and math (STEM). To this end, science literacy for all must be addressed. Science literacy starts with quality teachers and does not end until we have K through Gray continuing education. No one—no one company, academic institution, non-profit or government agency—can accomplish this task alone. Addressing such complex issues in a timely fashion requires strong collaborations and accelerated action plans. Plans that are implemented by starting with small pilot programs that, once successful, are force-multiplied into broader impacts.

We will put a spotlight on two exemplary efforts, the newly-formed American Association of Chemistry Teachers (AACT) and the model RetroFIT Philly "Coolest Block" Competition. We will do a deep dive into RetroFIT PHILLY which started with a "green" mayor, a creative company, a forward-thinking energy non-profit and a solid sustainability plan, Greenworks Philadelphia. Efforts such as these are proactively integrating innovation—*sustainable innovation*—into our cities, our schools and ourselves.

I firmly believe that working together as a science literate populous, thinking globally and acting locally, that we can make good decisions and set a sustainable path forward.

Chemistry at a Crossroads (*2*)

My primary objective as president of the American Chemical Society was to give a face and a voice to chemistry. "In the highly competitive, global economy of the 21st century, mathematics and science are no longer pursuits for the few. They are requirements for all (*3*)." In short, "the future well-being of our nation and people, depends…on how well we educate [the next generation] in mathematics and science specifically (*4*)." According to the Organization for Economic Cooperation and Development, the U.S. ranked 21 out of 23 countries in math and 17 out of 19 countries in problem solving (*5*). This is the definition of a failing grade.

Scientific literacy is essential to understanding and acting sustainably. To close this growing gap will require a focused effort on three fronts: education, collaboration and innovation. Education: to reach and connect with legislators, the media, the public, and—*perhaps most importantly*—the next generation. Collaboration: to build a strong, vibrant, and vocal technical community that is both internally connected across different disciplines and externally engaged with our non-technical neighbors. Innovation: to reignite our commitment to science and technology in order to revitalize our companies, our communities, and ourselves.

What Is Needed? Competency, Passion and Alignment!

To bridge this growing gap and transform the future will require a fully competent, completely passionate, and totally aligned team effort. Two out of three just will not suffice. Here's why: a) competency and passion without alignment constitutes a **personal hobby,** b) competency and alignment devoid of passion is, at best, a **distasteful chore,** and c) alignment and passion without competency makes one an **enthusiastic rookie**. Looking at it from the flip side, if your team is not performing, not delivering the desired outcomes, ask yourself. "What's missing?"

Time To AACT: Quality Teachers Matter

To effectively engage the next generation in science—and especially in chemistry—we need to start with teachers and we need to start now. Teachers can reach classrooms of students day after day, week after week, year after year. Mentoring one student at a time is wonderful and much needed, but to reach every student everywhere, we need to reach the teachers.

Quality teachers are the number one school-related predictor of student achievement (*6*). So, what do teachers need to have to be "quality" teachers? The operative word here is "need." New York State Master Teacher Sally Mitchell put it like this, "We need resources. We need lesson plans. We have so much squeezed into a day; we need timely resources that we can trust."

Based on extensive feedback and a collaborative team effort from secondary school teachers, professors, industry experts, and ACS leaders working together with American Chemical Society (ACS) staff, the American Association of Chemistry Teachers (AACT) was born. The official launch was September 2014 and they have hit the ground running. The growing AACT website is now a professional home through which the K–12 chemistry teaching community has access to customized resources and support—from staff and most importantly, from colleagues and peers (*7*).

What's the Plan? Greenworks Philadelphia

Educating legislators, the media and the public about sustainability will require more than K-12 teachers. It will require a compelling vision, a charismatic champion, and a plan. A plan based on systems thinking.

In his inaugural address in 2008, Mayor Michael A. Nutter shared his transformational goal to make "Philadelphia the greenest city in America." Nutter created the Office of Sustainability. In 2009 they published "Greenworks Philadelphia," a six-year plan divided into five overarching goals (Energy, Environment, Equity, Economy, and Engagement) with 14 individual targets and over 160 actionable initiatives to turn this dream into reality.

As a member of the Mayor's Sustainability Advisory Board and an R&D Director at The Dow Chemical Company, I was uniquely positioned to make an impact on Energy, Target 3: Retrofit 15 percent of housing stock [in Philadelphia] with insulation, air sealing and cool roofs. To paraphrase our Nobel prize-winning, former U.S. Secretary of Energy Steven Chu, this is called "weatherization" but I would rather call it "saving money by saving energy" (*8*). Weatherization may not sound sexy but reducing home heating and cooling costs by approximately 20% is a wallet–friendly, carbon footprint reducing, climate adaptation behavior.

With over 350,000 row homes in Philadelphia alone, it was clear that we'd never accomplish this ambitious target in a timely fashion (by 2015) by retrofitting one building at a time. What we needed was a force-multiplier of 10-100x. Fellow advisory board member Liz Robinson, executive director of the Energy Coordinating Agency of Philadelphia (ECA), suggested retrofitting an entire block. With 7,000 blocks in Philadelphia, most championed by a block captain, and all captains networked together through the Mayor's Office, this sounded daunting but not entirely impossible. We devised a competition led and executed by ECA, with products and building expertise donated by Dow and with networking and communication through the Mayor's Office.

The RetroFit PHILLY Competition was launched by Mayor Nutter on a cold day in February 2010 when the roofs were white with snow (*9*). The City of Philadelphia was forging a novel public private partnership with ECA and the Dow Building and Construction business group to host a competition in which neighborhood blocks from across the city would compete to become the "Coolest Block" in Philadelphia. The winning block would receive energy-saving cool roofs and other energy efficient products, such as insulation and air sealing, for the entire block.

Integrating Education and Job Training into the Plan

Education sessions were held by ECA at the Philadelphia Free Library, at local community centers and sometimes even in block captains' homes. These sessions explained the science, the potential savings, and the overall sustainability of insulation, air sealing and cool roofs, as well as the requirements to enter the contest. The information used to communicate the contest is still available at RetroFitPHILLY.com.

Green job training sessions—from blower door testing to insulation, air sealing and cool roof applications—were orchestrated by ECA in order to build up the necessary workforce to efficiently execute the en masse retrofit. A deadline was set for April 5, 2010, at 5:00 p.m., and entry forms started to flow in.

Fast forward to May 13, 2010. On a cool, energy saving, white roof— not just a roof white with snow—Mayor Nutter signed cool roof legislation into law for the city of Philadelphia and, at the same time, announced the winners of the RetroFit PHILLY "Coolest Block" Contest. "I would like to congratulate 1200 Wolf Street and thank all the neighbors who came together to participate in the 'Coolest Block' contest," said Mayor Nutter. "Many of the row homes that give our city its unique character were built long before today's energy-conscious environment. This contest and today's legislation will help Philadelphia become a city of the future and set an example for others throughout the country" (*10*). The residents of Wolf Street were not the only winners. Dow raised awareness of its sustainable building technologies and became actively engaged in Philadelphia, the city helped its citizens in a tangible (and photogenic) way, and ECA gained an opportunity to expand its workforce training and energy education efforts.

After the RetroFit: Telling Their Stories and Hearing Their Requests

Twenty-nine row homes on the 1200 block of Wolf Street received their “cool retrofits”, and the resulting energy savings and environmental benefits are adding upon year on year.

The side stories are heartwarming. One woman shared, “My nephew got ECA green job training and by chance, ended up on the team that retrofitted my home.” Another resident added, “I lost my white wine cooler! In the winter my bedroom is now so warm that I can no longer chill my wine there.” A third resident with a husky male bulldog added, “My bulldog loves the cool roof! And I love that he drools a lot less!” To a person, they all enjoyed the June South Philly-style block party celebration with the mayor.

The follow-up programs are inspirational. In response to residents who couldn’t enter RetroFit PHILLY because they did not have an intact roof on their home, ECA launched EnergyFIT Philly (*11*). This is an innovative approach to the prevention of homelessness by preserving and stabilizing affordable housing which is currently ineligible for energy conservation programs due to roof leaks and other home repair needs. There was a call for applications as recently as March 2015.

All that said, my favorite email came from a young girl who asked, “When are you going to have a Coolest School Contest?” What a great idea!

The Winning Hat Trick: Competency, Passion and Alignment!

This bringing together of the competency, passion and alignment of ECA, the City of Philadelphia, Dow Building and Construction and The Dow Chemical Company Foundation delivered a model not only for Philadelphia city blocks but also for urban cities worldwide with respect to energy saving, CO_2 mitigation, and climate adaptation. In truth, RetroFit PHILLY positively impacted all five of the overarching Greenworks sustainability goals: Energy, Environment, Equity, Economy, and Engagement.

Force-Multiplying Success: From RetroFit PHILLY to EnergyWorks

Five years into the six-year Greenworks Philadelphia implementation timeline, small programs have been force-multiplied into larger programs. More specifically, the RetroFIT PHILLY program was force-multiplied into a successful $25 million dollar Energy Efficiency Conservation Block Grant (EECBG) (*12*) program. The U.S. Department of Energy (DOE) created the EECBG program to develop, promote, implement, and manage energy efficiency and conservation projects that ultimately created jobs. The 3-year EnergyWorks (*13*) residential program was force-multiplied to include five counties (Bucks, Chester, Delaware, Philadelphia and Montgomery), completed more than 2,500 homes, and was expertly led by ECA. As of 2015, the commercial aspect of the program is still in effect and is managed by The Reinvestment Fund (TRF) and Philadelphia Industrial Development Corporation (PIDC) (*14*).

Think Globally, Act Locally: From GCCA to ECA

On a local level, we have great energy and weatherization teachers with Liz Robinson and her team at ECA. On a global level, we have the resources of the Kurt Shickman and the Global Cool Cities Alliance (GCCA) (*15*). GCCA released “A Practical Guide to Cool Roofs and Cool Pavements” a cool cities toolkit that explains just how to put this kind of program into practice, whether you are a sustainability director tasked with making your city the greenest, a block captain who wants to make your neighborhood more livable or a local resident interested in making your home more energy efficient. This timely toolkit is divided into two parts: 1) Ready to Learn: Primer to build your own cool surfaces knowledge base and then educate others, and 2) Ready to Act: Implementation Guide with best practices and case studies to start and/or grow your own cool surfaces program (*16*). This kit includes everything from the science behind the cost savings to existing research on climate adaptation and CO_2 mitigation to continuing education for all. This document has been force-multiplied into CoolRoofToolkit.org, a website with ongoing discussions and over 600 studies, articles, videos covering cool roofing and Urban Heat Island (UHI) programs. Additional resources and case studies can be found at the American Institute for Architects, the California Energy Commission, Case Studies (Toronto, Chula Vista, New York City, Walmart, and Delhi), the Global Cool Cities Alliance, Global Eco-Cities Survey, and the NYC °CoolRoofs Program.

Bridging the Gap, Transforming the Future: The ASK…

Now it is your turn to stand in the future and envision your own sustainability scenario, whether it’s science literacy for all or the greenest locale ever or something completely different. There’s no time like the present to put that vision into words and move those words into action.

I firmly believe that working together we can create a sustainable future. So, let’s get started!

My Hallmark Closing

Thank you for all you have done … and all that you are going to do!

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References

1. United States Department of Education, National Center on Education Statistics, Washington, DC. http://nces.ed.gov/ (accessed October 10, 2015).
2. Hunt, C. T. Chemistry at a Crossroads. *Chemical and Engineering News*, Jan. 1, 2007. http://cen.acs.org/articles/85/i1/Chemistry-Crossroads.html (accessed October 10, 2015).
3. A Commitment to America's Future: Responding to the Crisis in Mathematics and Science Education. Business-Higher Education Forum, 2005. http://www.bhef.com/sites/g/files/g829556/f/report_2005_commitment_to_americas_future_0.pdf (accessed October 10, 2015).
4. Before It's Too Late: A Report to the Nation from the National Commission on Mathematics & Science Teaching for the 21st Century. Commission Chair John Glenn, 2000. http://www.madscience.org/files/web/pdf/Beforeitstoolate.pdf (accessed October 10, 2015).
5. The Organization for Economic Cooperation and Development, October 2013, adopted from National Academy of Sciences (1996). National Science Education Standards (Report). National Academy Press. http://www.nap.edu/read/4962/chapter/4#22 (accessed October 10, 2015).
6. Rice, J. K. Understanding the Effectiveness of a Teacher's Attributes, Economic Policy Institute, 2003. http://www.epi.org/publication/books_teacher_quality_execsum_intro/ (accessed October 10, 2015).
7. American Association of Chemistry Teachers. https://www.teachchemistry.org/content/aact/en.html (accessed October 10, 2015).
8. Romm, J. ClimateProgress, October 31, 2009. http://thinkprogress.org/climate/2009/10/31/204889/energy-secretary-steven-chu-on-home-weatherization-save-energy-efficienc/ (accessed October 10, 2015).
9. Philadelphia's Mayor Nutter Launches "Coolest Block" Contest, Rowhouse Magazine, February 17, 2010. https://urbanrowhouse.wordpress.com/2010/02/17/philadelphias-mayor-nutter-launches-coolest-block-contest/ (accessed October 10, 2015).
10. Mayor Nutter Announces Winner of RetroFIT PHILLY "Coolest Block" Contest, Signs Cool Roof Legislation into Law, WordPress, May 13, 2010. https://cityofphiladelphia.wordpress.com/2010/05/14/mayor-nutter-announces-winner-of-retrofit-philly-%E2%80%9Ccoolest-block%E2%80%9D-contest-signs-cool-roof-legislation-into-law/.
11. EnergyFIT Philly. https://www.ecasavesenergy.org/services/home-energy-efficiency/energyfit-philly (accessed October 10, 2015).
12. Energy Efficiency and Conservation Block Grant (EECBG) is a funding program of the U.S. Department of Energy (DOE). http://energy.gov/eere/wipo/energy-efficiency-and-conservation-block-grant-program (accessed October 10, 2015).

13. EnergyWorks-Philadelphia is a DOE funded program. http://www.energyworksnow.com/ (accessed October 10, 2015).
14. EnergyWorks is by The Reinvestment Fund (TRF) and Philadelphia Industrial Development Corporation (PIDC). http://www.energyworksnow.com/commercial/partners/ (accessed October 10, 2015).
15. Global Cool Cities Alliance (GCCA) is a non-profit that works with cities, regions, and other stakeholders to accelerate a worldwide transition to highly reflective, cooler, healthier cities. http://www.globalcoolcities.org/ (accessed October 10, 2015).
16. Global Cool Cities Alliance and R20 Regions of Climate Action, A Practical Guide to Cool Roofs and Cool Pavements, January 2012 (accessed October 10, 2015). (Updates are available at: www.coolrooftoolkit.org.)

Chapter 3

Teaching and Learning about Sustainability: The View from CHED

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This chapter highlights the work of people from the Division of Chemical Education. Individually, they have won an award for incorporating sustainability into the chemistry curriculum from the ACS Committee on Environmental Improvement, contributed articles on sustainability to the Journal of Chemical Education, written a chapter in a recent ACS monograph on sustainability in the chemistry curriculum, and/or served on the author team of Chemistry in Context, an ACS undergraduate textbook that weaves sustainability into each chapter. Collectively, they speak to the successes, failures, joys, and/or challenges in bringing sustainability to the chemistry curriculum.

Introduction

"In the middle of the 20th century, we saw our planet from space for the first time. Historians may eventually find that this vision had a greater impact on thought than did the Copernican revolution of the 16th century, which upset the human self-image by revealing that the Earth is not the centre of the universe. From space, we see a small and fragile ball dominated not by human activity and edifice but by a pattern of clouds, oceans, greenery, and soils. Humanity's inability to fit its activities into that pattern is changing planetary systems, fundamentally. Many such changes are accompanied by life-threatening hazards. This new reality from which there is no escape, must be recognized—and managed." Our Common Future, Gro Harlem Brundtland, 1987 (*1*)

In Teaching and Learning about Sustainability; Levy, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

By their actions, members of the Division of Chemical Education (DivCHED) (*2*) have demonstrated their agreement with Brundland's statement. There *is* a new reality. When we engage our students in learning about sustainability in their chemistry courses, we play an important role in recognizing – and managing – this new reality.

This chapter highlights the work of people from DivCHED. In recent years, they have brought sustainability to the classrooms, laboratories, textbooks, and community-based experiences in which students learn. The venues include high schools, colleges, universities, and graduate schools. Through their experiences, instructors have gained expertise that enables them to speak to their successes, failures, joys, and challenges.

Contributors to this Chapter

DivCHED is over five thousand members strong. Individuals from this Division of the ACS were selected to contribute to this chapter on the basis of their achievements relating to sustainability in the chemistry curriculum.

One basis for inclusion was being an author in Sustainability in the Chemistry Curriculum, a monograph in the ACS Symposium Series published in 2011 (*3*). In 2010, each author gave a presentation in a symposium of the same title at the 239th National Meeting of the American Chemical Society in San Francisco. This monograph, published a year later, was dedicated to those "who have dedicated their talents to rethinking the undergraduate chemistry curriculum. They have explored and tested new pedagogical approaches in order to better convey the excitement and centrality of chemistry. They have contributed to the research on how people learn chemistry."

A second basis for inclusion was being a recent recipient of an award given by the ACS Committee on Environmental Improvement (CEI). This award, initiated in 2010, recognizes "individuals or groups who have made exemplary contributions to the incorporation of sustainability into chemical education." It encourages the dissemination of work that demonstrates how to incorporate sustainability into the chemistry curriculum (*4*).

A third basis for inclusion was being part of the author team of Chemistry in Context, an ACS textbook that engages students in learning chemistry in the context of societal issues (*5*). In addition to weaving sustainability through each chapter, the seventh and eighth editions of this text featured an opening chapter "Chemistry for a Sustainable Future." This chapter references Our Common Future, pointing out to students that "Brundtland's words carry a message to those who teach and learn: 'In particular, the Commission is addressing the young. The world's teachers will have a crucial role to play in bringing this report to them (*6*).' "

The fourth basis for inclusion was a recent publication in the Journal of Chemical Education (JCE) (*7*). Authors were selected whose papers used "sustainability" as a keyword. Although the list of JCE authors had a high degree of overlap with the previous three categories, the list did net a few more names for possible inclusion.

Once a list of possible contributors was assembled, each person was invited to add his or her voice to the SustainMix symposium in San Francisco on behalf of DivCHED. Each contributor was requested to submit one or two slides that illustrated a success, a joy, a failure, or a challenge in teaching and learning about sustainability in the chemistry curriculum. The response rate exceeded 90%, with 30 people sending submissions (Table 1).

One other group also contributed to this chapter, students in a class taught by the author of this chapter at the University of Wisconsin-Madison. On their final exam in the 2014 spring semester, these students were offered an extra credit question that asked them to provide a message – any that they might choose to write – for those attending the Sustain-Mix symposium. With their permission, two of their messages are included here, one written by Louisa Lincoln and the other by Danny Erickson.

The next section sets the stage for the remainder of this chapter, naming a primary challenge in teaching sustainability. The four sections that then make up the body of this chapter provide the details of the joys, successes, challenges, and failures of teaching (and learning) chemistry using topics that connect to sustainability.

For additional information about the content of sustainability and ways to engage students in learning it as part of their study of the chemical sciences, readers are urged to consult three sources. The first is the ACS Monograph, Sustainability in the Chemistry Curriculum (*3*). The second is the national meeting presentations of those who won awards for incorporating sustainability into the chemistry curriculum, archived by CEI on the ACS website (*4*). The third, a more general repository of curricular materials, Sustainability Improves Student Learning, is hosted by the Science Education Resource Center, SERC (*8*).

A Key Challenge in Teaching Sustainability

Teaching sustainability in the chemistry curriculum has many challenges, as will be described in a later section of this chapter. At the outset, the challenge provided by **Bettie Davis** from the Chemistry Department at Saint Vincent College in Latrobe, PA, is useful to frame those that follow. She writes:

> "… most people really don't know what sustainability is. It is not recycling, protecting endangered species, conservation, alternate power sources. But all of these are important to sustainability. Most people will pick out just one or two of these and dwell on them as sustainability."

A student of mine, **Louisa Lincoln**, echoed the sentiment expressed by Davis. In May of 2014, she composed this message on her final exam for me to convey to those attending this symposium:

"I think it is so valuable to realize that sometimes when we're so focused on one little thing, a relatively miniscule detail, it's so easy to be completely oblivious of these massive, massive issues right in from of us."

Table 1. Contributors to "The view from CHED"

Contributor	*Institution*	*ACS Monograph (3)*	*CEI Award (4)*	*Chemistry in Context Edition (5)*	*Journal of Chemical Education (7)*
Karen Anderson	Madison College		2015	7e, 8e	
Anne Bentley	Lewis & Clark College			7e-9e	
Michael Cann	U of Scranton	x	2010	7e, 8e	
Nancy Carpenter Ted Pappenfus Tim Soderberg	U of Minnesota, Morris		2012		x
Patrick Daubenmire	Loyola University Chicago		2015	9e	
Bettie Davis	Saint Vincent College	x			
Larry Duffy	U of Alaska, Fairbanks	x			
Jack Eichler	U of California, Riverside		2014		
Jamie Ellis	Ithaca College			7e, 8e	
Matthew Fisher	Saint Vincent College	x	2015		x
Avi Hofstein	Weizmann Institute of Science		2014		
Richard Jarman	College of DuPage		2013		
Andy Jorgensen	U of Toledo	x	2013		
Resa Kelly Ellen Metzger	San Jose State University		2013		
Mary Kirchhoff	American Chemical Society	x			
Mingming Lu	U of Cincinnati		2014		

Contributor	***Institution***	***ACS Monograph (3)***	***CEI Award (4)***	***Chemistry in Context Edition (5)***	***Journal of Chemical Education (7)***
Peter Mahaffy	The King's University College		2012		
Anne Marteel-Parrish	Washington College		2011		
Jeremiah Mbindyo	Millersville University	x			
Cynthia Maguire	Texas Woman's University				
Cathy Middlecamp	U of Wisconsin-Madison	x	2011	3e-8e	x
Brian Naasz	Pacific Lutheran University	x			
Glenn Odenbrett	Case Wetern Reserve University	x			
Marion O'Leary	Carnegie Institution for Science	x			
Laura Pence	U of Hartford				
Keith Peterman	York College				
Katie Purvis-Roberts	Claremont Colleges			7e-9e	
Judith Ramaley	Portland State University	x			
Richard Sheardy	Texas Woman's University	x			
Sara Skrabalak	Indiana University	x			
Sheri Strickland	Converse College	x			
Joseph Vicente Andrea Swenson	East Side Community HS		2013		
Mary Anne White	Dalhousie University		2012		
Uri Zoller	University of Haifa				x

Clearly, the term "sustainability" warrants further discussion. Davis is correct in that people tend to focus on one aspect, missing the bigger picture. Actually, this is not unique to sustainability; those who teach any subject tend to focus on one set of things to the exclusion of others. Fortunately, any definition can be construed as the start of a much longer conversation. In this sense, sustainability launches an interesting and timely conversation.

What perhaps makes sustainability different from many concepts in the chemistry curriculum is that it can find a home in most, if not all disciplines. Clearly, those who teach chemistry understand sustainability in different ways, as indicated by the different speakers in this symposium. However, those in the social sciences and humanities are likely to have even a greater range of understandings, and also have contributions to make to our collective understanding of the term sustainability.

Sustainability can be viewed both as content (involving nouns) and as a process (involving verbs). As a body of content, engaging students in learning about sustainability means offering them a body of knowledge. Knowing about sustainability means knowing how to work with ideas such as the Triple Bottom line, cradle-to-cradle, the Tragedy of the Commons, external costs, and carbon footprints. Collectively, ideas such as these form a coherent body of knowledge for students to master (*9*).

In another sense, sustainability is a process. Those who engage in thinking about sustainability as individuals, as local communities, and as nations generate new questions that help them imagine and achieve a sustainable future. The process of learning about sustainability can mean engaging in a new way of thinking. This way of thinking applies not only to chemistry but also to any field of study.

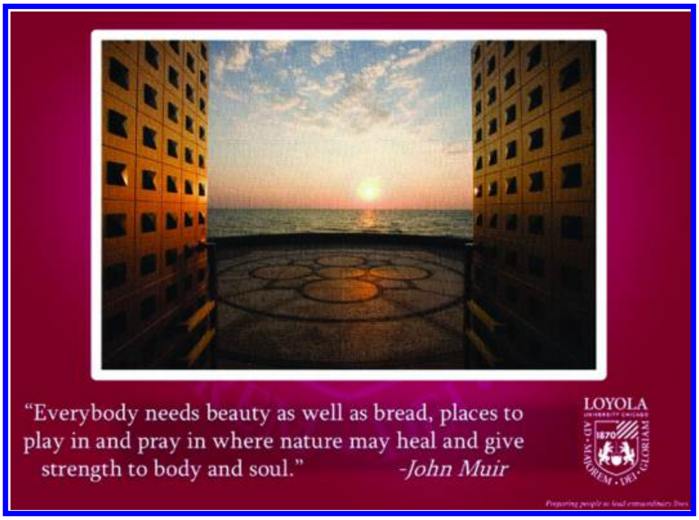
Both as content and as a process, sustainability presents instructors with challenges. The words of Bettie Davis challenge us to get our heads up to see the larger picture in which sustainability is situated. So do the words of my student Louisa Lincoln, noting how easy it is to be oblivious of the massive issues right in front of us. Lincoln also wrote: "I would like professors to hear Cathy's train story." This train story – and its connection to the larger picture in which sustainability is situated – will serve as the conclusion of this chapter. The next four sections summarize the joys, successes, challenges, and failures of bringing sustainability to our chemistry students.

The Joys of Teaching Sustainability

Five people chose to submit information relating to the joys of teaching and learning with sustainability. This section briefly describes the contribution of each one.

Karen Anderson (Chemistry Department, Madison College, Madison, WI) noted how, in a positive way, her students caught her attention through their writings about sustainability. Here is what one student stated: "I am interested to see what the future will bring for our world. I would like to see more bike trails and ways of getting around that don't use fossil fuels. … The more people know what the crisis is, the more they may choose to participate in the cause!"

Patrick Daubenmire (Department of Chemistry and Biochemistry, Loyola University Chicago, Chicago, IL) explained the rationale for his joy, saying "Earth is both our beauty and our bread, and so I feel compelled to incorporate sustainability into my courses. And it is a joy when students respond." Daubenmire also quotes John Muir: "Everybody needs beauty as well as bread, places to play in and pray in where nature may heal and give strength to body and soul (*10*)," as shown in Figure 1. A second slide in Daubenmire's submission included these words written by a Loyola student: "It is cool that people are trying to do some good. We could actually affect the environment by the small things we do."



"Everybody needs beauty as well as bread, places to play in and pray in where nature may heal and give strength to body and soul." -John Muir

Figure 1. A joy: people are "trying to do some good". (slide contributed by Patrick Daubenmire)

Mary Kirchhoff (Education Division, ACS) pointed to the joys experienced at the ACS Summer School on Green Chemistry and Sustainable Energy (*11*). This summer school, supported by the ACS Petroleum Research Fund, engages graduate students and postdoctoral scholars from the United States, Canada, and Latin America. The program has involved about 700 participants since 2003.

Mingming Lu (Department of Biological, Chemical and Environmental Engineering, University of Cincinnati, OH) described the joy of teaching sustainability in terms of its effects in the wider community. Her work with students involved producing biodiesel from trap grease and waste coffee grounds. She reported how her work with students is "taking roots in the community" and may even spin off a business from their innovative approaches to recover the oil without adding solvents new to the biodiesel producers.

Mary Anne White (Department of Chemistry, Dalhousie University, Halifax, Nova Scotia) reported that during the question period at a recent meeting, "one of our graduate students indicated that he had carried out a life cycle analysis of the use of a personal printer compared with a community-shared printer," and that "transportation of parts is a significant but hidden energy cost of the overall use of a printer." The visitor was caught rather flat-footed and then said that sustainability is a big future priority for the company." "Clearly," White states, "he was shown up by a first-year graduate student who had taken our Materials Sustainability graduate course. I was pretty proud!"

Successes in Teaching Sustainability

As a category, "Success" was utilized by contributors more than any other. This section includes the success stories of 15 individuals or teams.

Anne Bentley (Department of Chemistry, Lewis & Clark College, Portland, OR) highlighted her success with a class assignment that "made sustainability personal." Her students had the opportunity to research a Portland-based environmental chemistry issue of interest, conduct at least one off-campus interview, and share what was learned at the environmental studies community poster session. The work of her students included Oregon zoo composting, an organic, sustainable brewery, a biofuel-powered ski shuttle, waste management, Willamette River cleanup, and using poplars for biofuel.

Jack F. Eichler (Department of Chemistry, University of California, Riverside) contributed to the SENCER national curriculum reform project that engages students in learning science through real-world contexts (*12*). He successfully "SENCERized" his general chemistry course; that is, he infused environmental sustainability themes (*13*). He and his students worked on an investigative air quality lab project as well as on six new problem-based case studies with themes of environmental sustainability and renewable fuels.

Jamie Ellis (Chemistry Department, Ithaca College, NY) was pleased to describe her success as an author for the seventh and eighth editions of Chemistry in Context (*5*). She redesigned the chapter "Genetic Engineering and the Molecules of Life" to bring a new focus to genetically-modified crops. Using food as a context, she incorporated issues of sustainable food production and potential solutions to the problem of world hunger from chemistry, while at the same time introducing the necessary biochemistry concepts for general chemistry students. Her future plans include to "integrate examples from both health and environmental concerns into my biochemistry and advanced seminar courses."

Avi Hofstein (Department of Science Teaching, Weizmann Institute of Science, Rehovot, Israel) described a 25-year partnership between chemistry education and Israeli industry that encompassed three modes: (1) to apply the principles of green science to the teaching and learning of chemistry, (2) to contextualize learning chemistry with applications of sustainable science and technology practices, and (3) to have issues such as climate change, energy, and risk become the driver for science education (*14*).

Andy Jorgensen (University of Toledo, OH, and the National Council for Science and the Environment) focused on climate change as a key issue in sustainability. He reported success in changing the views of over a thousand audience participants in talks on climate change, showing data supporting that more people were able to view climate change as a major issue.

Brian Naasz (Department of Chemistry, Pacific Lutheran University, Tacoma, WA) described how he engaged students from an Environmental Chemistry class for non-majors by challenging them to write a term paper about the application of the chemistry to a real environmental challenge. Most of the students gave enthusiastic responses (with some whining). Sample titles of the term papers include

- "Hydraulic Fracturing: The New Energy Sourcing Method or a Fracking Environmental Disaster?"
- "Conflict within the Sustainability Triangle: Dilapidated Ships of the Puget Sound",
- "PCB's, PCBDE's and Their Impact on Salmon in the Puget Sound" and
- "The Prevalence of Hypoxia as a Result of Nutrient Pollution in the Chesapeake Bay Watershed."

Jeremiah K.N. Mbindyo (Department of Chemistry, Millersville University, PA) described a two-day campus conference held in 2012: "Stewards of Sustainability (*15*)." He described two tracks in the conference, environmental preservation, and economic development and social equity. Mbindyo explained how "students were involved in conference planning, including introducing speakers." In addition, there were follow-up discussions and in-depth treatment of topics discussed at the conference in class. He noted how the conference produced "very lively discussion about sustainability of nuclear power vs. solar power."

Cynthia Maguire (Chemistry and Biochemistry Department, Texas Woman's University, Denton, TX) described how her students "Learn by Doing." Students assess a local business to see how they might improve sustainability in their everyday operations. The improvements suggested by her students included insulating hot water heaters, installing LED light fixtures to replace fluorescents, installing solar panels, adding a rainwater catchment system and increasing recycling.

Ted Pappenfus, **Nancy Carpenter**, and **Tim Soderberg** (Chemistry & Biochemistry, University of Minnesota, Morris) have incorporated sustainability into the chemistry curriculum in lower level courses, upper level courses, and in undergraduate research. Carpenter also is the author of Chemistry of Sustainable Energy, a textbook for upper-level students (*16*). The University of Minnesota, Morris, was recognized by Second Nature with a Climate Leadership Award in 2014 (*17*).

Keith E. Peterman (Physical Sciences Department, York College, PA) highlighted his success with two examples of real-world learning. The first was a short-term study abroad trip that he led to Costa Rica. The second was a field trip to a nearby waste-to-energy power plant.

Katie Purvis-Roberts (W.M. Keck Science Department for Chemistry and Environmental Science, Claremont McKenna, Pitzer and Scripps Colleges) focused on sustainability in chemistry textbooks such as Chemistry in Context, a textbook for non-majors that has examples of sustainability woven throughout the text (*5*). The key ideas of green chemistry are printed inside the front cover! She also described how Chemistry of the Environment, 3rd edition (*18*), incorporates the key ideas of sustainability.

Richard Sheardy (Chemistry and Biochemistry Department, Texas Woman's University, Denton, TX) is charting a green path ahead, commenting "We have successfully completed a semester of organic chemistry using numerous green experiments." These included integrating discussion topics and green chemistry curriculum into the organic chemistry laboratory, integrating microwave chemistry into different chemistry courses and faculty research, and formulating a path towards our ultimate goal—complete sustainability.

Sara Skrabalak (Department of Chemistry, Indiana University, Bloomington, IN) said "the most successful experience I had bringing sustainability to the classroom was when IU had an entire semester dedicated to the topic, in which students enrolled in course bundles that enhanced interdisciplinary learning and provided campus wide programming. Examples of activities from Chem 100 include children's books on a sustainability topic, a Tour of IU's Heating Plant and Algae Project, as well as a student poster session on Sustainability topics." This "Thēm·es·ter" ran over an entire semester and is depicted in Figure 2.

thēm·es·ter

sustain•ability: Thriving on a Small Planet

Fall 2010

COLLEGE OF
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Bloomington

Figure 2. A success: Thēm·es·ter at Indiana University (19). (slide contributed by Sara Skrabalak. The Themester trademark is the property of the Trustees of Indiana University.)

Sheri Strickland (Department of Biology, Chemistry, and Physics, Converse College, Spartanburg, SC) successfully incorporated sustainability into her course "Concepts of Chemistry." Noting that it may be possible to apply a particular technological solution, she helped students raise the question "But should we?" To answer this, students need to identify risks and benefits, consider the relative importance of each, and use credible evidence to make a case. She also used case studies to explore whether or not the people assuming the risks were the same as those reaping the benefits. In some cases, the people assuming the risks are geographically separated (drifting of airborne pollutants) or are separated in time (storage of high-level nuclear waste).

Andrea Swenson and **Joe Vincente** (East Side Community High School, NY, NY) described their successes in a college preparatory class focused on Water Sustainability in Chemistry Education. Their students were presented with a question: “If water is an economic, environmental, and social equity issue, how are we responsible for it as a sustainable resource?” They reported success in conveying to students rigorous chemistry concepts and real-world sustainability issues and solutions. They also provided students with the opportunity to work on a creative project to demonstrate their understanding.

Challenges in Teaching Sustainability

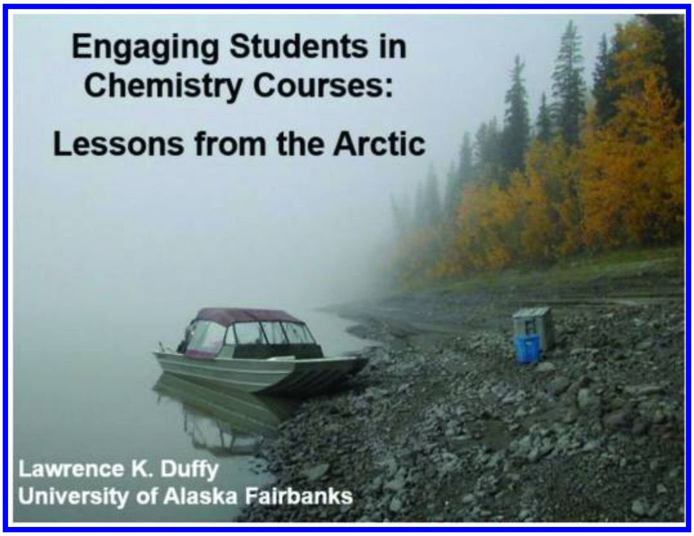
Eleven instructors or instructor teams chose to submit information relating to the challenges of teaching and learning with sustainability. This section briefly describes the contributions of ten submissions. The eleventh, by Bettie Davis, was described in an earlier section.

Michael Cann (University of Scranton, PA) named sustainability as *the* challenge of the century. He also posed a challenging question: “How do we weave sustainability and green technologies as prominent themes into chemistry education?” As part of the answer to this question, he catalogued the events relating to sustainability at a recent ACS national meeting.

Lawrence K. Duffy (University of Alaska, Fairbanks) spoke to the challenge of teaching sustainability in the region you live, at the same time bringing in issues from other regions of the globe. He pointed out that “interdisciplinary courses integrate chemistry concepts with topics of adaptation, mediation, and resilience.” He engaged his students in learning chemistry through local issues in the Arctic (Figure 3).

Matthew Fisher (Chemistry Department, Saint Vincent College, Latrobe, PA) spoke to the challenge of learning new things, “such as those related to renewable energy, design of new materials, or public health. Sustainability *always* brings us in contact with topics that weren’t part of our graduate school experience.” Fisher acknowledges being pushed out of his comfort zone when he teaches. But he also reframes the challenge: “It is one of the real joys and rewards of teaching sustainability. We get to learn new things all the time, a wonderful and energizing experience!"

Richard Jarman (College of DuPage, Glen Ellyn, IL) spoke to the challenges of complex partnerships. His project, “The Clean Fuels Depot Project,” turned yard waste into energy – and students into scientists.” He noted the challenge of maintaining momentum when several groups, including those off campus, worked in collaboration.



Engaging Students in Chemistry Courses:

Lessons from the Arctic

Lawrence K. Duffy
University of Alaska Fairbanks

Figure 3. A challenge: think locally and globally. (slide contributed by Larry Duffy)

Peter Mahaffy (The Kings University College in Edmonton, Ontario) reported that he employs climate literacy as a rich context to engage his students in learning general chemistry. He invited participants to "check out brand new resources to teach four topics in general chemistry, each beginning with an important sustainability question." The resources can be found at VC3, Visualizing the Chemistry of climate change (*20*).

Anne Marteel-Parrish (Washington College, Chestertown, MD) highlighted the challenge of course development. Their task was to adapt a one-semester Green Chemistry Sustainable Chemistry course to meet the demands of the 21st century. Their new objectives for this one-semester course included:

- introducing the world-wide scope of sustainability
- understanding business drivers
- practicing sustainable decision-making, and
- addressing quantitative aspects of sustainable practices.

Glenn Odenbrett (Great Lakes Innovative Stewardship through Education Network, Case Western Reserve University) highlighted the challenge of resources. He noted that his state of Ohio, like other states, "does not have enough professionals on staff to monitor the quality of the state's surface water frequently. He felt challenged in supporting the work of state environmental agencies with limited resources, including the need to maintain very high data collection standards."

Marion O'Leary (Carnegie Institution for Science, Stanford, CA) focused on water as a limited resource. He challenged instructors to include a discussion of the value of water in the chemistry curriculum, in order to "sensitize students to the idea that water is under-valued and increasingly becoming a limiting resource."

Judith Ramaley (President Emerita, Portland State University) commented on the challenge of being interdisciplinary:

> "While adding a wicked problem like sustainability to the chemistry curriculum is important, the challenge only takes on its full dimensions when chemists connect their work with insights and approaches from other fields and experiences. Until we do, we cannot expect our students to learn how to do this either."

Uri Zoller (Science and Science Education in Chemistry, University of Haifa) challenged instructors to restructure education at all levels, and to shift the paradigm. His examples included:

- algorithmic thinking to system/lateral thinking
- disciplinary teaching to interdisciplinary teaching
- technological, economic and social growth at all cost to sustainable development

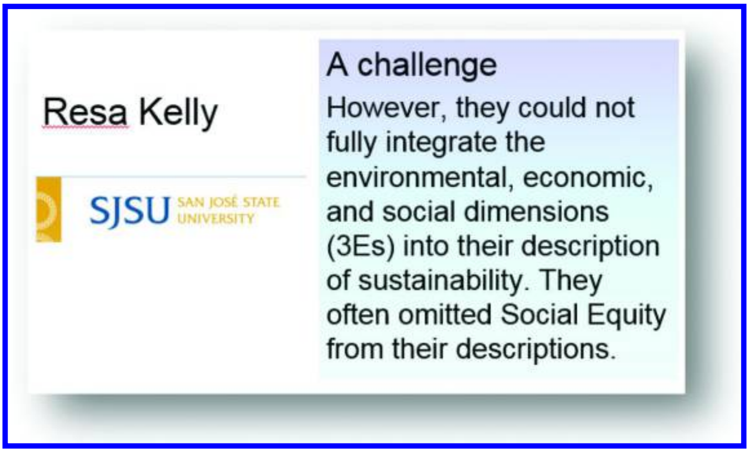
He named "the sustainability challenge" in bringing sustainability to the chemistry/science curriculum so that students become "capable literate and active participants (*21*, *22*)."

Failures in Teaching Sustainability

Let's call them shortcomings. Nobody contributed a failure, as such. However, two instructors mentioned a way in which their efforts fell short of a desired goal. For their willingness to be candid, we are in their debt. As Laura Pence noted, "There's work to be done here."

Resa Kelly and **Ellen Metzger** (Chemistry Department and Geology Department, San Jose State University) highlighted the success of a 3-day workshop for science teachers "Educating for sustainability." Prior to participating in the workshop, the teachers had a basic understanding of sustainability. This workshop formed the basis of a master's thesis by Cristina Chang, "Teachers' Understanding of Sustainability."

However, Kelly and Metzger also reported a shortcoming in regards to the understanding of sustainability shown by the teachers. Her words are shown in the slide she contributed (Figure 4).



Resa Kelly

SJSU San José State University

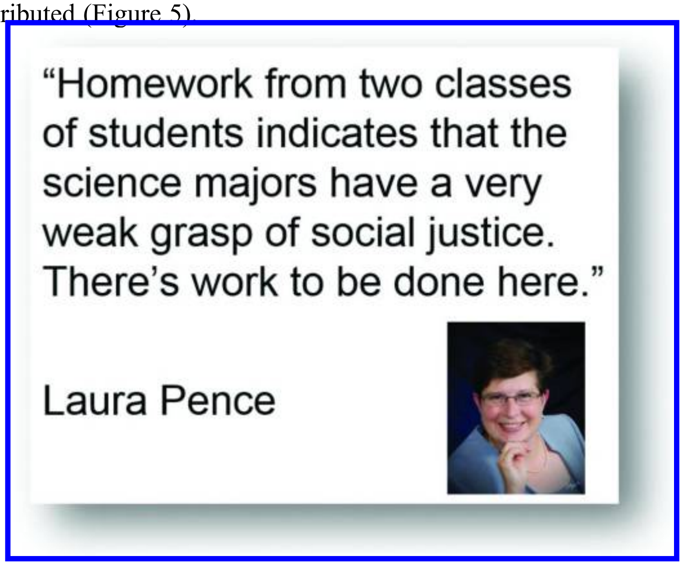
A challenge

However, they could not fully integrate the environmental, economic, and social dimensions (3Es) into their description of sustainability. They often omitted Social Equity from their descriptions.

Figure 4. A shortcoming. (slide contributed by Resa Kelly)

Laura Pence (Department of Chemistry, University of Hartford) pointed to her success with activities in her Environmental Chemistry course. "Throughout the course," Pence says, "I try to focus not only on the chemistry but also on the economic and social justice factors that work to assist or retard progress on environmental issues." The content that she used for the course was the Montreal protocol—the progression of phasing out different ozone-depleting chemicals, and the schedule was different for developed and developing nations. She later goes on to explain how "the different provisions of the treaty map onto the triple bottom line of Environment, Economy, and Social Justice."

However, Pence noted a shortcoming, and her words are shown in the slide she contributed (Figure 5).



"Homework from two classes of students indicates that the science majors have a very weak grasp of social justice. There's work to be done here."

Laura Pence

Figure 5. A shortcoming. (slide contributed by Laura Pence)

The Train: Concluding Story

As noted earlier, one of my students requested that I tell “the train story.” To what was this student referring? This section provides the answer.

Sustainability has many definitions and instructors approach sustainability in different ways. As an instructor, I struggle with how to convey a message about sustainability without getting lost in a definition (or two). Currently, the approach I take is to tell a story that goes like this.

On my campus, there is a set of rail-road tracks on which trainloads of coal were once hauled to the heating and cooling plant. The crossing has no gate because nowadays the trains are infrequent. A campus bicycle paths crosses these rail-road tracks. Conveniently, the path has a bend in it so that cyclists hit the tracks at a right angle, minimizing the chance that their bike wheels will get trapped in the space next to the metal rails of the track.

One day I was riding along this path. It was the hour at which classes change, so the street was busy with pedestrians, mopeds, cars, and other cyclists. Watching my wheels and at the same time trying not to hit any students (or get hit by a vehicle), I sped over the tracks at a nearly perfect right angle.

At the instant when I had cleared the tracks, the horn of a locomotive blared. Loudly! Ten feet away, an engineer was leaning out the window of the locomotive with a lady-how-come-you-didn’t-see-the-train look. I practically fell off my bicycle.

For a good decade, I still inwardly shuddered every time I crossed that intersection on the bike path. No, I didn’t get hit by a train but yes, it was a close call. And as you might imagine, I always now look up for a train.

But I no longer shudder. Why? A few years ago, I came across an article describing “Brain Games,” a set of materials published by National Geographic (*23*). It explained how one’s attention is like a spotlight and cannot possibly focus on everything at once. Not a train, but a revelation hit me. Of course I missed seeing the locomotive! I was so focused on the track bed, the pedestrians, the vehicles, and staying upright on my bicycle that I had sensory overload.

And I got to thinking. During my daily life at the university, I get so focused on preparing for class, answering email, going to meetings, collecting papers, and assigning grades, that I also experience sensory overload. And of course I miss seeing things!

And at this point, I connect the story to sustainability. Sustainability involves the things we may fail to notice. With heads down, we may miss the bigger issues. As I then explain (*24*),

> “Unlike the locomotive that warned me with its horn, the metaphorical locomotives coming down the train tracks in our world have no whistles. Changes right in our neighborhoods may be silently occurring. For example, discarded prescription drugs are making their way into the drinking water. The debris from plastic bottles is accumulating in the oceans. Carbon dioxide from the fuels we burn to generate electricity increases in the atmosphere.

> Larger changes on our planet similarly have no few if any whistles that we can hear. For decades, the ozone thinned silently in the stratosphere above us as a result of chlorofluorocarbons. Today, the tundra quietly thaws and releases methane. At increasing rates, species blink out of existence with neither a bang nor a whimper."

We need to look up! When we do, we will see the issues in our world that connect to the chemistry we teach. We can find real-world contexts that truly engage our students in learning.

The "train story" contains one other message that connects to sustainability: Pay it forward. People in the past have done things that have made our lives better today. Likewise, it is our responsibility to do things today that will make other people's lives safer, healthier, and happier in the future. The city engineer who put the bend in the bicycle path was one of the people who years ago did something that today makes my life better.

Pay it forward! The members of the Division of Chemical Education who contributed to this symposium are among those who have done this. I am grateful to them. So are people in ACS who helped to make this symposium possible financially, logistically, and intellectually through their support. I am grateful to them as well.

I would like to end with one more message from one of my students. He asked me to convey these words to those gathered at this symposium:

> "There's really nothing I can say that you already don't know or strive to accomplish in your professional lives. However, I have learned that becoming sustainable is the only way the human race and the Earth can survive. So keep up the hard and perilous work. Thank you."

Acknowledgments

With respect and appreciation, the author recognizes the many other instructors and students who contribute to sustainability on their campuses and in their communities but who could not be named in this chapter.

References

1. Report of the World Commission on Environment and Development: Our Common Future, United Nations, 1967. http://www.un-documents.net/our-common-future.pdf (retrieved August 1, 2015).
2. Division of Chemical Education, American Chemical Society. http://www.divched.org/ (retrieved August 1, 2015).
3. Middlecamp, C., Jorgensen, A., Eds. *Sustainability in the Chemistry Curriculum*; ACS Symposium Series 1087; American Chemical Society: Washington, DC, 2011.
4. Committee on Environmental Improvement, American Chemical Society, ACS-CEI Award for Incorporation of Sustainability into Chemical

Education, Committee on Environmental Improvement, American Chemical Society. http://www.acs.org/content/acs/en/about/governance/committees/cei/sustainability-in-the-curriculum.html (retrieved August 1, 2015).

5. Middlecamp, C.; Mury, M.; Anderson, K.; Bentley, A.; Cann, M.; Ellis, J.; Purvis-Roberts, K. *Chemistry in Context*, 8th edition; McGraw-Hill: Dubuque, IA, 2015.
6. Chapter 0: Chemistry for a Sustainable Future. *Chemistry in Context*, 8th ed.; available for download at http://www.acs.org/content/acs/en/education/resources/undergraduate/chemistryincontext.html (retrieved August 1, 2015).
7. *Journal of Chemical Education*, Division of Chemical Education, American Chemical Society. http://pubs.acs.org/journal/jceda8 (retrieved August 1, 2015).
8. SISL: Sustainability Improves Student Learning, The Science Education Resource Center. http://serc.carleton.edu/sisl/index.html (retrieved August 1, 2015).
9. Middlecamp, C. Sustainability! What, How, and Why Now for Our Chemistry Students. In *Sustainability in the Chemistry Curriculum*; Middlecamp, C., Jorgensen, A., Eds.; ACS Symposium Series 1087; American Chemical Society: Washington, DC, 2011.
10. Muir, J. *The Yosemite*; The Century Co.: New York, 1912. http://vault.sierraclub.org/john_muir_exhibit/writings/the_yosemite/ (retrieved August 1, 2015).
11. ACS Summer School on Green Chemistry & Sustainable Energy, American Chemical Society. http://www.acs.org/content/acs/en/greenchemistry/students-educators/summerschool.html (retrieved August 1, 2015).
12. Science Education for New Civic Engagements and Responsibilities, SENCER. http://www.sencer.net/ (retrieved August 1, 2015).
13. Eichler, J. F. Ground Level Ozone in Newton County, GA: A SENCER Model for Introductory Chemistry. In *Science Education and Civic Engagement: The SENCER Approach*; Sheardy, R. D., Ed.; ACS Symposium Series 1037; American Chemical Society: Washington, DC, 2010.
14. Burmeister, M.; Rauch, F.; Eilks, I. Education for Sustainable Development (ESD) and chemistry education. *Chem. Educ. Res. Pract.* **2012**, *13*, 59–68.
15. Stewards of Sustainability, 2012 International Policy Conference Agenda. http://www.millersville.edu/ccerp/files/IPC_agenda_2012.pdf (retrieved August 1, 2015).
16. Carpenter, N. E. *Chemistry of Sustainable Energy*; CRC Press: Boca Raton, FL, 2014.
17. Second Nature, University of Minnesota, Morris, 2014 Climate Leadership Award. http://www.secondnature.org/climate-leadership-awards/university-minnesota-morris (retrieved August 1, 2015).
18. Spiro, T. G.; Purvis-Roberts, K.; Stigliani, W. M. *Chemistry of the Environment*, 3rd ed.; University Science Books: 2012.
19. Themester 2010 Home, Indiana University Bloomington. www.themester.indiana.edu/themester2010 (retrieved August 1, 2015).

20. VC3, Visualizing the Chemistry of Climate Change. http://www.kcvs.ca/vc3/Lessons/ (retrieved August 1, 2015).
21. Zoller, U. Science Education for Global Sustainability: What Is Necessary for Teaching, Learning, and Assessment Strategies? *J. Chem. Educ.* **2012**, *89* (3), 297–300.
22. Zoller, U. Research-Based Transformative Science/STEM/STES/STESEP Education for "Sustainability Thinking": Teaching to "Know" to Learning to "Think". *Sustainability* **2015**, *7* (4), 4474–4491.
23. Brain Games, National Geographic Channel. http://channel.nationalgeographic.com/brain-games/ (retrieved August 1, 2015).
24. Middlecamp, C. Chemistry Education That Makes Connections: Promoting Sustainability. In *Chemistry Education: Best Practices, Opportunities, and Trends*; Garcia-Martinez, J., Serrano-Torregrosa, E., Eds.; Wiley-VCH, Verlag GmbH & Co. KGaA: 2015.

Chapter 4

Harnessing Advances in Biology and Computing To Advance Chemistry: A Regulatory Toxicology Perspective

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Continuing advances in high speed computing and in the understanding of the biological basis of life have enabled a systems approach to assess chemical toxicity. They provide a promise to more efficiently evaluate risk potential after chemical exposure to humans and the environment, and they also provide a promise to design sustainable chemicals and chemical products. Building on the National Research Council’s 2007 report “Toxicity Testing in the 21st Century: A Vision and a Strategy” this chapter presents an overview of the multidisciplinary approaches being developed to integrate science across enabling technologies to develop a mechanistic understanding of toxicology and to use this emerging understanding to predict adverse outcomes. National and international efforts to develop a new paradigm for risk assessment will be mentioned in the context of safe food and drugs, sustainable “green” chemistry, human health and environmental protection.

The Promise of Toxicity Testing in the 21st Century

The goal of this chapter is to describe the promise of “Toxicology Testing in the 21st Century” (Tox 21) to provide more informative and efficient data for risk assessment as described in the National Academy of Science’s National Research Council’s 2007 Report “Toxicity Testing in the 21st Century: A Vision and a Strategy” (*1*). The key roles of adverse outcome pathways (AOP) (*2–5*) and an

In Teaching and Learning about Sustainability; Levy, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

Integrated Approach to Testing and Assessment (IATA) (*5*, *6*) will be described in the context of how these might be used to help improve risk assessment and to help guide the development of "safer", "greener" chemical products. The focus of the chapter will be on US federal government and international efforts, primarily those of the Environmental Protection Agency (EPA) and the Organization for Economic Cooperation and Development (OECD).

Challenge and Need

The current paradigm for the use of a variety of tests to inform chemical safety evaluation is time-tested and provides an effective basis for risk management decisions (*7*). It relies on evolutionary similarity among mammals and incorporates a variety of test species (primarily rats, mice, hamsters, guinea pigs and dogs) (*8*). They are given chemical substances of concern under defined, worst case, test conditions (e.g., very high doses) to determine if the substance causes any toxicity. The logic is that if effects are seen in the animals under these conditions they may cause the same or similar effects in humans. Further, if nothing is observed following exposure to the chemical under such worst case conditions in laboratory animals it is very unlikely that it will cause any effects in humans exposed to the usually much lower doses that will be encountered in food, drugs, cosmetics and the environment.

The challenge is that while the future sale of food, drugs and cosmetics provides a means to recoup testing costs, this is not the case for orphan drugs for which there is little economic benefit, nor for chemicals released into the environment during manufacture, use, and disposal for which there is no economic benefit. As a result there is great uncertainty about whether such chemicals pose a challenge to human health and the environment, as there are many thousands of them, and they have been subjected to limited or no toxicity testing evaluation. Further, it is unlikely that they will ever be subjected to toxicity testing using traditional testing approaches, which are very costly (*5*, *9*). Such testing can range up to $10M or more to register a pesticide active ingredient for instance. Toxicity testing is also a time consuming process as studies that mimic cancer, developmental and reproductive effects are conducted over the lifetime of the test animals which means that the outcome is not known for several years. Finally, the standard animal tests are conducted using a routine experimental approach. While this provides a basis for comparisons between studies, the protocols are not easily adaptable when new issues arise, such as the need to test for endocrine disruption, to evaluate the potential effect of cumulative exposures to chemicals, or to evaluate the potential effects of exposures to nanomaterials.

For the past few decades it has been clear that it is not possible to evaluate the entire universe of commercial chemicals using traditional toxicity testing approaches given the tens of thousands of chemicals in commerce, the fact that only a small subset now have sufficient information to inform regulatory decisions (e.g., there are only around 500 well tested chemicals out of a roughly 70,000 commercial chemical universe), and the cost of testing. It would take centuries to systematically test each commercial chemical using current approaches, and it would cost more than society can bear. Further, given the biological differences between human and animal test species it would not provide the information needed to fully evaluate chemical safety, because more and more evidence is being found that the results of animal testing do not realistically predict human toxicity (*10*). This created the need for a testing approach that results in sufficient, targeted and credible information rather than the generation of encyclopedic information. Until recently, available tools, techniques, and knowledge have not permitted the development of such an informative and efficient testing approach.

Fortunately, recent advances in high speed computing, plus a better understanding of the nature of disease, as well as advances in understanding how chemicals enter the body and are distributed and transformed in it, show promise to realize the development and implementation of an improved and targeted testing approach. The question is how to harness these advances in knowledge and technology to build such a new testing approach, and how best to set it in motion to learn and readily adapt as our knowledge continues to grow?

2007 NRC Toxicity Testing in the 21st Century Report

Following EPA's development of a framework for computational toxicology in 2003 (*11*) and publication of the NIEHS roadmap for a 21st Century National Toxicology Program in 2004 (*12*), EPA tasked the National Research Council (NRC) of the National Academy of Sciences (NAS) to provide advice about how to develop a more informative and efficient testing process to inform decisions about chemical safety. In 2007 NAS published their recommendations in the report "Toxicity Testing in the 21st Century: A Vision and a Strategy" (*1*). The key to their recommendations, as shown in Figure 1 (*13*), is the recognition that life operates through a finite set of normal biological processes from conception to death acting through cellular-response pathways. These can be thought of in multiple ways, but in essence the key point is that if any pathway is perturbed by exposure, uptake and delivery of some chemical substance, or its metabolite, it can disrupt that pathway from its regular sequence of events and send it along another path that results in early cellular change. The NRC further recognized that these early cellular changes do not necessarily lead to disease, or some other adverse outcome, because the body possesses many adaptive response mechanisms, homeostasis, to correct such changes and return the altered pathway back to the normal cellular response pathway and normal biological function (*14*).

However, if the dose perturbing the normal cellular response pathway is sufficiently high, if it occurs over long periods of time, or if it the damage happens at the wrong place and/or at the wrong time the NRC recognized that the early cellular change can overwhelm the normal homeostatic mechanisms such that it cannot be repaired, and the cell becomes irreversibly committed to an adverse outcome pathway resulting in an adverse effect such as mortality, compromised reproduction or some other toxic endpoint (*15*). Thus, the NRC recommended that the key to building a new testing paradigm that provides the targeted, credible information needed to efficiently and effectively inform decisions, and that can be improved as knowledge is gained, is to be able to define adverse outcome pathways (AOPs) and to be able to distinguish between early cellular changes that cause AOPs from those that are returned to normal biological pathways.

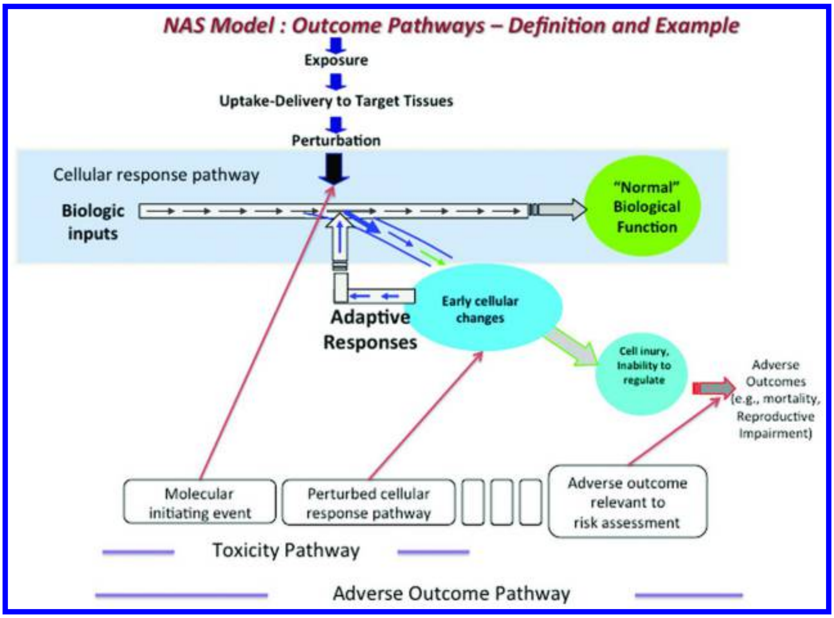


Figure 1. NAS Model for basis of Toxicity Testing in the 21st Century. (Reprinted with permission from ref (13). Copyright 2005 Elsevier.)

The NRC believed that this can be accomplished using cell-based (high throughput) assays employing human cells to understand how chemicals perturb normal cellular functions (i.e., toxicity pathway) and then to establish relationships between these perturbations and adverse outcomes, develop *in vitro* to *in vivo* extrapolation methods that cover the range of events in the AOP, and finally to integrate the results from such tests to predict hazard/risk.

The concept is being applied by EPA (*16*) and others now to help advance their programs. For instance, in May 2011 EPA held a Science Advisory Panel review entitled "Integrated Approaches to Testing and Assessment Strategies: Use of New Computational and Molecular Tools" to receive expert feedback and recommendations about how to improve its plans to apply AOPs through IATA for its pesticide regulatory program (*17*).

The NRC recommended the use of human, not animal, cells in efforts to reach their Tox 21 vision to ensure that the new approaches are most informative about human risk, because they recognized the growing body of evidence that animal based models are not sufficiently predictive of human responses. (However, it should be noted that animal testing and tests using animal cells are highly relevant to inform safety evaluations about potential ecological risk.) Their recommendation to use high throughput methods was to create efficiencies and cost savings that would facilitate rapid testing of tens of thousands of chemicals in hundreds of tests covering the entire range of biological responses to provide a thorough evaluation of chemicals and endpoints. While the NRC vision for Tox 21 has the potential to predict toxicity, and to provide a means to design safer chemicals, the challenge is to convert the Tox 21 promise into reality.

Tailor Testing to the Need

Implementation of the NRC vision for Tox 21 will involve a major paradigm shift in how toxicity testing is planned, conducted and evaluated, and a major hurdle will be achieving acceptance of the new approaches. Overcoming this acceptance hurdle will involve a variety of legal, social and cultural changes in addition to the challenge of showing scientific validity and practical utility of the methods and models that are developed. Thus, given the magnitude of the culture change full implementation of the Tox 21 paradigm will likely take decades (*18*). However, it can be implemented in phases and used for certain applications through a "fit for purpose" approach as experience with, and confidence is gained in, the various models and methods, and as new advances are shown to be useful and reliable. In fact a number of Tox 21 methods and models are being used now.

The term "fit for purpose" means to use the Tox 21 method, model or data to meet a defined need after it has been shown that that method, model or data are appropriate for that purpose. If, for instance, the need is to screen a list of chemicals to identify those that possess some property that may be a signal of potential toxicity for the purpose of identifying which subset of chemicals merit follow up testing, one simply needs information suggesting that a substance has the ability to elicit biological change that may lead to harm (e.g., positive results in mutagenicity tests might suggest that further evaluation of the substance for its ability to cause cancer is warranted).

Fit for purpose is not a new concept. Regulatory agencies, industry and others have long tailored their testing to meet the need. For instance, pharmaceutical companies (Pharma) do not conduct complete toxicity testing for every promising drug candidate. Rather they make small quantities of drug candidates and run them through testing screens designed to identify those substances with the biological properties desirable for the drug purpose in mind and to weed out all the rest as early as possible. For those few candidate drugs with promising biological activities larger quantities of the drug candidate are then synthesized to allow further screening to be conducted to satisfy the manufacturer that the drug does indeed elicit the desired biological properties and that it is likely to be safe and effective for use. As a drug candidate continues show promise, successively larger amounts of the material are made, and the successive testing becomes more rigorous and expensive. This iterative screening-first approach, developed by Pharma, provides the model for the Tox 21 efforts. However, there is a key difference in how the approach is applied for the development of pharmaceuticals compared to how it is used to identify hazardous pollutants for environmental protection. For Pharma, identification of substances that possess the sought after biological activity (drug efficacy) is a measure of success. By contrast for those concerned with environmental protection identification of substances that possess the sought after biological activity (toxicity) is a measure of concern.

Launching the Toxicity Testing in the 21st Century Vision

After publication of "Toxicity Testing in the 21st Century: A Vision and A Strategy" (*1*) the federal government formed the Tox 21 Consortium to pool resources and to share expertise to achieve the NRC vision (*19*). The Environmental Protection Agency (EPA), the National Institutes of Health Sciences (NIEHS), and the NIH Chemical Genomics Center (NCGC) were the original partners. They signed a memorandum of understanding in 2008, and they were joined by the Food and Drug Administration (FDA) in 2010 (*20*). Each agency in the Tox 21 Consortium is contributing to the overall goal by applying its expertise and mission focus through complementary activities.

The initial work is being conducted in three phases that correspond to the timelines outlined by EPA in its Tox 21 strategic plan (*21*) with near- and mid- to long-term goals. The agency's near-term goals were first to strengthen priority setting and screening for data-poor compounds, next to develop and subsequently use new predictive methods to fill data gaps, and then to use this information to guide targeted *in vivo* testing. In the mid- to long-term the agency plans to move in a credible and transparent manner to hypothesis-based, mechanism-driven, and risk-based approaches that focus on effects most relevant for risk assessment to inform risk management.

Phase I was a proof of concept effort to show that the NAS Tox 21 vision was feasible. In this first phase, completed in 2009, EPA screened 320 compounds (309 unique chemical structures, primarily pesticide inactive ingredients and some putative endocrine disrupting compounds) in around 550 high throughput assays in its ToxCast I program (*22*). The NCGC screened 2,870 compounds in 140 quantitative high throughput assays through its NCGC/NCATS Phase 1 program (*23*). Because these efforts were designed to evaluate the feasibility of the NRC's vision, well-characterized compounds of known toxicity were selected so that the results of the hundreds of high throughput screening tests could be compared with existing toxicity data to evaluate the predictivity of the Tox 21 approaches and to provide a means to optimize the screening battery, including discarding non-predictive tests.

Phase II was designed to develop approaches to screen large inventories of a diverse set of chemicals with various properties to refine the approach developed under Phase I for a variety of toxic, primarily endocrine, responses. In this phase chemicals were screened to identify biological activity, and then the results were examined to determine how that biological activity could be used to identify what follow-up testing might be appropriate (*24*). The focus, though not the exclusive focus, of Phase II was to work out the logistics for the use of large scale testing to help identify chemical substances that have biological activity that may be associated with endocrine disruption, and how to use this information to identify what specific and limited follow up testing is required. EPA screened around 1700 compounds for a variety of endpoints associated with endocrine disruption in this phase. The NCGC screened a 10,000 compound library in 30 assays with a primary focus on nuclear receptor activation and cellular response pathways. Between EPA and NCGC 8,307 unique compounds were tested given that some of the chemicals were tested in replicate across the agencies. Dose response information was generated by the NCGC, because it conducted quantitative high throughput screening employing three separate 14-point dose response curves for each chemical tested in each assay. A special emphasis was placed on quality control. Around 7,000 LC/MS analyses were performed on the test plates with follow-up analysis conducted after the test substances had been on the plates for four months. Phases I and II of the Tox 21 programs are completed, and they largely achieved their goals.

The goal of Phase III, not yet started at the time of the writing of this chapter, is to help build the basis to use data from Tox 21 approaches in risk assessment by developing the means to understand how the results relate to adverse effects in the human body. The goal is to improve biological coverage and human relevance by building on the experiences gained in Phases I and II to help develop the means to use data from high throughput approaches to inform risk assessments. As mentioned earlier in the chapter one needs an enhanced interpretation about what the data mean with respect to an AOP before they can be used to inform risk assessments. Just how much needs to be known before a comfort level is reached that these new approaches to toxicity testing are suitable for risk assessment is determined by whether the results are "fit for that purpose." The level of certainty required before a comfort level is reached that Tox 21 tests are fit for a particular type of risk assessment is determined by the importance of the decision to be made. This in turn is determined by the size and nature of the exposed populations, the potential impacts of adverse effects on those populations, the cost of remedy, legal and legislative requirements and a variety of other non-scientific factors.

High- and mid-throughput toxicology testing (i.e. *in vitro* robotic testing plus bioinformatics and biocomputational tools) are very promising first approaches to quickly generate hazard data on thousands of chemicals for tens- to hundreds- of endpoints, and they are less expensive than traditional toxicity testing. However, high throughput tests have some limitations. For instance, as currently configured they are not well suited to evaluate the effects of volatile chemicals or chemicals that require metabolism. Screening level tests are also not now able to evaluate the complex interactions that occur in the body of multicellular organisms, like humans, nor can they assess the interactions that occur between multicellular organisms such as the effects of chemicals on the nervous system and behavior or the immune system. In addition, they can't now be used to predict the formation of cancer, reproduction and development with any degree of certainty.

Expanding the Toxicity Testing in the 21st Century Vision

EPA has been collaborating with member countries comprising the Organization for Economic Cooperation and Development (OECD) to adopt Tox 21 approaches to inform regulatory decisions worldwide. The OECD mission is to remove the non-tariff trade barriers that might arise between countries if differing standards for regulation were implemented around the world. Applying the concept of adverse outcome pathways (AOP) (*2–5*) through an integrated approach on testing and assessment (IATA) (*5*, *6*) are considered to be the keys to achieve this goal. OECD established an AOP development program to identify new *in vitro* Tox 21 test methods as candidates to become OECD Test Guidelines. As part of this effort OECD also established the OECD QSAR Project for the identification of new methods/profilers for grouping chemicals, and various OECD Hazard Assessment activities for the development of Integrated

Approaches to Testing and Assessment (IATA), also known as Integrated Testing Strategies, for defined hazard endpoints.

Integrated Approach on Testing and Assessment

In OECD parlance, an Integrated Approach to Testing and Assessment (IATA) is "a narrative which delineates the documented, plausible, and testable processes by which a chemical induces molecular perturbations and the associated biological responses which describe how the molecular perturbations cause effects at the subcellular, cellular, tissue, organ, whole animal and (if required) population levels of observation." It is called an "Integrated Approach to Testing and Assessment", because it integrates existing information about what is known about a chemical, its chemical properties and impacts on biological systems with estimates of exposure to predict risk. It is a systematic process involving the formulation of plausible and testable hypotheses, and it is also used to identify what is not known to target subsequent testing on chemicals and endpoints of concern. The IATA process is designed to evolve as knowledge is gained so that future assessments will be better than those conducted now, and as time passes it is designed to rely more and more on efficient, informative and cost-effective biologically based alternative non-animal approaches and less and less on animal testing (Figure 2).

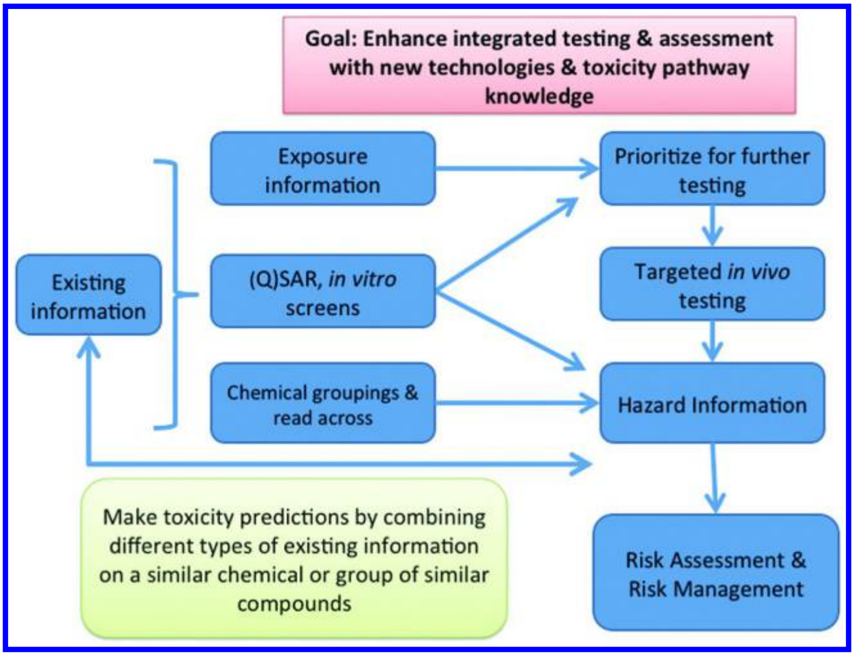


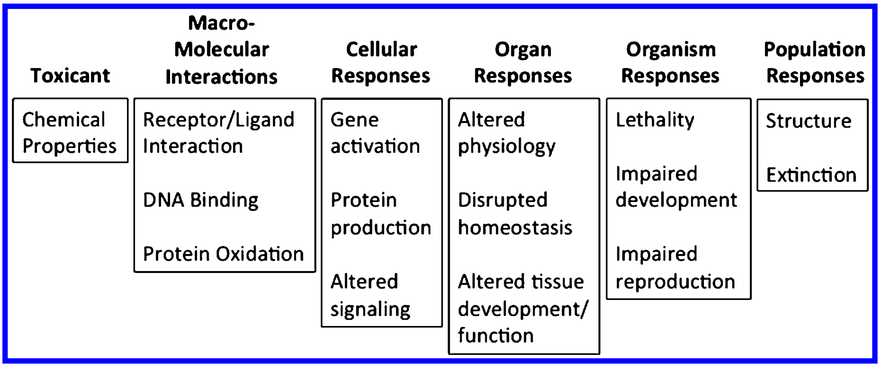
Figure 2. Integrated Approach on Testing and Assessment (IATA). (Reprinted with permission from ref (17). Copyright 2011 US EPA SAP.)

Adverse Outcome Pathways

An Adverse Outcome Pathway (AOP) is the key to any IATA. It formalizes the NRC Tox 21 concept of perturbations of normal cellular response pathways leading to adverse outcomes if the damage is not corrected by normal adaptive responses. In an AOP the initial damage to the cellular response pathway is referred to as a molecular initiating event (mie), and the toxic endpoint is referred to the adverse outcome. These are the two anchors of the AOP, beginning and end, respectively (Figure 1). Key events are not necessarily fully defined mechanistic steps, but they are measurable biological responses that occur along the pathway between the mie and the adverse outcome and it needs to be shown that they must occur in sequence for an adverse outcome to result. Figure 3 summarizes the types information needed to define an AOP, including the definition of an mie and an adverse outcome as well as key events between these two anchoring events.

Then various models, tests and other information from the data streams that inform the pathway relating to the adverse outcome are each mapped against that pathway to identify which part of it they adequately cover (Figure 4).

AOPs provide a basis to link predictive models and test results together to cover the full range of events leading from an mie to an adverse outcome. They also provide a basis to assess and/or predict risk for a variety of purposes, including the design of safer and greener chemicals (*25*).



Toxicant	**Macro-Molecular Interactions**	**Cellular Responses**	**Organ Responses**	**Organism Responses**	**Population Responses**
Chemical Properties	Receptor/Ligand Interaction	Gene activation	Altered physiology	Lethality	Structure
	DNA Binding	Protein production	Disrupted homeostasis	Impaired development	Extinction
	Protein Oxidation	Altered signaling	Altered tissue development/ function	Impaired reproduction	

Figure 3. Schematic representation of an Adverse Outcome Pathway. (Reprinted with permission from ref (3). Copyright 2103 OECD.)

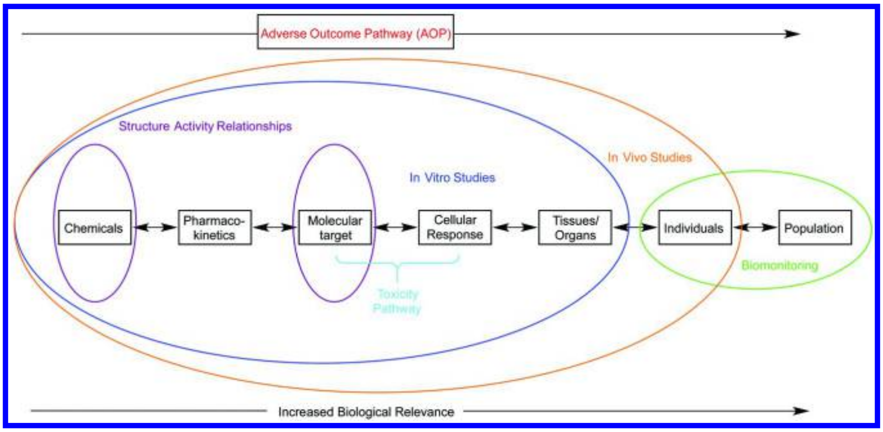


Figure 4. Adverse Outcome Pathway and the data streams that inform it. (Reprinted with permission from ref (17). Copyright 2011 US EPA SAP.)

Testing in the 21st Century Applications To Advance Chemistry for Sustainability

The development and application of Tox 21 has enabled the field of "green toxicology" and many Tox 21 tools are available now that can be used from the beginning of, as well as throughout, the design process to select less risky and more sustainable chemical options. Knowledge about the chemicophysical properties of a substance that determine its biological activity, as well as the biological properties of related chemicals that share the same chemical structure space, can be used to target screening level efforts to separate the greener chemistries from less green ones. Table 1 "The 12 Principles of Green Chemistry" provides a basis to define the role for Tox 21 approaches in sustainable chemistry (*26*). Principles 3-5 and 10-12 provide a framework for application of Tox 21 tools for the specific purpose of green design by offering a coherent intellectual framework for the application of these tools to assess exposure and risk and to identify where the available Tox 21 tools need to be augmented.

Figure 5 depicts the major thrusts of green toxicology, which include benign design and early testing to avoid exposure to hazardous substances and thus avoid risk by developing "…less toxic products, safer processes, and less waste and exposure" (*26*).

The OECD has developed a "Substitution and Alternatives Assessment Toolbox" as well as other tools to help guide the development of greener chemicals and to help select safer alternatives (*27*). As shown in Figure 6 these tools, including Tox 21 methods, models and data, are designed to be applied throughout the entire chemical enterprise from the design of safe and effective commercial chemicals, foods, drugs, and cosmetics, through their appropriate use and to their proper disposal (*26*). Figure 6 also makes clear that it is essential for a variety of scientists, engineers and other technical experts to work in multidisciplinary teams from the beginning of design efforts throughout the process to ensure safe and sustainable product manufacture, use and disposal.

Table 1. The 12 Principles of Green Chemistry[a]

1. Prevent Waste
2. Atom Economy
3. Less Hazardous Synthesis
4. Design Benign Chemicals
5. Benign Solvents & Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis (vs. Stoichiometric)
10. Design for Degradation
11. Real-Time Analysis for Pollution Prevention
12. Inherently Benign Chemistry for Accident Prevention

[a] Adapted with permission from reference (*25*). Copyright 2014 ALTEX.

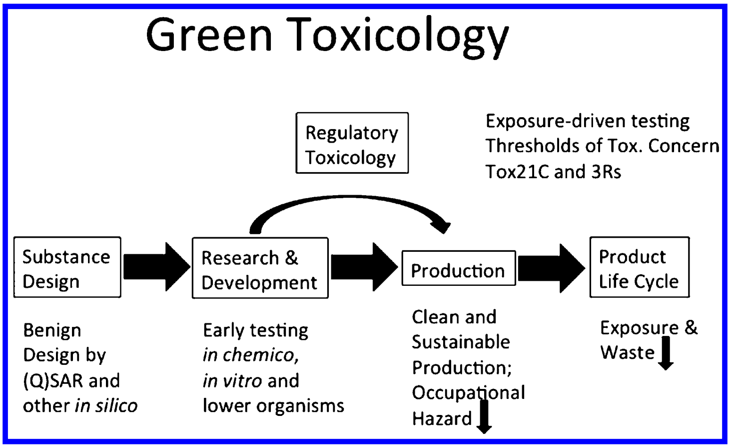


Figure 5. Principles of green toxicology. (Reprinted with permission from ref (26). Copyright 2014 US ALTEX.)

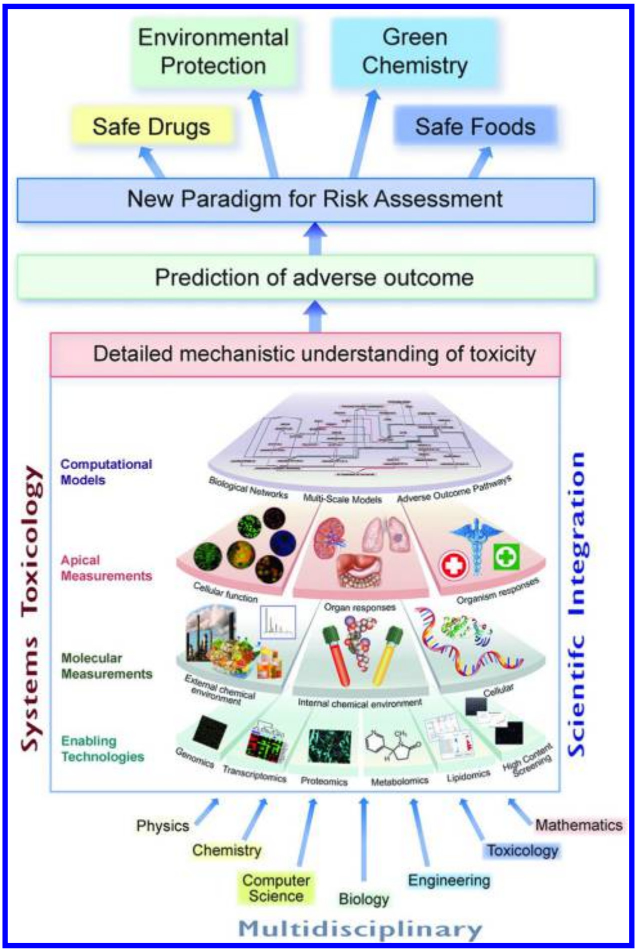


Figure 6. Potential Tox 21 Applications. (Reprinted with permission from ref (25). Copyright 2014 US EPA American Chemical Society.)

As noted earlier in the chapter, Tox 21 needs to be applied in a fit for purpose manner. It was also noted that while there are a number of Tox 21 tools that can now be used to screen large inventories of chemical substances to identify testing needs, they are not yet sufficiently mature for use in risk assessment to inform regulatory decisions. Risk assessments evaluate whether a chemical substance likely causes a biological response (hazard) in combination with the potential for contact to the substance under various scenarios (exposure) to identify the potential for harm (risk). The culmination of the risk assessment process is a description of the potential for harm in terms of the strength of the evidence as well as the uncertainties of the assessment and variability of the data to provide context (risk characterization) for use of the assessment by risk managers and others (*28*).

The chemicophysical properties of a chemical substance determine what the body will do to the chemical (pharmacokinetics) and what the chemical will do to the body (pharmacodynamics). These properties are key to risk assessment, because they determine a chemical's absorption, its distribution in the body and how it will be metabolized and excreted. They also determine what damage, if any, will be caused by the parent compound, and its metabolites, that may lead to an adverse outcome.

Figure 7 summarizes some of these steps and highlights the importance of systematically considering the entire life cycle of a chemical substance. Comparative exposure assessment is a critical component of risk, and an essential consideration in green chemical design (*29*), because there is a potential for exposure to the substance, its feedstock components, its contaminants and break down products throughout the life cycle of the substance. Thus, each step must be carefully identified and evaluated. Green chemistry design involves a systems approach that considers every exposure scenario, from cradle to grave for each of the alternatives being compared in context with their biological properties to provide the basis for green chemical design. This evaluation requires input from a number of disciplines, and partnerships between chemists and toxicologists throughout the chemical design process are a necessary requirement to produce safer chemicals.

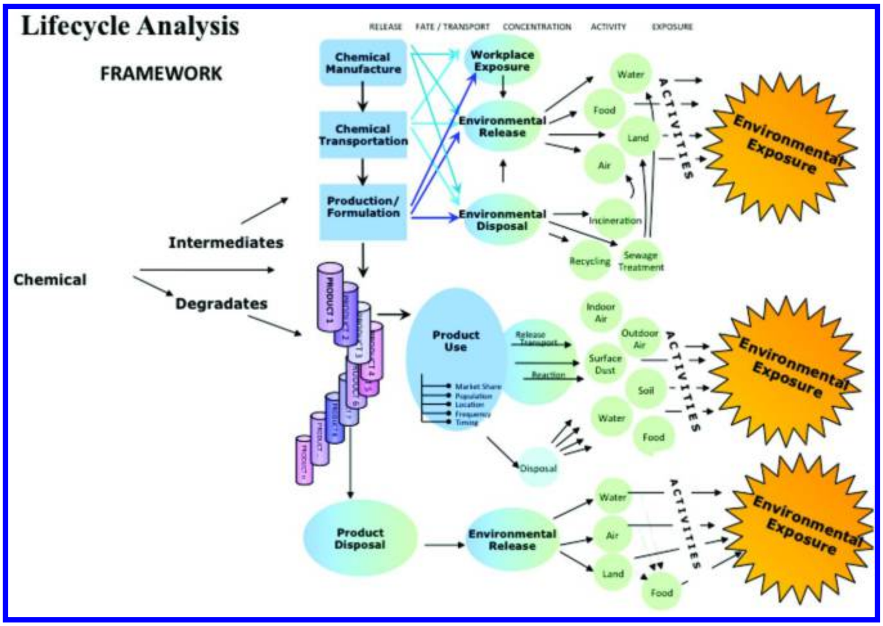


Figure 7. Key components of Life Cycle Analysis (29).

To help advance the means to achieve green design EPA recently asked the NAS to convene a panel of experts to "…*identify the scientific information and tools required by regulatory agencies and industry to improve and increase consideration of potential health and environmental impacts early in the chemical design process.*" In 2014 this resulted in publication of "A Framework to Guide

Selection of Chemical Alternatives” (*30*), which describes a 13 step process (Figure 8) to help develop safer chemicals, to avoid regrettable substitutes as well as other recommendations.

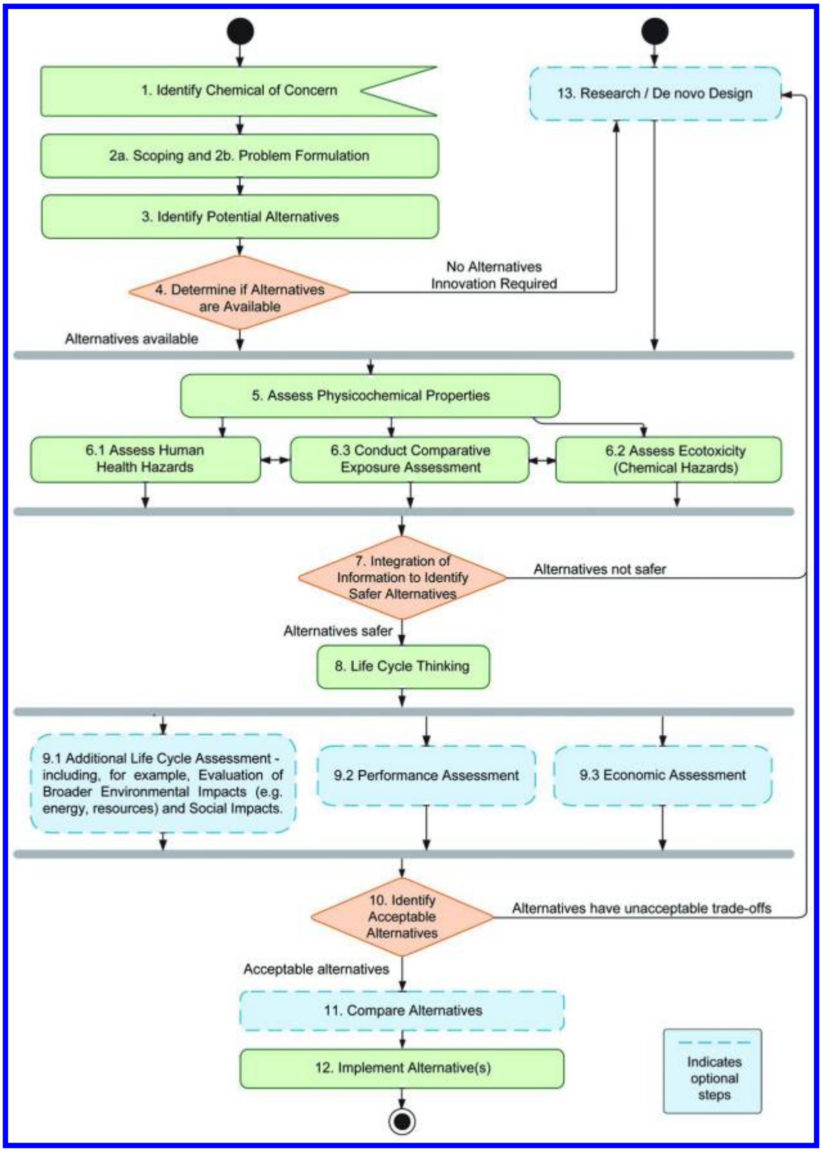


Figure 8. NAS Framework to Guide Selection of Chemical Alternatives. (Reprinted with permission from ref (30). Copyright 2014 National Academy of Science.)

The NAS emphasized scoping and problem formulation as a key initial steps in the process to identify how and why the chemical will be used, what are its alternatives, how will they be evaluated, and how will uncertainty and variability be addressed. They also recommended determination of stakeholder engagement needs in recognition that safety is as much an issue of social concern as it is of scientific assessment, and so involvement by those who will be affected is important. Subsequent steps involve identification of the chemical function, application and performance requirements as well as identification of human and environmental health effects of concern to provide a baseline for comparison with potential alternatives. The recommended process is outline in Table 2. The Academy recommended the use of novel *in vitro* and *in silico* data (i.e. data from Tox 21 approaches) as well as the more traditional data stream to inform this process.

Table 2. Components of Green Toxicology[a]

Benign Design	Toxicologists partner with chemists to identify moieties with undesirable traits
Test early, produce safe	Front load inexpensive, predictive, fast screening level tests
Avoid exposure	Increase the efficiency of production process
Make testing sustainable	Reduce the number of animals used for testing
Use tests not yet mature for regulating	Provides biological activity information, can be targeted to particular chemistries, and builds capability and capacity
Green Toxicology as a driver for 21st Century Toxicity	Experience in green design provides basis for demonstrating utility of computational and other Tox 21 approaches

[a] Adapted with permission from ref (*30*). Copyright 2014 National Academy of Sciences.

Alternative Whole Organism Testing To Supplement High Throughput Tests

As noted earlier, Tox 21 tests cannot be used to assess risk at this time, because they do not realistically model some effects of concern that occur in humans with any degree of certainty (e.g., effects of chemicals on the nervous and immune systems, formation of cancer, alterations of the reproductive system, developmental effects and behavior). Over time a variety of Tox 21 approaches will be shown to produce data that are appropriate for risk assessment, but until that time animal testing will still be necessary. Currently, traditional toxicity testing on rats, mice and other mammals is usually employed to meet this testing need despite the cost and time required. However, alternative whole animal tests have been developed and refined in the last decade, and they are increasingly being used in place of the rodent species traditionally employed for animal testing. Also pioneering efforts to develop “organs on a chip” that can be combined in modular units to mimic the full range of functions of an intact organism have recently been funded by the Defense Advanced Research Projects Agency

(DARPA), FDA and the NCGC. They offer exciting hope for the future (*31*), but they are not ready for application yet.

A major hurdle to the acceptance and use of any Tox 21 method is the need to demonstrate that it is health protective. Since the advent of toxicity testing in the 1930's and 1940's a huge amount of traditional toxicity data have been developed using animal testing. Many risk assessments have been based on this information, and countless decisions have been informed by such testing in government and in the private sector. As a result hundreds of laws and regulations have been developed requiring or recommending the use animal data, and many key legal decisions have been made concerning how to interpret the results from such testing. While not perfect, experience with the traditional approaches has shown them to be protective of human health and the environment, because "society" reached a social contract by "agreeing" more than 50 years ago to accept the results from these tests to inform policy decisions even given their flaws.

If we are to move to the future envisioned by the National Academy of Sciences, it must be shown that the Tox 21 approaches are at least as realistic and protective, if not more so, than the traditional toxicity tests to inform environmental and human health decisions. Such information is needed before we reach a new social contract and "agree" that the results from Tox 21 approaches, though not perfect, are as good as or better than 20th Century toxicity test results and are fit to inform safety decisions. [It should be noted that legislation in the European Union now precludes the use of animal tests on cosmetics (e.g. REACH Cosmetics Directive) (*32*). In other words, the EU has decided that non-animal approaches are "fit for purpose" to assess the risks from exposure to cosmetics.]

A bridging step between the current rodent based testing paradigm and the Tox 21 future is the use of alternative animal methods. Major drivers for the move to alternatives to animal tests were the efforts of Russell and Burch who in 1958 called for an end of the use of traditional species in toxicity testing for ethical reasons, and because scientific evidence indicated that the results from traditional toxicity tests do not mimic human toxicity well. They recommended a process they called the 3 R's (*33*) which stands for "Refine, Reduce and Replace." More specifically, their recommendations call for the "**R**efinement" of animal tests to reduce pain and suffering, the "**R**eduction" in the number of animals used for testing, and where possible the "**R**eplacement" of animals used for testing. While some success was made towards this goal over the next forty years, it wasn't until Tox 21 provided a means to achieve the 3 R's that this has been more generally feasible.

Progress towards the 3 R's has been accomplished in part through the development of alternative whole organism tests (e.g., Zebrafish, *Caenorhabditis elegans*, *Drosophila*). These are considered refinements of animal testing in 3 R parlance, because they employ organisms in lower taxa than mammals. However, like mammals they are multicellular and provide a means to test for nervous, immune, and reproductive effects as well as birth defects and cancer following chemical exposure. They also provide for more efficient and less costly testing in a shorter period of time than do the traditional toxicity tests, because of their much shorter lifespans, smaller size and less costly husbandry and housing requirements. For example, Zebrafish are multicellular, multitissue, multiorgan species that exhibit behavior and undergo rapid development. One is able to test all life stages in Zebrafish within a few weeks, and the endpoints measured are conserved across species including humans.

Much work needs to be done to build the links showing how the key events leading to toxicity in alternative species compare to those that occur in humans before such alternative tests can be used routinely to inform risk assessments, but they have promise to serve as important tools to inform risk decisions by serving as a link between the data produced by Tox 21 approaches, such as those used to date in screening and prioritization efforts, and those provided by animal testing traditionally used to evaluate risk to humans. Perhaps more importantly they can serve as appropriate model species when evaluating certain ecological risks, and they can serve as a key component in sustainable chemical design.

A stepwise, iterative, learn as we go approach will likely be necessary to be able to compare the results from alternative animal and Tox 21 tests with traditional animal test results to demonstrate how well the new approaches stack up against the old ones. To the extent this is done in a systematic way to identify and diminish gaps, and to first move from data and information to knowledge and then finally to understanding, the more successful it will be. The use of AOPs through IATA will help build the necessary knowledge and understanding, and by working in teams through partnerships between chemists, toxicologists, systems biologists and others this can be done in such a way as to provide a firm basis for sustainable chemistry. To the extent that we build tools that are “fit for purpose” we can achieve a sustainable future more quickly and economically by proceeding efficiently in a directed way to harness knowledge about chemicophysical properties and then using this to conduct focused testing whose results progressively lead towards knowledge and ultimately wisdom about the potential chemical impacts on environmental and human health.

The Role of Science Is To Inform Decisions Not Make Them

Chemists need to think in new ways and begin to harness toxicology for chemical design. This means that chemists, toxicologists and other scientists need to work in partnership to shift beyond current animal based regulatory frameworks. It must be recognized that it will be important to demonstrate that the new approaches are at least as good if not better than the old ones to achieve management and public acceptance. Thus, risk managers, other key decision makers and the public need to be engaged early and often in the process. Scientists need to work as partners with lawyers too as there will likely be legal challenges to the implementation of the new approaches given the existing requirements of current laws and regulations.

No doubt mistakes will be made in the move towards Tox 21 implementation, but to the extent that the efforts are conducted in the open, are transparent, and that the concerns of the public are heard and valued, the effort will proceed more quickly and efficiently. To the extent that chemists, toxicologists, regulators and other decision makers clearly and consistently demonstrate that they are trying their best to harness Tox 21 to make the safety evaluation process more informative, more efficient and less costly, the more likely the effort is to succeed. It will be an interesting journey that will likely proceed in fits and starts, but to the extent that we learn as we go and apply the lessons learned to improve the process, the greater the prospects that we will achieve the vision and reap the benefits of the National Academy of Sciences Toxicity Testing in the 21st Century.

As scientists we sometimes wonder and occasionally get frustrated when others are not compelled by data to arrive at conclusions logically the way we are trained to do. An important fact of life is that many factors go into decision making besides science, especially on issues with potentially significant human and environmental health consequences, such as food and drug safety or environmental protection, and large economic impacts. Figure 9 is a diagram of the risk assessment/risk management process showing that while the risk assessment process is largely a scientific endeavor the risk management process is largely a social endeavor (*34*).

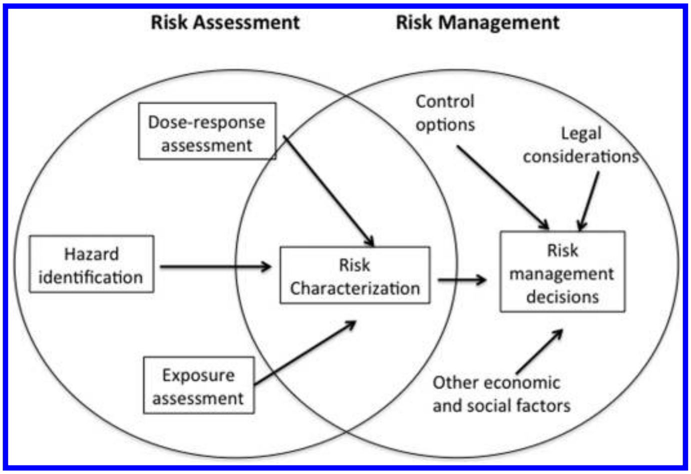


Figure 9. Risk Assessment/Risk Management Process. (Adapted with permission from ref (33). Copyright 2000 US EPA.)

To be most effective scientists need to have an understanding of the political, legal, economic and other social factors considered by decision makers and to recognize that while science informs decisions, the decisions are made in the context of policy (i.e. science informs, policy decides). To the extent that the policies and culture of the government and the work environment are understood by a scientist, the more effective he/she can be working in that environment and in designing studies that are fit for purpose and in communicating the results of those studies in the most useful format and context to inform decisions. NAS recommends that principles or tools be developed that support the benchmarking and integration of high throughput data on chemical effects "*especially in the context of different regulatory requirements*" in their 2014 Framework to Guide the Selection of Chemicals report (*30*).

International Harmonization Is Essential

The NRC vision for Tox 21 and its applications for sustainable chemistry will only be realized to the extent they are adopted. Given the multifaceted nature of society, working with partners to achieve these goals is required as noted in the previous section. Additionally, given the global economy, international harmonization of regulatory efforts is also critically important, and there is a need to be aware of international requirements so that sustainable products are designed with global acceptance in mind.

No one organization, or even one country, is able to achieve the Tox 21 vision alone, so it is important to build on the experiences of others so worldwide information sharing, common application tool boxes, mutually accepted test guidelines, harmonized testing frameworks and assessment guidance are developed. Many efforts are now underway to accomplish this through OECD, North American Free Trade Agreement (NAFTA), International Program on Chemical Safety (IPCS), European Food Safety Agency (EFSA) and others.

Within countries stakeholder engagement is also the key to achieve acceptance of Tox 21 approaches. One example as a model of how this might be accomplished is the Pesticide Program Dialog Committee established by the US EPA (*35*). Representatives from more than 70 stakeholder groups representing environmental organizations, animal rights advocates, farm workers, pesticide manufacturers, children's rights groups, Indian tribes and others regularly meet with EPA to learn of the agency's plans to implement Tox 21, to provide feedback to EPA, and then to go back to their respective organizations to educate them about the new approaches thus reducing resistance and maximizing the chance for success.

Summary

The National Academy of Sciences 2007 report "Toxicity Testing in the 21st Century: A Vision and Roadmap" recommended the use of high throughput screens that cover the full range of events in biological processes to develop the means to know when normal cellular response pathways are sufficiently altered by chemical exposure that they lead to adverse outcomes. The OECD extended these concepts through Integrated Approaches to Testing and Assessment based on adverse outcome pathways as a means to use data from 21st Century Toxicity Testing Technologies (Tox 21) to initially know what to test, when to test it and how and ultimately to assess risk and inform decisions. The first applications have been to screen large inventories of previously untested chemicals to identify those that merit follow up toxicity testing, to decide which follow up tests are required and to schedule the order in which they are tested. The ultimate goal is to reach the point where tests will only be required as needed and animal testing will be rare and only conducted when absolutely necessary. When it is possible to achieve the Tox 21 vision, most decisions will be informed by the inherent properties of the chemical. Even now these properties, plus results from the current Tox 21 test approaches, can help guide green chemistry. Reaching these goals can only be achievable with strong scientific and stakeholder support through a transparent process involving scientific, legal, economic and other social factors.

References

1. National Research Council of the National Academies. *Toxicity Testing In The 21st Century: A Vision And A Strategy*; The National Academies Press: Washington, DC, 2007; 216 pages.
2. OECD. *The adverse outcome pathway for skin sensitisation initiated by covalent binding to proteins*; OECD Series on Testing and Assessment No. 168; Part 1: Scientific Evidence. ENV/JM/MONO(2012)10/PART1; Paris, France, 2012. Available: www.oecd.org/officialdocuments/displaydocumentpdf/?cote=env/jm/mono(2012)10/part1&doclanguage=en.
3. OECD. *Guidance document on developing and assessing adverse outcome pathways.* OECD Series on Testing and Assessment No. 184; ENV/JM/MONO(2013) 6; Paris, France, 2013. Available: www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=env/jm/mono(2013)6&doclanguage=en.
4. OECD Adverse Outcome Pathway Program. Available: http://www.oecd.org/chemicalsafety/testing/adverse-outcome-pathways-molecular-screening-and-toxicogenomics.htm.
5. Willett, C. E.; Bishop, P. L.; Sullivan, K. M. Application of an Integrated Testing Strategy to the U.S. EPA Endocrine Disruptor Screening Program. *Toxicol. Sci.* **2011**, *123* (1), 15–25.
6. OECD. *Guidance Document On An Integrated Approach on Testing and Assessment (IATA) for Skin Corrosion and Irritation*; Environment, Health and Safety Publications Series on Testing and Assessment; No. 203; ENV/JM/MONO(2014) 19; Paris, France, 2014; 64 pages.
7. Fowle, J. R., III; Jacobs, A.; Fitzpatrick, S. Regulatory Testing to Inform Decisions: National and International Requirements. In *Reducing, Refining and Replacing the Use of Animals in Toxicity Testing*; Allen, D. G., Waters, M. D., Eds.; Issues in Toxicology; Royal Society of Chemistry: Cambridge, U.K., 2014; pp 44−98.
8. Gad, S. C., Ed. *Animal Models in Toxicology*; CRC Press: Boca Raton, FL, 2013; 1152 pages.
9. Knight, J.; Rovida, C. Safety Evaluations Under the Proposed US Safe Cosmetics and Personal Care Products Act of 2013: Animal Use and Cost Estimates. *ALTXEX* **2014**, *31* (2), 177–208.
10. Martić-Kehl, M. I.; Schibli, R.; Schubiger, P. A. Can animal data predict human outcome? Problems and pitfalls of translational animal research. *Eur. J. Nucl. Med. Mol. Imaging* **2012**, *39* (9), 1492–1496.
11. Kavlock, R. J.; Ankley, G. T.; Blancato, J. N.; Collette, T. W.; Fowle, J. R., III; Francis, E. Z.; Gray, L. E., Jr.; Hammerstrom, K.; Swartout, J.; Tilson, H. A.; Toth, G. P.; Veith, G. D.; Weber, E. J.; Wolf, D. C.; Young, D. M. *A Framework for a Computational Toxicology Research Program in ORD*;

EPA 600/R-03/065 (NTIS PB2005-105438); U.S. Environmental Protection Agency: Washington, DC, 2003.

12. National Toxicology Program. *A National Toxicology Program for the 21st Century: A Roadmap for the Future*; National Institutes of Environmental Health Sciences: Research Triangle Park, NC, 2004; 14 pages. https://ntp.niehs.nih.gov/ntp/about_ntp/ntpvision/ntproadmap_508.pdf.
13. Andersen, M. E.; Dennison, J. E.; Thomas, R. S.; Connolly, R. B. New directions in incidence dose modeling. *Trends Biotechnol*. **2005**, *23* (3), 122–127.
14. Gregus, Z. Mechanisms of Toxicity. In *Toxicology: The Basic Science of Poisons*, 8th ed.; Klaassen, C. D., Ed.; McGraw-Hill Education Medical: New York, NY, 2013; pp 87−91.
15. Ankley, G. T.; Bennett, R. S.; Erickson, R. J.; Hoff, D. J.; Hornung, M. W.; Johnson, R. D.; Mount, D. R.; Nichols, J. W.; Russom, C. L; Schmieder, P. K.; Serrano, J. A.; Tietge, J. E.; Villeneuve, D. L. Adverse outcome pathways: A conceptual framework to support ecotoxicology research and risk assessment. *Environ. Toxicol. Chem*. **2010**, *29* (3), 730–41.
16. Fowle, J. R., III. Use of Tox 21 Tools from Prioritization for Screening to Risk Assessment in the Context of Endocrine Disruption. *ALTEX Proc. 1/12, Proceedings of WC8* **2012**, 101–103.
17. US EPA FIFRA Science Advisory Panel review of OPP's "Integrated Approaches to Testing and Assessment Strategies: Use of New Computational and Molecular Tools". http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2011-0284-0032.
18. Kotter, J. P. *Leading Change*; Harvard Business Review Press: Cambridge, MA, 2012; 195 pages.
19. Collins, F. S.; Gray, G. M.; Bucher, J. R. Toxicology. Transforming environmental health protection. *Science* **2008**, *319* (5865), 906–907.
20. Memorandum Of Understanding On High Throughput Screening, Toxicity Pathway Profiling, and Biological Interpretation of Findings Between The U.S. Department Of Health and Human Services (HHS) National Institutes of Health (NIH) National Institutes of Environmental Health Sciences (NIEHS)/National Toxicology Program (NTP) and the U.S. Department Of Health and Human Services (HHS) National Institutes of Health (NIH) National Human Genome Research Institute (NHGRI) NIH Chemical Genomics Center (NCGC) and the U.S. Environmental Protection Agency (EPA) Office of Research and Development and the U.S. Department Of Health and Human Services (HHS) U.S. Food and Drug Administration (FDA). Washington, DC, 2010.http://www.epa.gov/ncct/download_files/tox21/MOU_EPA-NTP-NCGC-FDA-Without-Signature-Page.pdf, 7 pages.
21. US EPA Office of the Science Advisor. *The U.S. Environmental Protection Agency's Strategic Plan for Evaluating the Toxicity of Chemicals*; EPA /100/K-09/001; Washington, DC, 2009; 35 pages.
22. Judson, R. K.; Houck, A. R.; Kavlock, J.; Knudsen, T. B.; Martin, M. T.; Mortensen, H. M.; Reif, D.; Rotroff, D.; Shah, I. A.; Richard, A. M.; Dix, D. J. In Vitro Screening of Environmental Chemicals for Targeted Testing

Prioritization: The ToxCast Project. Environ Health. Perspect. **2010**, *118* (4), 485–92.

23. Xia, M.; Huang, R.; Witt, K. L.; Southall, N.; Fostel, J.; Cho, M. H.; Jadhav, A.; Smith, C. S.; Inglese, J.; Portier, C. J.; Tice, R. R.; Austin, C. P. Compound cytotoxicity profiling using quantitative high-throughput screening. Environ Health Perspect. **2008**, *116* (3), 284–91.
24. Toxicology in th 21st Century, NIH, National Center for Advanicing Translational Sciences. Available: http://www.ncats.nih.gov/research/reengineering/tox21/tox21.html.
25. Sturla, S. J.; Boobis, A. R.; Fitzgerald, R. E.; Hoeng, J.; Kavlock, R. J.; Schirmer, K.; Whelan, M.; Wilks, M. F.; Peitsch, M. C. Systems Toxicology: From Basic Research to Risk Assessment. Chem. Res. Toxicol. **2014**, *27*, 314–329.
26. Maertens, A.; Anastas, N.; Spencer, P. J.; Stephens, M.; Goldberg, A.; Hartung, T. Food for Thought… Green Toxicology. ALTEX **2014** (31), 243–249.
27. OECD Substitution and Alternatives Assessment Toolbox. http://www. oecdsaatoolbox.org/Home/Index. OECD Meta review. http://www.oecdsaatoolbox.org/Home/AAGuides. http://www.oecdsaatoolbox.org/Home/FrameworkMatrix.
28. National Academy of Sciences. *Risk Assessment in the Federal Government: Managing the Process*; National Academy of Sciences Press: Washington, DC, 1983; 189 pages.
29. Wolf, D. Syngenta Crop Protection, formerly US EPA, ORD, RTP, NC. Personal communication, 2015.
30. National Academy of Sciences. *Framework For Chemical Selection*; National Academy of Sciences Press: Washington, DC, 2014; 264 pages.
31. Human on a chip. http://www.ncats.nih.gov/research/reengineering/tissue-chip/tissue-chip.html; see also http://wyss.harvard.edu/viewpage/461/.
32. Seventh Amendment of the European Union Cosmetics Directive banning animal testing. https://www.cosmeticseurope.eu/publications-cosmetics-europe-association/european-union-cosmetics-directives.html?view=item&id=14.
33. Russell, W. M.; Burch, S., R. L.; Hume, C. W. *The principles of humane experimental technique*; Johns Hopkins Center for Alternatives to Animal Testing: Baltimore, MD, 2005. http://altweb.jhsph.edu.
34. Fowle, J. R., III; Dearfield, K. L. *U.S. Environmental Protection Agency Risk Characterization Handbook*; EPA 100-B-00-002; December 2000; 160 pages.
35. US EPA, Pesticide Advisory Committees and Regulatory Partners. Available: http://www2.epa.gov/pesticide-advisory-committees-and-regulatory-partners/pesticide-program-dialogue-committee-ppdc.

Chapter 5

The Chemical Health and Safety Role in Supporting Safe, Sustainable Labs in the 21st Century

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Laboratories have significantly larger environmental footprints than other types of buildings. These footprints are driven by scientific requirements for flexible workspaces that can support the safe use of a diverse group of hazardous chemicals. Reducing these environmental impacts will require careful planning and risk assessment in order to "right-size" energy use and materials requirements in the research setting. To address this concern, "Green Laboratory" communities of diverse stakeholders that support development of more sustainable laboratory techniques will necessary. This chapter highlights the key considerations involved in this issues and provides references to sources of useful information.

After the 2011 Fukushima earthquake, power shortages forced Japan to cut back its electricity use significantly. This impact was felt by laboratory scientists at the University of Tokyo, which cut its electricity use by up to 40% during peak periods of demand. This was done by turning off lights, reducing ventilation demand, shutting down elevators, and running energy-intensive experiments during off-peak hours.

As reported at Nature.com, researchers at the university said that their low-energy lives were inconvenient, but largely manageable. Restricting the use of some equipment to off-peak hours is "realistic and feasible" said neurochemist Haruhiko Bito, although he added that scheduling researchers' energy use can

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be time-consuming. Chemist Eiichi Nakamura said that the loss of instruments and computer systems slowed research. “The electricity shortage made us realize that we can indeed save energy easily by 10%, but that 30% cuts will impact productivity in the longer term” (*1*).

The Lab Greening Opportunity

Estimates suggest that research laboratories consume five times as much energy as general academic floor space and ten times as much as residential spaces (*2*). The Japanese experience demonstrates that modern laboratories, while resource-intensive workspaces, contain opportunities to improve their environmental sustainability.

Much of this environmental footprint can be attributed to safety considerations included in the programming, design and development of laboratory spaces. The top priorities in this process are generally:

1) flexibility of the space to support an evolving research agenda;
2) deadline pressures to deliver the space as soon as possible to support the missions of the occupants of the space; and
3) facility construction costs.

These priorities often mean that considerations related to energy conservation and facility operating costs fall by the wayside, as tradition and liability concerns lead to retaining historical design specifications based on 20th century chemical uses. Unfortunately, because the facility operating costs are not directly connected to research funding, there is little financial incentive for the laboratory community to understand their magnitude and ways to manage them. Climate action concerns related to carbon emissions from academic campuses are changing this situation.

Addressing and reforming these design habits will require education of many stakeholders. These include laboratory designers, facility operating staff, laboratory leadership (administration and faculty), and laboratory staff in ways that laboratory design and operation can be “right-sized” to conduct chemical operations safely, while minimizing the environmental impacts of the facility it is performed in. These changes will require financial investments, but energy cost savings from those changes are likely to pay for this cost, often in less than 10 years, while saving on carbon emissions over that period. Estimates of these savings can be determined using the Lawrence Berkeley National Laboratory’s Laboratory Fume Hood Energy Model (*3*).

At the heart of this change will be an increased understanding by all stakeholders of the risk assessment process necessary to prudently address laboratory safety issues. The experience at the University of Tokyo suggests that such an effort will provide significant (at least 10%) savings without impacting the productivity of laboratory science. Some laboratory designers have higher ambitions, for example reaching Net Zero Carbon by 2030 (*4*). If academic campuses are to meet the terms of the American College and University

Presidents' Climate Commitment, these more ambitious approaches must be considered.

This chapter provides an overview of three key environmental impacts associated with laboratories and identifies opportunities for green laboratory operations while maintaining a safe workplace. Specifically, it discusses:

1) optimizing laboratory ventilation operations to appropriately balance laboratory health and safety and energy conservation concerns;
2) the role of risk assessment in supporting reductions in the environmental footprints of laboratories; and
3) development of Green Laboratory communities that support more sustainable laboratory practices.

The Carbon Footprint of Laboratory Ventilation

As described above, laboratories use much more energy than other facilities, resulting a large carbon footprint associated with their operations. This is because of the wide variety of hazardous chemicals potentially used in the laboratory environment. This requires broad protection strategies for control of the concentration of airborne chemicals in the laboratory. Laboratory air from the outside environment is pulled into the laboratory building, heated and cooled, delivered to the laboratory workspace, and then immediately exhausted from the building, either through the fume hood or the general exhaust system. Thus, the energy required to treat and move the air is much higher than in equivalent floor space of other types of workspaces, where conditioned air can be recirculated.

As a result, the EPA estimates that one fume hood's energy use is the equivalent of three households in the same climate. For this reason, ventilation is the largest user of energy in labs, representing about 60% of the energy use associated with a laboratory (*5*). This design strategy means that the ventilation of laboratory spaces is responsible for the largest portion of the laboratory facilities' carbon footprint; what proportion of this footprint it is will depend on the local climate of the facility. This factor can be assessed using the fume hood energy model cited above.

Sustainable management of the ventilation energy associated with laboratory space requires careful building design and ongoing monitoring of laboratory activities to assure that a safe and sustainable amount of air is delivered to each laboratory. Fortunately, modern ventilation control systems are designed with appropriate flexibility to support this process. Operators of the system can use the ANSI Z9.5 standard for Laboratory Ventilation, in combination with the ANSI Z10 standard for Occupational Health and Safety Management Systems to appropriately balance safety and sustainability considerations. One example of such a program is that found at Cornell University, Ithaca, NY (*6*); the conceptual basis for this program is described in Stuart and Sweet (2012) (*7*).

The primary driver of this program is a "control banding" risk assessment process performed on a regular basis by Cornell Environmental Health and Safety staff that allows ventilation mechanics to continuously commission laboratory ventilation to meet the needs of the laboratory operations while assuring that spaces are not over-ventilated (*8*). The value of this program is demonstrated by data in the Cornell Climate Action Plan that reports level energy consumption at the Ithaca campus despite a 12% increase in laboratory floor space between 2000 and 2010 (*9*). This plan describes not only energy conservation initiatives undertaken to reduce the campus' climate impact, but also a variety of other innovative approaches to addressing this issue in the academic environment.

Right-Sizing and Risk Assessment

Since 2009, there has been growing concern about safety conditions in academic laboratories. For example, reports from the Chemical Safety Board (*10*), the National Academy of Sciences (*11*), and the American Chemical Society (*12*) have raised concerns about systematic problems in academic lab safety. Chief among these concerns is the need for the development of laboratory risk assessment skills to be incorporated into the chemistry and chemical engineering curriculum.

While this concern is based on high profile incidents in academic laboratories which have resulted in serious injuries and deaths, there are also laboratory sustainability implications associated with this issue. Without careful risk assessment of laboratory operations to inform facility planning and operations, uncertainties result in overdesign of laboratory spaces, as exemplified in the ventilation discussion above.

This redesign of a laboratory facility to "right-size" its energy requirements to the work being conducted in the building requires careful risk assessment of the chemistry involved in the work. One example of this is reducing the number of fume hoods that are operating on a campus. It is common to observe that a minority of fume hoods on a diverse campus are actively being used for chemical processes. In these cases, the hoods can be "hibernated" to reduce their air flow and thus their energy needs (*13*). In order to develop such a program, communication between lab staff about their ventilation needs to control risks and the facility operators must occur on a reliable basis. This communication is often facilitated by Environmental Health and Safety staff who understand both the chemical risk assessment process and building operation considerations.

One reason for the traditional lack of explicit risk assessment documentation in academic laboratories is the lack of best practice guidance that identifies and describes methods for assessing and controlling hazards for both teaching and research purposes. Fortunately, recent developments in chemical safety can address this need.

The first significant development in this regard is the promulgation of the Globally Harmonized System of Classification and Labeling of Chemicals by the United Nations. This system organizes and rationalizes the definition of chemical hazards with both scientific and communication considerations in mind. Thus, it forms the basis for a systematic identification and evaluation of hazards associated with specific laboratory processes.

A second important development is the description of a chemical safety paradigm that can be used in a wide variety of laboratory settings. This risk analysis and management for projects (RAMP) paradigm, described in Hill and Finster (*14*), provides an avenue for identifying chemical information needs to perform a risk assessment of chemical processes that falls into the OSHA definition of a laboratory (*15*).

With such a risk assessment in hand, the various management options for addressing chemical hazards can be prioritized and balanced in a way that allows for more sustainable laboratory operations. The management options for chemical hazards include replacing the hazard, engineering controls, housekeeping and oversight, personal protective equipment, and emergency planning. For example, changing the chemicals used in a chemical process to those that are less hazardous may allow for less use of disposable personal protective equipment, or improved laboratory housekeeping may reduce the need for ventilation in a laboratory.

The third major development is the publication of the American Chemical Society Committee on Chemical Safety's document on Identifying and Evaluating Hazards in Research Laboratories (*16*). The methods described in this document provide a scalable risk pathway that allows the level of detail involved to be matched to the level of risk associated with the work under consideration. Included in these methods are laboratory sustainability techniques such as minimization of hazardous and solid waste, identification of safer processes, and appropriate oversight of laboratory conditions for both safety and environmental concerns.

Developing Green Lab Communities

Creating a laboratory community can have both safety and sustainability benefits. Green Chemistry Principle #12 describes "Inherently Safer Chemistry for Accident Prevention" as choosing substances used in a chemical process to minimize the potential for chemical accidents including releases, explosions, and fires (*17*). While this is a generic statement, it can be applied to laboratory operations as part of the risk assessment process described above. It is important to recognize that using Green Chemistry to improve laboratory sustainability is most effectively done in Green Laboratory communities that promote laboratory workers to communicate with each other about improved techniques for reducing the environmental footprints of their work.

In an environment such as academic, which has a high turnover of lab personnel can be a significant challenge. In addition, the stakeholders involved in "greening" laboratories include a diverse set of professions, including:

- Laboratory scientists and staff, who determine the laboratory goals and methods to be used;
- Laboratory administration, who determine which spaces will be assigned to which work within a laboratory facility;
- Design architects and engineers, who develop the specifications for the spaces based on the information provided by the two groups above;

- Facility operators, who adjust the building’s settings to accommodate comfort and safety issues associated with the work being conducted;
- Environmental health and safety staff ,who provide oversight of the results of the above work to assure they stay within prudent health and safety expectations;
- Campus energy management staff, who are responsible for assuring that the campus’ financial and energy resources are used as effectively as possible; and
- Green Labs organizers, who serve the community by highlighting laboratories’ environmental aspects and impacts, not simply with regard to ventilation energy use, but also with regard to other concerns such as solid waste management, management of laboratory electrical loads and best practices that support both the progress and the sustainability of the laboratory mission. Examples of such issues were described in a 2011 article by The Scientist (*18*).

Organizing this diverse set of stakeholders can be a significant challenge, because of resources limits, not only in terms of researcher’s time and attention, but also the financial mechanisms necessary to enable implementation of proactive measures. To overcome this hurdle, government agencies and utility suppliers have developed programs that can provide starting capital for this process (*19*).

Another challenge is that the stakeholders mentioned earlier gain their peer information through separate professional networks that speak different languages with different priorities. For example, while laboratory staff are oriented toward scientific societies, laboratory designers work with standards written by their professional groups, and Environmental Health and Safety staff focus on occupational health and safety regulations. Developing communication among these various groups is a key role of the Green Laboratory profession that is developing.

Despite these challenges, several campuses have developed such programs, often financed by facilities departments and led by staff with significant academic laboratory experience. Because sustainability issues are often tied to local environmental conditions (for example, water conservation is a more pressing issue in the Southwestern United States than in the Northeast), peer to peer education at the same campus is an important Green Labs strategy. This approach has been implemented at campuses including the University of Colorado Boulder (*20*), University of California Davis (*21*), and Cornell University (*22*).

Reviewing their web sites, one can see that the issues addressed at each campus have common themes with campus-specific variations which reflect local issues and the infrastructure available to support Green Labs activities. As with risk assessment and personal protective equipment, one size does not fit all when it comes to Green Laboratories.

Conclusion

The environmental impact of 21st century laboratories is significant. However, emerging technologies and paradigms present important opportunities for reducing those impacts without impacting the fundamental scientific missions of this important workplace. A partnership between laboratory planners, designers, building operators, administration, and workers will help move laboratory science in a more sustainable direction for the 21st century.

References

1. Japan rethinks its energy policy; Renewables come to the forefront as universities take the lead on electricity conservation. http://www.nature.com/news/2011/110518/full/473263a.html?message=remove&s=news_rss&utm_source=feedburner&utm_medium=feed&utm_campaign=Feed%3A+news%2Frss%2Ftoday+(NatureNews+-+All+articles+published+today) (accessed March 10, 2015).
2. Renovating Research Laboratories for Zero Carbon by 2030. http://www.wbdg.org/resources/renovatinglabs.php (accessed March 10, 2015).
3. Laboratory Fume Hood Energy Model. http://fumehoodcalculator.lbl.gov (accessed April 27, 2015).
4. American College & University Presidents' Climate Commitment. http://www.presidentsclimatecommitment.org/about/commitment (accessed March 10, 2015).
5. Posner, S.; Stuart, R.; Thompson, G. A conceptual model for laboratory ventilation greenhouse gas planning. *J. Chem. Health Saf.* **2011**, *18*, 34–42.
6. Cornell University Laboratory Ventilation Management Program. http://sp.ehs.cornell.edu/lab-research-safety/chemical-safety/lab-ventilation/Documents/Cornell_LVMP.pdf (accessed March 10, 2015).
7. Stuart, R.; Sweet, E. A systems approach to an institutional laboratory ventilation management plan. *J. Chem. Health Saf.* **2013**, *20*, 31–37.
8. Sweet, E.; Stuart, R. Identifying general laboratory ventilation requirements using a control banding strategy. *J. Chem. Health Saf.* **2014**, *21*, 9–14.
9. Cornell University Climate Action Plan. http://www.sustainablecampus.cornell.edu/initiatives/climate-action-plan (accessed March 10, 2015).
10. "Experimenting with Danger" Focuses on CSB Case Study on Texas Tech University Accident; Laboratory Deaths at UCLA and Dartmouth. http://www.csb.gov/csb-releases-new-video-on-laboratory-safety-at-academic-institutions/ (accessed March 10, 2015).
11. Safe Science: Promoting a Culture of Safety in Academic Chemical Research (2014). http://dels.nas.edu/Report/Safe-Science-Promoting-Culture/18706 (accessed March 10, 2015).

12. Advancing Graduate Education in the Chemical Sciences. http://www.acs.org/content/dam/acsorg/about/governance/acs-commission-on-graduate-education-summary-report.pdf (accessed March 10, 2015).
13. Modal Fume Hood Hibernation, Cornell University. http://www.sustainablecampus.cornell.edu/pages/modal-fume-hood-hibernation (accessed April 27, 2015).
14. Hill, R. H.; Finster, D. *Laboratory Safety for Chemistry Students*; Wily: 2010.
15. 29 CFR 1910.1450 Occupational exposure to hazardous chemicals in laboratories. https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_id=10106&p_table=STANDARDS (accessed March 10, 2015).
16. Identifying and Evaluating Hazards in Research Laboratories. http://www.acs.org/content/dam/acsorg/about/governance/committees/chemicalsafety/identifying-and-evaluating-hazards-in-research-laboratories-draft.pdf (accessed March 10, 2015).
17. Inherently Safer Chemistry for Accident Prevention. http://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/principles/green-chemistry-principle--12.html (accessed March 10, 2015).
18. How Green Is My Lab? Doing science sustainably. http://www.the-scientist.com/?articles.view/articleNo/30697/title/How-Green-Is-My-Lab-/ (accessed April 27, 2015).
19. Second Edition of Clean Energy Finance Guide Released. http://energy.gov/public-services/funding-financing (accessed March 10, 2015).
20. University of Colorado Green Labs Program. http://www.colorado.edu/ecenter/greenlabs (accessed March 10, 2015).
21. University of California Davis, Take Action: Green Your Lab. http://sustainability.ucdavis.edu/action/green_workplace/green_labs.html (accessed March 10, 2015).
22. Cornell University Green Your Lab. http://www.sustainablecampus.cornell.edu/initiatives/green-your-lab (accessed March 10, 2015).

Chapter 6

Sustainability Challenges for Organic Chemistry: ORGN Perspective

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The issue of sustainability is becoming increasingly important in science, as researchers strive to create systems and technologies that can provide ongoing benefit to earth's population. The role that the various technical divisions of the American Chemical Society can play in this important enterprise was a focus for a 'Sustain Mix' event held during the ACS National Meeting in San Francisco, in August 2014. As the 2014 chair of the ACS Division of Organic Chemistry (ORGN), I participated in this event, and here summarize some thoughts and trends relating to the global sustainability challenge and how an organization such as the ACS Division of Organic Chemistry can play a useful role in helping to build a sustainable future.

Introduction

I am glad to have the opportunity to represent the ACS Division of Organic Chemistry (ORGN) in this important volume on the topic of sustainability and chemistry. What I present here roughly follows the talk on this subject that I delivered at the ACS National Meeting in San Francisco, in August 2014. As the 2014 chair of ORGN I felt obligated to participate in the SustainMix event, despite my lack of expertise on this subject. The Organic Division does have a long history of promoting green chemistry, although few within our leadership had, at the time of the San Francisco meeting, devoted much thought to the

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long term sustainability of the organic chemistry enterprise. Organic chemists, particularly those of the process chemistry persuasion, do enjoy the challenge of designing chemical syntheses to meet specific design constraints, and while these constraints have historically been concerned with the production of high quality products meeting required performance standards with minimal starting material and processing costs, the rapid rise of green chemistry and engineering in recent years suggests that organic chemists may be up to the challenge of optimizing for sustainability as well. These reflections are compiled from my own personal views and from valuable discussions with other organic chemists on how organizations like the ACS Division of Organic Chemistry can play a useful role in helping to build a sustainable future. I am particularly grateful to Ingrid Mergelsberg, Rob Maleczka, Mike Doyle, Oliver Reiser and David Constable.

Is Sustainability at Odds with 3.5 Billion Years of Evolution?

The sustainability challenge for humans on earth in the 21st century is daunting. We can summarize by saying that we have too many people, not enough resources and too much degradation. Before pondering potential fixes, it is useful to reflect on some fundamental truths about life as we know it. In San Francisco, with exceptional vineyards and wineries close at hand, I likened our situation on Earth to winemaking, where grape juice (containing the key resource, sugar) is placed into a vessel, then inoculated with a living colony of yeast organisms. The yeast eat the sugars, grow and multiply until either the food runs out or the growing colony generates so much toxic waste (ethanol) as a byproduct of their growth that the system crashes and the organisms within the vessel die. If we take pity on the dying yeast colony, coming to the rescue to remove ethanol or provide more sugars, the yeast just do it all over again, selfishly increasing until they once again crash the system. It could be argued that this kind of behavior is a core attribute of all life on earth, which if given the chance, will multiply unchecked to take advantage of available resources. Luckily, unlike the yeast trapped within a sealed vat, the earth is not an entirely closed system, receiving an ongoing supply of sunlight that provides the foundation for (almost) all life on earth. Nevertheless, the distribution of this sun-derived food among the web of life on earth is dynamic and constantly changing, complete with runaway resource depletion and system crashes akin to the winemaking example. We humans would like to believe that we are more intelligent than the yeast, being able to foresee and take steps to avert an impending system crash. However, the reality is quite stark. The world's population continues to balloon well past a safe 'carrying capacity', continued growth is called for by economists and planners, with the plateauing or declining population growth of countries such as Japan being pointed to as a harbinger of impending economic disaster (*1*). We are far away from being able to create and enact a plan that would transform a world spiraling out of control in terms of population growth and resource depletion into one that could be sustainably managed.

Stay and Fix vs. Move on to Fresh Pastures

The family histories of many Americans are filled with stories of immigrant ancestors escaping closed systems with dwindling resources, relocating in a new land of opportunity where hard work and an abundance of unexploited resources allowed them to thrive and multiply. But, after a few years or a few generations they often moved on because of increasing competition and decreasing resources. From Massachusets to New Jersey to Kentucky to Ohio to Indiana to Illinois to Nebraska to California, continually seeking new horizons and fresh pastures. This pioneer spirit and appreciation for the open road is an integral part of not just American culture, but a common theme among many peoples. Using a chemistry analogy, we could say that humans love the initial rate portion of the reaction curve, where every appropriate collision of starting materials, A and B, leads to the formation of product, C. We love the simplicity of this initial burst regime, but as time goes on the reverse reaction begins to limit progress, ultimately leading to that particularly dissatisfying situation where for every C that is formed, one is consumed and destroyed… gridlock… stasis… equilibrium.

We would much rather be like Robinson Crusoe coming ashore on an uninhabited island filled with untapped resources. Recent archeological investigations have been shedding light on early inhabitants of the Americas, whose immediate forebears crossed the Bering land bridge to encounter a world untouched by humans. Several weeks before our meeting in San Francisco, the scientific press was filled with reports of the discovery of a Clovis culture site in northern Mexico containing the butchered skeletons of two gomphotheres, a mammoth relative, along with stone tools (*2*). Two things are significant about this finding: First, the site dates to 13,400 years ago, very soon after humans came to the Americas. Second, gomphotheres had been thought to be extinct prior to the arrival of humans in the Americas, clearly a hypothesis now in need of revision. Megafauna extinctions have often occurred when humans come into contact with isolated environments (*3*). For example, eleven species of flightless moas became extinct within a hundred years of the arrival of humans in New Zealand about eight hundred years ago (*4*). Viewed from our current perspective, these extinctions are difficult to understand; why would people kill the last moa rather than fighting to preserve them as a sustainable resource? But, viewed from the perspective of a participant at a moa or gomphothere barbeque, the dilemma becomes more easily understood – with local and short term considerations outweighing global and long term impacts.

How To Avoid the Tragedy of the Commons?

This kind of situation where optimization of individual interests leads to degradation of shared resources is often referred to as the “tragedy of the commons” from a 1968 *Science* article by Garrett Hardin (*5*). The key features can be illustrated in a scenario where a village shares a communal pasture, and one villager gets the idea to graze a cow on the pasture. The cow grows fat, the owner profits, and decides to put a few more cattle onto the pasture. Inspired by his success, neighbors add their cattle as well. In time, the cattle become crowded, growing more slowly, and the pasture begins to show signs of degradation. While less profitable than before, those raising cattle are still making profits, so the practice continues. But as all could foresee but none could prevent, an overabundance of cattle on the pasture ultimately leads to complete degradation and system collapse. History is replete with examples of how accumulation of seemingly innocent actions by individuals ultimately spells disaster for a shared resource. Anthropogenic climate change, overfishing of the world's oceans and the imminent extinction of rhinos, elephants, tigers, gorillas and saiga to meet demands for trophies and folk cures are just a few grim examples of the tragedies we are currently facing (*6*).

For the example of the cows and the village green, a relatively straightforward solution may be possible. A village council can shift the equilibrium to achieve a 'sustainable steady state' by introducing variable grazing fees, applying an economic pressure that over time would reduce the number of cattle and limit environmental degradation. Alternatively, a 'sustainable cycle' can be achieved if the council prohibits all grazing when pasture degradation reaches a certain critical level, mandating a fallow period to regenerate the degraded resource before grazing resumes. While both of these strategies could, in principle, lead to a sustainable outcome, the problem of how the council decides on a course of action, and how they arrange to enforce their decision now and into the future can be quite complex, even at the level of a small village. The situation becomes considerably more complex when the resource in question is shared between several towns or several states or several nations, or when it is shared by the entire globe.

Early pioneers escaped such degraded environments by moving to unspoiled locations and fresh pastures, but this strategy is becoming increasingly non-viable as ever more of the earth's surface and resources become developed. While colonization of the arctic, ocean seamounts or space may be possible, it is increasingly clear that our challenge today is to devise sustainable systems and ways of operating that will allow us to avoid 'tragedy of the commons' outcomes.

Can't We All Just Get Along?

A natural response when faced with such problems is to ask "why doesn't everybody just do the right thing? Do we really need to create laws and policing mechanisms to keep people from doing the wrong thing?" Unfortunately, the strategy of expecting people to do the right thing suffers from several important flaws:

- *Awareness:* Sometimes the right thing is just not obvious. The effects that cumulatively lead to resource degradation can, in some cases, be small and subtle, with participants in the tragedy not even realizing that what they are doing has a negative consequence.

- *Difference of Opinion:* Sometimes different people see the issue in different ways. The patient buying rhinoceros horn powder in China sees the impact of their actions differently than the conservation officer in Botswana or the environmentalist in California, and the ‘climate change denier’ sees the link between anthropogenic carbon dioxide and climate change differently than does an atmospheric scientist or the majority of the scientific community. While both of these examples may involve a minority opinion at odds with common sense, not every case of differences of opinion is so cut and dried. For example, in areas of the Pacific Northwest, continued harvest of threatened species such as salmon or whales is guaranteed to certain Native American tribes by treaty, but these species are threatened or endangered, and protected from harvest in other parts of the region. Clearly, after a dismal history of broken and revoked treaties between the US government and Native American peoples there is little appetite for challenging the perpetual rights to fishing and whaling granted in existing treaties. However, as the threatened fish and whale species continue to decline, some are advocating exactly this course of action.
- *Free Riders:* Sometimes, despite all best efforts at creating a fair and equitable system, individuals will chose to ‘cheat the system’, pursuing their own selfish actions even though they know this will cause harm to the larger community. Examples are numerous: urban graffiti and vandalism, tax cheats, bank robbery, insurance scams and, perhaps closer to home, the aggravating problem of the shared workplace refrigerator that is always a terrible mess. While perhaps disappointing from a moral or ethical standpoint, evolutionary theory tells us that the parasitic strategies employed by free riders can be successful, provided the ratio of free riders to those that they parasitize remains low (*7*). The presence of free riders is dilemma of long standing, as fifth century BC Greek general and historian, Thucydides, tells us:

  > “*…they devote a very small fraction of time to the consideration of any public object, most of it to the prosecution of their own objects. Meanwhile each fancies that no harm will come from his neglect, that it is the business of somebody else to look after this or that for him; and so, by the same notion being entertained by all separately, the common cause imperceptibly decays*” (*8*).

Can Scientific Societies Help?

The questions of ‘who decides?’ and ‘who polices’ are central to the creation of sustainable systems. Agreement on these issues across international lines is notoriously difficult, even with the existence of trans-governmental bodies such as the United Nations. The frustratingly slow progress of the Intergovernmental Panel on Climate Change in addressing the anthropogenic carbon dioxide problem is a recent example that serves to illustrate this point. Extragovernmental organizations are increasingly playing a role in building consensus and effectively driving political change, a case in point being the role of Greenpeace in ending commercial whaling.

Heretofore inwardly focused scientific societies may be helpful in constructing a common, scientific evidence-based viewpoint that spans traditional boundaries, helping to inform the general population and drive change at the local, national or international levels. The membership of the American Chemical Society (ACS), the American Association for the Advancement of Science (AAAS), the Royal Society of Chemistry (RSC), the International Union for Pure and Applied Chemistry (IUPAC), the ACS Division of Organic Chemistry (ORGN) and similar organizations span across a wide range of nations and beliefs, but these members all share a common training in evidence-based inquiry and scientific problem solving. Perhaps these scientific organizations can drive consensus on identifying the most urgent problems and help to focus innovation efforts so as to bring about positive change while promoting education, understanding and training on the emerging science of sustainability.

It will be a challenging task for scientific societies to begin playing a larger role in galvanizing public opinion and driving political change. On the other hand, scientific societies have historically shown a commitment to taking charge in building consensus within their own ranks, creating and maintaining the infrastructure of science and showing a commitment to stay and fix rather than abandoning problems to move on to fresh pastures. The scientists committed to these organizations are certainly not free riders, and could be an important element in addressing the sustainability challenge. Success in this effort will depend on several key points:

- We will need to move quickly and work in concert. Our world is already seriously degraded, and we simply don’t have time to waste in unproductive sidetracks and misaligned approaches to the sustainability problem.
- We will need to involve a greater proportion of our members, going beyond the rather small percentage of active ‘doers’ who have historically been involved in society matters. Effective strategies for converting free riders to volunteers will be needed to increase the frequency of the volunteer phenotype in the general population.
- We will need to actively open our society leadership to members with fresh ideas and boundless energy for tackling tough problems. Established leaders will need to provide guidance and council but must resist the temptation to hold onto power past the point where progress toward the ultimate goal becomes slowed.
- We will need to be bold and courageous to propose and implement global solutions that are capable of addressing the problem at hand, but that are fair and equitable and that preserve the freedom and dignity of the earth’s inhabitants. This is not the time or place for half measures and inaction, or for lopsided strategies that exploit one part of the population for the benefit of another.

The Scientific Good Citizen

Scientific infrastructure can easily be taken for granted, falling prey to the tragedy of the commons when too many choose to be free riders and too few participate in essential maintenance. The importance of building and maintaining the infrastructure of science was something that was impressed on me during my training as an organic chemist at the University of Illinois. Roger Adams was an important figure at Illinois who was a prolific scientific infrastructure builder, playing an important role in creating the model for the educational and research systems in organic chemistry in the 20th century, including many elements still in play today (*9*). Adams was also the 1921 chair of the ACS Division of Organic Chemistry, a historical link that I am proud to share with him. The importance of such role models for scientific good citizens cannot be overemphasized, and the expectation that all scientists have an obligation to contribute to the 'care and feeding' of scientific infrastructure is an essential civics lesson that deserves more explicit treatment in graduate training programs. Scientific infrastructure-building requires planning and a clear vision of the desired future state. The random walk approach to arriving at the right scientific infrastructure is slow, inefficient and ultimately not a viable path forward for creating a sustainable future.

What Can the ACS Division of Organic Chemistry Do?

The mission of the Organic Division is to foster and promote the advancement of the field of organic chemistry. We accomplish this by providing professional development and training, maintaining networks between practicing organic chemists, communicating cutting-edge science in our field, sponsoring awards that help to exemplify excellence in the field and by coordinating excellent programming at ACS National meetings. This outstanding programming is what initially attracted me to the Organic Division, long before I became involved in anything having to do with the running of the division.

The division employs a very open process for selecting symposium topics for the national meetings, and consequently the focus of programming varies from year to year, reflecting the changing interests of our members. An open call for symposium proposals can be found on the division website (www.organicdivision.org). The increasing importance of green organic chemistry as a topic of interest to the division provides a nice illustration of how this system works. Only a decade ago we had very little programming on this topic. Initial forays into this at first unfamiliar topic were met with some skepticism, but the popularity of these sessions and the excellence of the science presented therein led to acceptance and growth, to the point where green chemistry topics have become a mainstay of today's ORGN program.

The Organic Division has a number of member-oriented activities that help to support our community and draw our members closer together. The National Organic Symposium is a biannual conclave of organic chemists that has been bringing together organic chemists since 1925. An outstanding overview of the history of this event has been chronicled by Edward Fenlon and division webmaster, Brian Meyers (*10*). This symposium has played an important historical role in shaping the field or organic chemistry, and will continue to do so for years to come.

We have no doubt that organic chemistry will continue to be a vibrant area of scientific investigation well into the future. This division is actively investing in the next generation in terms of education, training and leadership. Longstanding programs sponsored by the division include fellowships for both graduate students and undergraduate researchers as well as symposia honoring outstanding achievement by early career scientists in both academia and industry. When we talk with young students and emerging new organic chemists we find them to be very passionate about using their knowledge to solve global problems and to help build a sustainable future. In an effort spearheaded by John Gupton, the division recently launched an ACS Division of Organic Chemistry Outstanding Undergraduate Chemistry Student in Organic Chemistry Award that recognizes the top organic chemistry student at US universities and colleges. In 2014, 279 different schools participated, and the program continues to grow. The winning students are incredibly enthusiastic about putting their training to work in a career that will make a difference in the world.

In a very successful ACS Division of Organic Chemistry Graduate Student Symposium developed by Gary Molander and Andy Evans, rising fifth-year graduate students in organic chemistry are brought together for four days of intensive workshops with student presentations and posters. The program is supported by industry, and helps define a year class among these students. As they go on to finish their studies, some go to careers in industry, others to academia, but it is our hope that they will continue to hang together as a collaborative unit over time. The program is now entering its sixth year, and the passion of these young students for using their knowledge and training to go out and tackle the problems of the world is very impressive and gratifying.

Toward Sustainable Organic Chemistry: Recent Examples

David Constable has done a great job of providing a sobering view of the unsustainable situation with regard to accessing many of elements that are routinely used in organic chemistry such as rhodium, indium and palladium (*11*). Organic chemists are rising to the challenge, replacing a number of these unsustainable metal catalysts with earth-abundant metals such as iron, nickel and cobalt (*12–14*) or by the use of organocatalysts which contain no metal at all (*15*, *16*). Biocatalysis continues to thrive, being used at increasingly large scale and taking on chemical transformations that were heretofore considered out of scope (*17*, *18*). Other organic chemists are investigating renewable feedstocks (*19*), solar energy (*20*), carbon sequestration (*21*) and conversion of abundant methane to higher molecular weight fuels and feedstocks (*22*, *23*). Still other chemists are taking advantage of recent developments in analytical technologies to push the scale of routine organic synthesis to unprecedented levels of miniaturization (*24*), or to use sustainable, non-toxic solvents to enable the function of chemical analysis devices that can be brought out of the laboratory and into the everyday world (*25*). Finally, recent trends in the use of inexpensive remote meeting and collaboration technologies may help to both reduce the costs of participation in science, while simultaneously increasing the pool of participants – both important elements for the development of a sustainable global scientific enterprise (*26*, *27*). Excellent reviews of the exciting progress in these and other areas offer ample testimony to the fact that the creativity and ingenuity of organic chemists will play an important role in facilitating the transition to a more sustainable world.

Please Join the ACS Division of Organic Chemistry

I would like to take this opportunity to request that interested readers help the Organic Division to remain an ongoing source for good in our field. Membership is only $15 per year at this writing. The Organic Division, like many ACS divisions, is currently fighting an ongoing decline in membership as the organic chemistry jobs in the US are reduced and as volunteerism continues to decline. Our membership has dropped about twenty-five percent over the past ten years. Many organic chemists know the ACS Division of Organic Chemistry and appreciate the programming, awards and other services that it provides, but are not members. Please, be a scientific good citizen, become involved and take this opportunity to join at the division website (www.organicdivision.org). The Organic Division is committed to fostering and promoting the advancement of the field of organic chemistry to create a sustainable world, and we welcome your involvement in helping us to achieve this mission. We are facing significant challenges, but even the longest journey begins with a single step.

References

1. Japan's demography: The incredible shrinking country. *The Economist*; March 25, 2014.
2. Sancheza, G.; Holliday, V. T.; Gaines, E. P.; Arroyo-Cabrales, J.; Martínez-Tagüeña, N.; Kowler, A.; Lange, T.; Hodgins, G. W. F.; Mentzer, S. M.; Sanchez-Morales, I. Human (Clovis)-gomphothere (Cuvieronius sp.) association ~13,390 calibrated yBP in Sonora, Mexico. *Proc. Natl. Acad. Sci. U. S. A*. **2014**, *111*, 10972–10977.
3. Sandom, C.; Faurby, S. Global late quaternary megafauna extinctions linked to humans, not climate change. *Proc. R. Soc. London, Ser. B* **2014**, *281*, 20133254.
4. Holdaway, R. N.; Jacomb, C. Rapid Extinction of the Moas (Aves: Dinornithiformes): Model, Test, and Implications. *Science* **2000**, *287*, 2250–2254.
5. Hardin, G. The Tragedy of the Commons. *Science* **1968**, *162*, 1243–1248.
6. Dirzo, R.; Young, H. S.; Galetti, M.; Ceballos, G.; Isaac, N. J. B.; Collen, B. Defaunation in the Anthropocene. *Science* **2014**, *345*, 401–406.
7. Ertan, A.; Page, T.; Putterman, L. Who to punish? Individual decisions and majority rule in mitigating the free rider problem. *Eur. Econ. Rev.* **2009**, *53*, 495–511.

8. *The history of the Peloponnesian war, Thucydides*; tr. by R. Crawley; 1874; Book I, p 92 (Google eBook).
9. Tarbell, D. S.; Tarbell, A. T. *Roger Adams Scientist and Statesman*; American Chemical Society: 1981.
10. Fenlon, E. E.; Myers, B. J. Profiles in Chemistry: A Historical Perspective on the National Organic Symposium. *J. Org. Chem*. **2013**, *78*, 5817–5831.
11. Constable, D.; Chirik, P.; Matharu, A. *Endangered Elements: Critical Materials in the Supply Chain*; Presentations On Demand, 18th Annual Green Chemistry & Engineering Conference, June 17−19, 2014, http://www.acs.org/content/dam/acsorg/events/technology-innovation/Slides/2014-06-09-elements-gci.pdf (accessed Aug 28, 2015).
12. Jagadeesh, R. V.; Surkus, A. E.; Junge, H; Pohl, M. M.; Radnik, J.; Rabeah, J.; Huan, H.; Schünemann, V.; Brückner, A.; Beller, M. Nanoscale Fe2O3-Based Catalysts for Selective Hydrogenation of Nitroarenes to Anilines. *Science* **2013**, *342*, 1073–1076.
13. Zuo, W.; Lough, A. J.; Li, Y. F.; Morris, R. H. Amine(imine)diphosphine Iron Catalysts for Asymmetric Transfer Hydrogenation of Ketones and Imines. *Science* **2013**, *342*, 1080–1083.
14. Friedfeld, M. R.; Shevlin, M.; Hoyt, J. M.; Krska, S. W.; Tudge, M. T.; Chirik, P. J. Cobalt Precursors for High-Throughput Discovery of Base Metal Asymmetric Alkene Hydrogenation Catalysts. *Science* **2013**, *342*, 1076–1080.
15. Holland, M. C.; Gilmour, R. Deconstructing Covalent Organocatalysis. *Angew. Chem*. **2015**, *54*, 3862–3871.
16. Atodiresei, I.; Vila, C.; Rueping, M. Asymmetric Organocatalysis in Continuous Flow: Opportunities for Impacting Industrial Catalysis. *ACS Catal*. **2015**, *5*, 1972–1985.
17. Sheldon, R. A.; van Rantwijk, F. Biocatalysis for sustainable organic synthesis. *Aust. J. Chem*. **2004**, *57*, 281–289.
18. Turner, N. J.; Truppo, M. D. Biocatalysis enters a new era. *Curr. Opin. Chem. Biol*. **2013**, *17*, 212–214.
19. *Feedstocks for the Future: Renewables for the Production of Chemicals and Materials*; Proceedings of the 227th National meeting of the American Chemical Society held 28 March−1 April 2004 in Anaheim, CA; ACS Symposium Series 921; American Chemical Society: Washington, DC, 2006.
20. Dittrich, T. *Materials Concepts for Solar Cells*; Imperial College Press: 2014.
21. Smit, B.; Reimer, J. R. *Introduction to Carbon Capture and Sequestration*; Imperial College Press: 2014.
22. Lunsford, J. H. Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. *Catal. Today* **2000**, *63*, 165–174.
23. Konnick, M. M.; Hashiguchi, B. G.; Devarajan, D.; Boaz, N. C.; Gunnoe, T. B.; Groves, J. T.; Gunsalus, N.; Ess, D. H.; Periana1, R. A. Selective CH Functionalization of Methane, Ethane, and Propane by a Perfluoroarene Iodine(III) Complex. *Angew. Chem*. **2014**, *53*, 10490–10494.
24. Buitrago-Santanilla, A.; Regalado, E. L.; Pereira, T.; Shevlin, M.; Bateman, K.; Campeau, L. C.; Schneeweis, J.; Berritt, S.; Shi, Z.

C.; Nantermet, P.; Liu, Y.; Helmy, R.; Welch, C. J. Nanomole Scale High-Throughput Chemistry for the Synthesis of Complex Molecules. *Science* **2015**, *347*, 49–53.

25. Welch, C. J.; Nowak, T.; Joyce, L. A.; Regalado, E. L. Cocktail Chromatography: Enabling the Migration of HPLC to Nonlaboratory Environments. *ACS Sustainable Chem. Eng.* **2015**, *3*, 1000–1009.
26. Welch, C. J.; Ray, S.; Melentez, J.; Fare, T.; Leach, M.; Ray, S. Virtual conferences becoming a reality. *Nat. Chem.* **2010**, *2*, 148–152.
27. Davies, H. M. L.; Morton, D. C-H Functionalization: Collaborative Methods to Redefine Chemical Logic. *Angew. Chem.* **2014**, *53*, 10256–10258.

Chapter 7

Green Chemistry and Innovation

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People often discuss “barriers” to the implementation of green chemistry. This leads to the impression that there is some form of “push back” in the market for sustainable technologies. However, if a technology has attractive performance and cost attributes, it is unlikely that the additional presence of “sustainable” attributes will inhibit its adoption. Most often the “push back” in the market is related NOT to the sustainability aspect, but to the absence of sufficient performance and cost aspects of a product. History has shown us that for a technology to be successful in the market place, it cannot depend solely on its “sustainability” but must also be consistent with traditional drivers. Developing successful green chemistry technologies therefore is fundamentally a challenge in innovation at the molecular level. An important reason why technology organizations have a difficult time meeting this challenge is that most academic chemistry and materials science programs do not adequately teach students techniques to help them design products that are sustainable. Universities around the world are finding ways to add the principles of green chemistry into their curriculum, and one day most, if not all, scientists will have the adequate training - but this will take time. Until the entire chemistry work force is fully trained in green chemistry, organizations that have internalized green chemistry for themselves will enjoy significant competitive advantage.

In Teaching and Learning about Sustainability; Levy, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

Green Chemistry, Sustainability, and Small Business

How do green chemistry, sustainability, and small business mix? Before we address this, I first would like to begin by saying that I am a medicinal chemist. I graduated from Princeton University in 1988 and my advisor was Professor E. C. Taylor. I had the opportunity of working in anti-cancer chemotherapy, on the drug Alimta (*1*), sold by the Eli Lily Company. Alimta is an extremely successful anti-cancer drug for solid tumors. It was a huge program at Princeton in the 1980s, with hundreds of people working on it. In 2012, Princeton opened up a multi-story chemistry building built on the proceeds of Alimta. Needless to say, I assume Princeton is very happy with this molecule.

I had every expectation of going into academia and working as a medicinal chemist. Then, one day, I met a vice president of the Polaroid Corporation, by the name of Lloyd Taylor,who invited me to lunch and offered me a job in exploratory research. I informed him that I was a medicinal chemist planning to go into academia. When he told me how much he wanted to pay me and I said, "When do I start?" and I began working at Polaroid.

Edwin Land, one of the founders of Polaroid, is one of my absolute heroes and, although I never met him, working at Polaroid was a wonderful opportunity. In the eighties, Polaroid was probably one of the best places on the planet to work as a chemist. To have the scientific freedom that I was given was great.

You are probably asking yourself, "So what would a medicinal chemist do at a place like Polaroid?" I was very introspective and was thinking about how, for over 180 years of chemistry, we have been doing things a certain way. As chemists, we heat things under high temperature, we apply high pressure, and we use all kinds of solvents. It's amazing the things we do, and the drugs, materials, the fabrics that we make. Yet, when we look out at nature, I would argue that nature out-performs us hands down from a perspective of molecular complexity and diversity. Not only that, but nature also manufactures everything at room temperature and ambient pressure, and for the most part, uses water as a solvent.

I am not the only person to think about this idea of nature out-performing human science. Janine Benyus has published a book titled "Biomimicry" (*2*) and many chemists have published examples. But I started to explore questions such as, "Why do we heat reactions to high temperature? Why do we manufacture the way we do?"

When you study organic chemistry, you learn that molecules have certain geometries. An S_N2 reaction requires the nucleophile to come in at an angle of 180 degrees to displace the leaving group. For an electrophilic aromatic reaction, the oncoming electrophile has to approach at a 120-degree angle because of the hybridization of the orbitals. All of these geometries are dictated. When we put things into a solvent and heat, these molecules are just banging into each other at absolutely random directions, so most of the time nothing happens. The only way we humans can make chemistry happen is by speeding molecular velocity so that the molecules collide more often. This increased frequency of collision translates into an increased probability for these collisions to happen with the correct trajectory.

But in nature there is never a reactive collision! If you think about it—cells, tissues, plants and leaves—everything is in a semi-condensed state where molecules diffuse through a more complicated, facilitated process in which they “snuggle up” to each other first. Only after they snuggle up to each other do they react. Thus, there is never a random reactive collision. Essentially, molecules first must derivatize themselves through non-covalent forces before the covalent chemistry happens, a process I called noncovalent derivitization (*3*). This observation led me to look at how molecular self-assembly could facilitate materials properties.

While at Polaroid, one of our inventions was based on this concept of noncovalent derivatization (*4*). In the United States, when a company wants to begin to manufacture something at “real world” scale, it needs to obtain EPA approval. For anyone familiar with this process, the documents are known as a Low Volume Exemption and a Pre-Manufacturing Notification.

Through the process of learning how EPA approval happens, I was reacquainted with a dear friend, Paul Anastas, with whom I grew up and attended college. He was working at the EPA in the Office of Pollution Prevention and Toxics and was starting a “green chemistry” program with a group of people. My chemistry fit right into his program by basically attempting to focus on synthesizing things to be environmentally benign in the first place rather than prevent pollution afterwards.

As an example of our collaboration, Paul and I wrote (*5*) *Green Chemistry: Theory and Practice*, a book that defined green chemistry as “the design of chemical products and processes that reduce or eliminate the use of and/or generation of hazardous substances.”

In my opinion, the most important component of green chemistry is the Twelve Principles. Unlike most programs that say *what* we should do, the principles of green chemistry advise you on *how* to do it. The Twelve Principles of Green Chemistry is not a panacea to solve all the world’s problems; rather, it is an attempt to get the organic chemists, the analytical chemists, the physical chemists, the polymer chemists, and the computational chemists to all say, “Yes, we have a role to play.” The Twelve Principles of Green Chemistry tell us all the things we *should* do. In a way, the Twelve Principles is a toolbox to enable the American Chemistry Society’s constituency, and all other chemists, to participate in solving the problems of society, as opposed to merely articulating them.

In my opinion, green chemistry has a huge philosophical and pedagogical component, but that is not enough. In order for green chemistry to change the world, it cannot just be a discussion or a journal article. Rather, to accomplish its goals, it needs to be practiced. In order to do so, it has to be more environmentally benign and less toxic than traditional approaches. Furthermore, it has to provide good performance. No one will buy a cleaner that doesn’t clean just because it was developed using the principles of green chemistry. It also has to have the right cost structure because society should not pay more than it needs for a product. (Safety must be affordable to all.) This focus on practice is not to say that we need not publish; of course, we must publish to grow a science. But if people cannot make use of the technologies, then we are not accomplishing our goals. So, only if all three are present—safety, performance, and cost—will we get something successful on the market.

After working for a decade at Polaroid, I decided it was time for me to go into academia. I thought to myself, here I am with a PhD in chemistry, and yet I have never had any coursework regarding what makes a molecule toxic or what resources are available to find out what makes a molecule toxic. If I wanted to make a red dye I can point to the class that taught me how to make a red chromophore; if I wanted to make it stick to a fabric, I can point to the class that talked about how things stick to each other; if I wanted to make it not fade in light I remember the P-chem and photochemistry class that taught me that. But not one of my classes taught me about toxicology, and I felt that this needed to be changed.

So at UMASS Boston, we decided to start a doctoral program in Green Chemistry. In doing so, we took nothing out of the chemistry program, but added a one-semester class, "Introduction to Mechanistic Toxicology". A one-semester class about toxicology doesn't make someone a toxicologist, but it provides one with the necessary resources to use when information is needed about a molecule. We also added a one-semester class in environmental mechanisms and a one-semester class in law and policy.

Industry has recognized the value of this type of training. More often than not, a person fresh out of the university has a great idea. This person works very hard to reduce the idea to practice. But when it comes time to commercialize the great idea, the company cannot because the process uses a solvent or a reagent that can't be scaled up because of some toxicological or environmental reason. This forces the company to re-invent the process a second time (if possible) with "real world" appropriate conditions. It would be beneficial if university students were given training for the real world, and taught how to invent their ideas correctly the first time around. Interestingly enough, the industries that "get it" realize that that is exactly what Green Chemistry is.

Since the vast majority of our chemistry graduates take positions in the industry (*6*), we owe it to them to let them be successful, and so the Green Chemistry PhD program at UMASS was a pilot program. I do not believe all universities should have PhD programs. But I do believe that every student should graduate one day having some of this training. There is a moral and ethical component, however. How can we hand a student a diploma and say, "go invent for society" without giving them some skills in toxicology and environmental health sciences? This is unacceptable.

This is why we need to work with toxicology, not to make junior toxicologists but rather to provide a conduit of conversation so that curriculum and green chemistry provides a step forward. We have a lot of good work ahead of us, but many people are on board and I am 100% confident that we will get there. The Green Chemistry Commitment run by Beyond Benign (*7*) is a testament to the momentum being witnessed in chemistry departments, to adapt and change.

In 2007, in history's worst economy ever, I decided to give up tenure and started a for-profit company, with Jim Babcock, the Warner Babcock Institute for Green Chemistry. We wanted a research facility that had every piece of equipment necessary to invent and develop green chemistry. While the lab and the equipment are spectacular, they pale in comparison to the people working there. They are amazing, passionate, and hard-working people. We do not publish many papers, nor do we speak at many technical conferences. Rather, we solve problems.

Some of the examples of things done in the pharmaceutical arena include an Alzheimer's drug (*8*) and a Parkinson's disease drug (*9*), both of which we hope to see in clinical trials. We also have a biomimetic hair process (*10*), which we modeled after the process called sclerotization, or the way a beetle changes its exoskeleton from white to black over a short period of time, which is a tyrosinase cascade. The product doesn't color your hair but rather restores the human melanin pigment. So if you had black hair and it turned gray, the product makes your hair black again; likewise, if you had brown hair and it turned gray, the product makes your hair brown again. It restores the exact color your hair was before it turned gray and it is not a dye, which is pretty amazing. This product known as Hairprint Technology is a very successful product on the market.

We also have a paving product. We have an additive (*11*) called "Delta-S" and a spinoff company called "Collaborative Aggregates" that allows pavers to use over 65% recycled material and pave at reduced temperatures.

Other examples include electronics recycling (*12*), solar energy (*13*, *14*), oncology drugs (*15*, *16*), BPA free thermal images (*17*), and bromine free flame retardants (*18*, *19*) to name a few.

While we have been very productive at the Warner Babcock Institute for Green Chemistry, I do not feel that we are any "better" or "smarter" than any other group of scientists. The point is, that when a group of people approach a problem from a different direction, the group often comes up with different solutions. Anything that one applies at the beginning of a research process that has them approaching it from a different perspective is good. What better different perspective than reduced toxicity and environmental impact. I would say that we are not successful in spite of green chemistry, but that we are successful because of it.

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References

1. Taylor, E. C.; Liu, B. A new route to 7-substituted derivatives of n-[4-(2-[2-amino-3,4-dihydro-4-oxo-7H-pyrrolo(2,3-d)pyrimidin-5-yl]ethyl)benzoyl]-L-glutamic acid. *J. Org. Chem.* **2001**, *66*, 3726–3738.
2. Benyus, J. M. *Biomimicry: Innovation Inspired by Nature*; Harper Collins: New York, 1997.
3. Guarrera, D.; Taylor, L. D.; Warner, J. C. Molecular Self-Assembly in the Solid State. The Combined Use of Solid State NMR and Differential Scanning Calorimetry for the Determination of Phase Constitution. *Chem. Mater.* **1994**, *6*, 1293.

4. Taylor, L. D.; Warner, J. C. Process and Composition for Use in Photographic Materials Containing Hydroquinones. U.S. Patent 5,177,262. Filed July 19, 1991, Published January 5, 1993. EP 0523470. Filed July 3, 1992, Published February 3, 1993. CA 2070450. Filed June 4, 1992, Published January 20, 1993. DE 69218312. Filed July 3, 1992, Published April 24, 1997. JP 06230540. Filed July 16, 1992.
5. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, 1998.
6. National Science Foundation, National Center for Science and Engineering Statistics.. *Doctorate Recipients from U.S. Universities: 2013*; Special Report NSF 15-304; Arlington, VA, 2013. http://www.nsf.gov/statistics/sed/2013/ (accessed Sep. 12, 2015).
7. The Green Chemistry Commitment, Beyond Benign Foundation, Wilmington, MA. http://www.greenchemistrycommitment.org/ (accessed Sep. 12, 2015).
8. Warner, J. C.; Nguyen, D.; Gladding, J. A.; Cheruku, S. R.; Loebelenz, J. R.; Norman, J. J.; Thota, S.; Lee, J. W.; Rosenfeld, C. Dihydro-6-Azaphenalene Derivatives for the Treatment of CNS, Oncological Diseases and Related Disorders. U.S. Pat. Appl. US 20140094487. Published April 3, 2014. PCT Int. Appl. WO 2014052906. Published April 3, 2014. CA 2886749. Published April 3, 2014.
9. Warner, J. C.; Chreuku, S. R.; Hari, A.; Norman, J. J. *Metal Complexes and Methods of Treatment*; PCT Int. Appl. WO 2015070177. Published May 14, 2015.
10. Warner, J. C.; Muollo, L.; Stewart, A. Formulation and Processes for Hair Coloring. PCT Int. Appl. WO 2015057254. Published April 23, 2015.
11. Warner, J. C.; Muollo, L. R.; Walker, R. L.; Bianchini, J. R. Asphalt Binder Additive Compositions and Related Materials. PCT Int. Appl. WO 2015070180. Published May 14, 2015.
12. Poe, S. L.; Paradise, C. L.; Muollo, L. R.; Pal, R.; Warner, J. C.; Korzenski, M. B. Method for the recovery of lithium cobalt oxide from lithium ion batteries. U.S. Pat. Appl. US 20140306162. Published October 16, 2014.
13. Warner, J. C.; Van Benschoten, H.; Cannon, A. Systems and Methods for Preparing Components of Photovoltaic Cells. PCT Int. Appl. WO 2011103494. Published August 25, 2011.
14. Warner, J. C.; Vanbenschoten, H.; Cannon, A. Semiconductor Compositions for Dye-Sensitized Solar Cells. PCT Int. Appl. WO 2011103503. Published August 25, 2011.
15. Warner, J. C.; Gladding, J. A.; Gero, T. W.; Cheruku, S. R. Rilyazine derivatives and compositions for the treatment of cancer. PCT Int. Appl. WO 2015034785. Published March 12, 2015.
16. Warner, J. C.; Gladding, J. A.; Gero, T. W.; Cheruku, S. R. Preparation of Rilyazine Derivatives Useful in Treatment of Cancer. U.S. Pat. Appl. US 20150065510. Published March 5, 2015.
17. Warner, J. C. Thermal Imaging. U.S. Pat. Appl. US 20140371064. Published December 18, 2014.

18. Warner, J.; Tang, P.-I.; Stewart, A.; Kelly, C. Bromine-Free Fire Retardant (FR) Agents Capable of Using a Cyclization Mechanism. PCT Int. Appl. WO 2015050542. Published April 9, 2015.
19. Warner, J.; Tang, P.-I.; Stewart, A.; Kelly, C. Structured endothermic fire-retardant agents encapsulated in thermally-sensitive material and fire-retardant composition comprising polymer matrix and microcapsules incorporating fire-retardant agents. PCT Int. Appl. WO 2015026353. Published February 26, 2015.
20. Warner, J. C.; Pont, J. L. Green Chemistry and innovation: SCHB perspective. Presented at the 248th ACS National Meeting, San Francisco, CA, United States, August, 2014; CHED-130.

Chapter 8

Environmental Perspective on Sustainability and Water Reclamation

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Water availability and quality must be maintained to assure life on Earth. Sustainability demands we use water judiciously and reclaim the contaminated water. A number of inorganic and organic compounds from arsenic to zinc can pollute our groundwater. Arsenic contamination of groundwater has been affecting around 200 million people worldwide including in the United States; however, it is most pronounced in Bangladesh, where naturally occurring arsenic contaminates millions of wells that were installed to solve the problem of microbial contamination. Arsenicosis, resulting from drinking arsenic-contaminated water can lead to a slow and painful death. To seek viable solutions, workshops were organized by the author in Bangladesh and India, and several symposia were planned at meetings of the American Chemical Society (ACS), UNESCO (United Nations Educational and Scientific Organization), and the International Union of Pure and Applied Chemistry (IUPAC). We need to maintain water quality by monitoring water resources for various known and unknown contaminants rigorously and regularly. Discussion of the problem will focus on how groundwater is contaminated with arsenic, desirable methods for monitoring arsenic contamination at ultratrace levels, and the best options for reclamation. This chapter highlights solutions that offer significant improvements in water purification technologies, at reasonable costs.

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1.0. Introduction

After air, water is the most essential material for human survival. Without water, life as we know it would not be possible. Therefore, it is absolutely necessary that we achieve water sustainability (*1–5*). The definition of sustainability is obvious, as it is constructed from two words—*sustain* (to provide what is needed for something or someone to exist) and *ability* (the power or skill to do something). To achieve sustainability, we must assure that we meet our needs and avoid compromising the ability of future generations to meet theirs (*6*). We will have to address technical, economic, and social issues (*4*) to attain this objective. Most importantly, we will have to use water judiciously and reclaim contaminated water. Water reclamation (the act or process of recovering) is absolutely essential because we have managed to pollute our surface water, and even groundwater in some cases, to a point that water needs to be purified for drinking (see Chapter 1 in reference (*1*)).

A number of inorganic and organic compounds from arsenic to zinc can pollute our groundwater (*7*). The discussion below briefly covers various contamination problems with water. The most horrendous water-contamination problem relates to arsenic contamination of groundwater in Bangladesh. It has been affecting around 200 million people worldwide, including the United States. In Bangladesh, naturally occurring arsenic contaminated millions of wells that were installed to solve the problem of microbial contamination (see detailed discussion in Section 4). Arsenicosis resulting from drinking arsenic-contaminated water can lead to a protracted painful death.

To seek viable solutions to this problem, workshops were organized by the author in Bangladesh (2005) and India (2011, 2014), and several symposia were planned during that period at ACS, UNESCO, and IUPAC meetings. A short discussion is provided later on how groundwater is contaminated with arsenic, desirable methods for monitoring arsenic contamination at ultratrace levels (below one part per million), and the best options for reclamation. Solutions that offer significant improvements in water purification technologies, at reasonable costs, are highlighted.

2.0. Water Availability and Quality

Here are some important facts about the availability and quality of our water supplies worldwide:

- Freshwater comprises only 3% of the total water available. Of that, only 0.06% is easily accessible.
- Over 80 countries in the world have water shortages.
- Almost 1.2 billion people drink unclean water today.
- Water-related diseases kill 5–10 million people, mostly children, around the world yearly.
- The United Nations estimates that 2.7 billion people will face a water shortage by 2025.

2.1. Water Quality Worldwide

Underdeveloped and developed countries have different, yet similar, problems with water quality.

2.1.1. Underdeveloped Countries

People need to be careful when they drink water in Africa, Asia, and Latin America. The rivers in these areas are frequently considered the most polluted in the world. These rivers have 3 times as many bacteria from human waste as the global average and 20 times more lead than rivers in developed countries. In 2004, water from half of the tested sections of China's seven major rivers was found to be undrinkable because of pollution. The Yangtze, China's longest river, is loaded with pollution. The pollution from untreated agricultural and industrial waste could turn the Yangtze into a dead river within a short time. This would make it impossible to sustain marine life or provide drinking water to the booming cities along its banks. For more information on water quality in China, please see Chapter 2 in Volume 4 of *Comprehensive Water Quality and Purification* (*5*).

As mentioned in the Introduction, Bangladesh has the most polluted groundwater in the world: the major contaminant is arsenic. Around 85% of the total area of the country has contaminated groundwater.

2.1.2. Developed Countries

The quality of water in Europe's rivers and lakes became worse between 2004 and 2005. Almost one-third of Ireland's rivers are polluted with sewage or fertilizer. The Sarno River in Italy is the most polluted river in all of Europe, featuring a mix of sewage, untreated agricultural waste, industrial waste, and chemicals. The Rhine, which flows through many European countries, is regarded by many as the dirtiest large river; almost one-fifth of all the chemical production in the world takes place along its banks. The King River is Australia's most polluted river, suffering from a severe acidic condition related to mining operations. Canadian rivers are also polluted.

Nearly 40% of the rivers in the United States are too polluted for fishing, swimming, or aquatic life. The Mississippi River drains nearly 40% of continental United States, including its central farmlands, and carries an estimated 1.5 million metric tons of nitrogen pollution into the Gulf of Mexico each year. Nearly 1.2 trillion gallons of untreated sewage, storm water, and industrial waste are discharged into U.S. waters annually (*8*). Lakes are even worse—46% of them are highly polluted. Two-thirds of U.S. estuaries and bays are either moderately or severely degraded from eutrophication (nitrogen and phosphorus pollution). Even the most advanced country like the United States is facing a water crisis. Most experts agree that the U.S. water policy is in chaos. Decision making about allocation, repair, infrastructure, and pollution is spread across hundreds of federal, state, and local agencies.

- Over 700 different chemicals have been found in the U.S. drinking water as it comes out of the tap!
- The EPA classifies 129 of these different chemicals as being particularly dangerous.
- The EPA sets standards for approximately 90 contaminants in drinking water (*9*)

The failure of safety measures relating to production, utilization, and disposal of a large number of inorganic/organic compounds can cause contamination of our water supplies.

2.2. Sources of Contamination

Drinking water comes mainly from the following sources: rivers, lakes, wells, and natural springs. These sources are exposed to a variety of conditions that can cause contamination of water. Some of the sources of contamination include:

- Combustion of coal/oil
- Detergents
- Disinfectants
- Drugs (pharmaceuticals)
- Fertilizers
- Gasoline (combustion products) and its additives
- Herbicides
- Insecticides
- Pesticides

A large amount of antimicrobials and antibiotics are administered to healthy animals on U.S. farms each year (*10*). A 2002 U.S. Geological Survey found pharmaceuticals (hormones and other drugs) in 80% of the streams sampled in 30 states. These contaminants are suspected in the rise of fish cancer, deformities, and feminization of male fish.

The world's seas are beset by a variety of water pollution problems. Table 1 shows major water bodies most affected by a range of pollutants.

The extensive use of plastics and their careless disposal has led to pollution of various water bodies as well. Large parts of the Pacific Ocean are referred to as "plastic oceans," where enormous gyres, about the size of Texas, are covered with plastic debris. The Pacific is the largest ocean realm on our planet, approximately the size of Africa—over 10 million square miles—and is the home of two very large gyres. The Atlantic Ocean contains two more gyres, and other plastic oceans exist in other bodies of water.

Table 1. Major Bodies of Water with Serious Problems[a]

Area	*Most Acute Problem*
Gulf of Mexico	Microbiological
Caribbean Sea	Suspended solids, spills
Baltic Sea (N Europe)	Eutrophication
Aral Sea (Kazakhstan)	Microbiological, high salinity
Yellow Sea (NE coast of China)	Eutrophication
Bohol Sea (in South Pacific)	Eutrophication
Congo Basin	Eutrophication, solid waste
Benguela Current (W coast of Africa)	Chemicals, radionuclides, solid wastes, spills
Victoria Lake (Central Africa)	Microbiological, eutrophication, suspended solids
Pacific Islands	Solid wastes, radionuclide

[a] Adapted from UNEP SEO Report, 2004—2005.

3.0. Monitoring Water Contaminants

The sad fact is our civilization has managed to pollute our waters to the point where we have to purify water for drinking. To assure water purity, we need to monitor contaminants from arsenic to zinc (*7*).

In the 1978 Metrochem meeting, organized by the New York Section of ACS, the author emphasized the need to analyze very low levels of various contaminants, in a paper entitled "In Search of Femtogram" (a femtogram is 10^{-15}g, or one part per quadrillion), to fully understand their impact. For example, dioxin (2,3,7,8-tetrachloro-dibenzodioxin) can cause abortion in monkeys at the 200 parts-per-trillion (ppt) level (*11*). PCBs at the 0.43 ppb (parts-per-billion level can weaken the backbones of trout (*12*).

Ultratrace analysis is necessary to monitor materials like PCBs and dioxin. In 1980, the author wrote an article explaining the importance of ultratrace analyses" in *CHEMTEC* (*13*). Soon thereafter, the author edited a book on *Ultratrace Analysis of Pharmaceuticals and Other Compounds of Interest* (*14*). The book describes methods for testing a large variety of compounds, including arsenic, and shows how analytical chemistry is the backbone of various fields of chemistry. In another book, *Trace and Ultratrace Analysis by HPLC,* in 1992 (*15*), the need is stressed for such analyses in food, pharmaceuticals, cosmetics, and the environment.

We have known for some time now that water that we call potable may actually contain many contaminants at parts per trillion (ppt) level, as exemplified by an analysis of Ottawa drinking water (Table 2; (*16*)).

Table 2. GC/MS Analysis of Ottawa Tap Water[a]

Compound	*Concentration Detected in Water (ppt)*
α-Benzene hexachloride	17
Lindane	1.3
Aldrin	0.70
Chlordane	0.0053
Dibutyl phthalate	29
Di(2-ethylhexyl) phthalate	78

[a] GC/MS: Gas chromatography/mass spectrometry.

In 2010, a United Nations resolution declared the human right to "safe and clean drinking water and sanitation."A simple definition of potable water is any water that is clean and safe to drink. National Primary Drinking Water Regulations control water quality in the United States. In response to public concern about degraded water quality and the widespread view that pollution of our rivers and lakes was unacceptable, the Clean Water Act became law in 1972. Control of point-source contamination, traced to specific "end of pipe" points of discharge or outfalls, such as factories and combined sewers, was the primary focus of the Clean Water Act. Other nations adopted similar measures and have seen improvement in point-source contamination as well. In the United States, potable water must be cleaner than the maximum contaminant level mandated by local, state, and federal guidelines (*17*). The tests commonly performed on drinking water are turbidity, total organic carbon, chlorite, chlorine dioxide, fluoride, sulfate, and orthophosphate (*18*). Some unregulated substances are also tested. Surprisingly, testing of arsenic is not carried out routinely. A variety of contaminants and their impact on water quality are discussed below briefly (*19*).

3.1. Color of Water

Most colors that have been ascribed to water relate to the materials that may be present in it (see below). It is important to note that water is a colorless liquid, though a layperson might describe the color of water as white or blue.

- Blue water generally refers to ocean water, which gets its color from the reflection of the color of the sky; however, we do have seas that are described by various other colors because of their appearance: Red Sea, Yellow Sea, Black Sea, and White Sea.
- Green water is caused by single-cell algae, which remain suspended in the water.
- Grey water is that generated from activities such as laundry, dishwashing, and bathing.
- Black water is water which has come into contact with fecal matter
- Brown water results from excessive iron.

3.2. Odors in Water

At times, municipal water may have an odor. Frequently, that odor relates to the chlorination of water. A musty odor in drinking water may be the result of by-products of blue-green algae.

Many utilities and beverage companies analyze water for the presence of compounds such as isopropyl-methoxypyrazine (IPMP), isobutyl-methoxypyrazine (IBMP), methylisoborneol (MIB), and geosmin. All of these compounds can be analyzed by solid-phase microextraction (SPME) and gas chromatography. Detectabilities range from 10 to 20 ppt.

3.3. Inorganic Compounds

A large number of inorganic compounds containing the following elements can be present in water: lithium, carbon, nitrogen, oxygen, fluorine, manganese, sodium, aluminum, silicon, phosphorus, sulfur, chloride, potassium, calcium, iron, cobalt, nickel, copper, zinc, bromine, strontium, cadmium, tin, iodine, cesium, and arsenic.

3.4. Organic Compounds

Volatile organic compounds (VOCs) can enter directly into our water resources from various spills, by improper disposal, or from the atmosphere, in the form of rain, hail, and snow.

In general, VOCs have high vapor pressure, low-to-medium water solubility, and low molecular weights. These properties allow them to move freely between water and air.

By contrast, semi-volatile organic compounds (SOCs) have a higher boiling point than VOCs; however, they can be volatilized under various environmental conditions and may pollute water.

According to the EPA, the following volatile organic contaminants are most likely to be found in drinking water:

- Benzene
- Carbon tetrachloride
- Chlorobenzene
- *o*-Dichlorobenzene
- *p*-Dichlorobenzene
- 1,1-Dichloroethylene
- *cis*-1,1-Dichloroethylene
- *trans*-1,1-Dichloroethylene
- Dichloromethane
- 1,2-Dichloroethane
- 1,2-Dichloropropane
- Ethylbenzene
- Styrene
- Tetrachloroethylene

- 1,2,4-Trichlorobenzene
- 1,1,1,-Trichloroethane
- 1,1,2-Trichloroethane
- Trichloroethylene
- Toluene
- Vinyl chloride
- Xylene

A number of SOCs can be detected in our water supplies, as well. They are ubiquitous because of anthropogenic activities, and they have the potential to accumulate in polar and mountainous regions. They can undergo atmospheric long-range transport via large-scale winds. The EPA has classified certain SOCs as persistent, bioaccumulative, and toxic (PBT) chemicals. VOCs and SOCs can be analyzed by gas chromatography.

3.5. Disinfectants

To protect public health, disinfectants are used to reduce the number of pathogenic microorganisms in water. Chemical disinfection has been an integral part of drinking water-treatment processes in the United States, since the early 1900s. Almost 70 years later, scientists identified the formation of chloroform ($CHCl_3$) and other volatile halogen-substituted organics in drinking water. Alternate chemical disinfectants such as ozone and chlorine dioxide form by-products of their own. The EPA regulates disinfection by-products and the permissible levels of disinfectants in drinking water.

3.6. Herbicides and Pesticides

Utilization of herbicides and pesticides is important to agriculture production. History shows the importance of water and food to the population's well-being. Various studies have been conducted on water samples from around the world to determine the use and concentrations of these materials. Regulations have been issued to assure better quality water, increased yields of grain, and changes in production practices.

3.7. Pharmaceuticals

The growing use of pharmaceuticals worldwide has become a new environmental problem. Wastewater treatment plants (WWTPs) are major contributors of pharmaceuticals in the environment. Over 3,000 chemical substances are used in human and veterinary medicines. The first report regarding this problem in the United States was issued in the 1970s. Diclofenac, for example, is frequently detected in aquatic matrices, and it has adverse effects on both rainbow trout and vultures.

Among pharmaceutical contaminants, the problem of endocrine disruptors is gaining greater significance. This problem received greater attention when the impact of the birth-control pill (ethynyl estradiol) on fish was established.

Recently, it was reported that infant liquid formula is the biggest culprit in exposing infants to bisphenol A, a potential hormone-disrupting chemical (*20*).

3.8. Radioactive Compounds

Radioactive compounds pose a double threat from both toxicity and damaging radiation. The extreme energy potential of many of these materials makes them both useful and toxic. Mining, production, use, and disposal of radioactive compounds provide potential pathways for their release into the environment. It is important to study sources, uses, and regulation of radioactive compounds, including biogeochemical processes that control mobility in the environment.

3.9. Wanton Contamination

After September 11, 2001, a new fear dawned on the water-supply industry relating to intentional water contamination. A vast array of possible contaminants can be used by terrorists at countless sites that would require quick detection. A backflow attack can occur when a pump or siphon is used to overcome the pressure gradient of the distribution system's pipes. This is usually around 80 lbs/in^2 or less and can be easily overcome by using a pump or siphon that injects a contaminant, using the Bernoulli Effect. Studies by the U.S. Air Force and Colorado State University have shown that this is a very effective means of contaminating a system.

4.0. Tackling a Major Problem: Arsenic Contamination

Arsenic is a notorious poison because it is colorless, tasteless, and odorless (*21*). There are many stories of its use to intentionally poison somebody. In the 5thcentury B.C.E., Hippocrates used it to treat ulcers. Fowler's solution (created in 1786) was used for a variety of treatments from asthma to cancer for more than 150 years. Arsenic compounds are still used for African sleeping sickness.

When arsenic gets into water by any of a variety of ways, it becomes a major problem. Arsenic contamination of groundwater has been reported in a large number of countries in the world including the United States, Australia, and a number of countries in Asia, Europe, and South America. Bangladesh and Bengal (India) suffer most.

As mentioned before, millions of wells installed in Bangladesh in the 1970s to solve the problem of microbial contamination were not tested for natural contamination by arsenic. Prolonged drinking of arsenic-contaminated water can lead to arsenicosis and, ultimately, to a slow and painful death. One-hundred million people are at risk who consume arsenic-contaminated water at levels of 10 ppb or greater. Inorganic arsenic above the 10 ppb level can increase the risk of lung, skin, bladder, liver, kidney, and prostate cancers. More than 200 million people may be affected by this problem worldwide

4.1. Sources of Arsenic Contamination

Arsenic compounds are used commercially for the following applications:

- Pesticides: monosodium methyl arsonate, disodium methyl arsonate
- Insecticide: dimethylarsenic acid
- Aquatic weed control and sheep and cattle dip: sodium arsenite
- Defoliating cotton bolls: arsenic acid, arsenic pentoxide
- Some pharmaceuticals and decolorizing glass: arsenic trioxide

Large areas in the west, midwest, and northeast U.S. have high arsenic concentrations. In my home state (NC), arsenic has been found in 960 wells statewide since January 2000.

According to the *Star News* (*22*) "Half the state's [NC] population depends on groundwater. Some filtration systems can remove arsenic from tap water."NC state toxicologist Ken Rudo noted, "for new wells, arsenic test is pretty much not done."

Microbially mediated reduction of assemblages comprising arsenic sorbed to ferric oxyhydroxides has gained consensus as the dominant mechanism for the mobilization of arsenic into ground-water. A recent microcosm-based study provided the first direct evidence for the role of indigenous metal-reducing bacteria in the formation of toxic, mobile As(III) in sediments from the Ganges delta.

4.2. Arsenic Uptake in Crops

Studies on arsenic uptake by crops indicate that there is great potential for the transfer of ground-water arsenic to crops. Green leafy vegetables act as arsenic accumulators, with *arum* (kochu), gourd leaf, *Amaranthus,* and *Ipomea* (kalmi) topping the list.

Speciation of Bangladeshi rice shows the presence of As(III), DMAV, and As(V); greater than 80% is in the inorganic form. More than 85% of the arsenic in rice is bioavailable. The fate of arsenic in irrigation water and its potential impact on the food chain is of great importance.

4.3. Ultratrace Analysis of Arsenic

A number of methods can be used for analyzing arsenic in water at 10 ppb or an even lower level.

- Flame atomic absorption spectrometry
- Graphite furnace atomic absorption spectrometry
- Inductively coupled plasma-mass spectrometry
- Atomic fluorescence spectrometry
- Neutron activation analysis
- Differential pulse polarography
- Atomic absorption: Flame—0.5 ng/mL; electrothermal: 0.1 ng/mL
- Atomic fluorescence: Laser excited—0.1 ng/mL

- X-ray fluorescence: Sample filtered through a freshly prepared sulfide layer for determining ng/mL of As
- Hydride generation for ICP: Sodium tetrahydroborate used as reductant; detection limits below 1 ng/mL

The speciation of arsenic requires separations based on solvent extraction, chromatography, and selective hydride generation. Detection limits for arsenic down to 0.0006 μg/L can be obtained with inductively coupled plasma mass spectrometry (ICP-MS). HPLC-ICP-MS is currently the best technique available for determination of inorganic and organic species of arsenic. The main problem is the high cost.

Using hydride generation (HG), arsenic can be determined by a relatively inexpensive atomic absorption spectrometer or atomic fluorescence spectrometer (AFS) at single-digit μg/L.

For developing countries, there is a need for low-cost, reliable instrumentation and dependable field test kits.

4.4. Remediation

The following methods can be used for remediation of arsenic contamination of water:

- Coagulation with ferric chloride or alum
- Sorption on activated alumina
- Sorption on iron oxide-coated sand particles
- Granulated iron oxide particles
- Polymeric ligand exchange
- Nanomagnetite particles
- Sand with zero-valent iron
- Hybrid cation exchange resins
- Hybrid anion exchange resins
- Polymeric anion exchange
- Reverse osmosis

Two filters that stand out in terms of their usefulness for serving a small family or a community are described below briefly.

4.4.1. Single Family System

These systems are based on solid sorbents to obtain potable water. Special emphasis has been placed on iron-based filters because they appear to be chemically most suitable for arsenic removal, they are easy to develop, and are environmentally benign. Arsenic removal mechanisms for a SONO filter (Figure 1) are based on surface complexation reactions, sorption dynamics, and kinetics (see details in Chapter 12 in reference (*2*)). This is one of the four filters approved by the Bangladesh government for public use. The manufacturer claims that the filtered water meets Bangladesh standards (50 ppb of arsenic; the requirements in the U.S. are 10 ppb), has no breakthrough, works without producing toxic waste, based on EPA guidelines (*3*). It costs about $40, lasts for five years, and produces 20–30 L/hour for the daily drinking and cooking needs of one or two families. A large number of these filters have been used all over Bangladesh and continue to provide more than a billion liters of safe drinking water. This innovation was recognized by the National Academy of Engineering Grainger Challenge Prize for Sustainability with the highest award for its affordability, reliability, ease of maintenance, social acceptability, and environmental friendliness.

The flow rate may decrease 20–30% per year if the groundwater has high iron levels (>5 mg/L), because of formation and deposition of natural HFO (hydrous ferric oxide) in sand layers. The sand layers (about one-inch thick) can then be removed, washed and reused, or replaced with new sand. Pathogenic bacteria may still be found in drinking water because of unhygienic handling practices or utilization of water from shallow tube wells located near unsanitary latrines and ponds. A protocol for elimination of bacteria should be used once a week in areas where coliform counts are high. It should be noted that, as with all commercial filters, the consumer needs to be alert to manufacturing defects, quality of water related to natural disasters such as flooding, and mechanical damage because of mishandling during transportation.

4.4.2. Community-Based Filter

This filter (Figure 2) can serve about 200 households and requires no chemical addition, pH adjustment, or electricity (see Chapter 13 in reference (*2*)).

A large number of these filters have been installed since 1997. The filter has these characteristics:

- Utilizes activated alumina as a regenerable adsorbent media
- Purifies Influent arsenic solutions ranging from 100 μg/L to 500 μg/L, containing both As(III) and As(V) species

When the filter is exhausted, the media can be replaced and the spent media is taken to a central regeneration facility for further reuse. An arsenic-laden spent regenerant form is converted to a small volume of sludge that can be contained in an aerated coarse sand filter. The process is claimed to be environmentally sustainable because the treatment residues are not toxic under normal environmental conditions. It is also economically sustainable, as the villagers collectively maintain the units by paying a monthly water tariff of about $0.40.

Figure 1. SONO filter

Figure 2. A community-based filter

4.4.3. Potential Solutions for Remediating Arsenic Contamination

The following potential solutions can be recommended, based on various workshops and symposia for solving the problem that Bangladesh and other countries face in purifying arsenic-contaminated water:

- Piped surface water should be the intermediate to long-term goal. This requires total commitment of local governments and funding agencies.
- Other surface water options such as sand water filters, rainwater harvesting, and dug wells should be utilized.
- The next best option is deep tube wells (located and installed properly, with the assurance that they won't be affected by other contaminants).
- Arsenic-removal filtration systems can work on a small scale; however, their reliability initially or over a period of time remains an issue. Other contaminants in water, including microbial contaminant, can affect their performance.

5.0. Wastewater Reclamation

Because we don't have an unlimited supply of safe water for our needs, water reclamation is absolutely necessary (*18*, *19*). Some examples of wastewater reclamation are discussed below.

5.1. Recycling Wastewater to Groundwater

Orange County Water District (OWCD) in California treats and injects 70 mM gallons/day into groundwater. It takes treated sewer water that otherwise would be discharged into the ocean, purifies it to near distilled quality, and then recharges it into the groundwater basin. OCWD ensures the OC groundwater basin is free of contamination and that usage is sustainable. It uses microfiltration, reverse osmosis, and UV to purify wastewater. Micro filtration (MF) removes bacteria and protozoa, and it also removes particles and suspended solids. Reverse osmosis (RO) removes viruses, bacteria, and chemical contaminants such as dissolved salts, metals, organic compounds such as endocrine disruptors and other pharmaceuticals. UV inactivates microbes and prevents replication, and UV with hydrogen peroxide is used to destroy small organics.

5.2. Recycling Wastewater to Surface Water

A preliminary treatment process used by NEWater in Singapore removes the debris and sandy materials from used water. The primary treatment process allows the solid pollutants in suspension (primary sludge) to settle to the bottom of the tanks and lighter materials like scum or greasy materials to float to the surface of the tank. The secondary treatment takes the upper layer of water and puts it into the aeration tank which is a bio-reactor and final clarifier. The used water is mixed with a culture of microorganisms known as activated sludge in the aeration tank. The microorganisms absorb and break down the organic pollutants. The clear supernatant water at the top of the tank is collected and discharged from the tanks as the final effluent. The sludge is allowed to remain in the digesters for 20–30 days. Anaerobic digestion of the organic matter in sludge produces biogas, which contains 60 –70% methane.

5.3. Reclaiming Wastewater for Drinking

Singapore gets 30% of its water requirements via the purification process developed by NEWater. To produce drinking water, the following treatment steps are used in addition to those listed above:

- Membrane filtration
- Reverse osmosis
- Elimination of bacterial impact
- Capture of nutrient value

The amount of testing done to reclaimed water should relate to how it is going to be recycled. For example, if it is recycled into a surface water supply, its quality after purification should match or exceed the requirements of the surface water to which it is being added. Similar rules may be followed for mixing with groundwater. Recycled wastewater for drinking must meet potable water requirements, with the added assurance by ultratrace analysis that no toxic contaminants are present (*4*).

6.0. Conclusions

Water pollution in our modern society is inevitable. We need to improve monitoring of point and nonpoint source pollution. It is important to employ effective safety measures that can prevent further pollution. To achieve water sustainability, water must be used judiciously and production of wastewater should be minimized. Rain and snow are nature's way of recycling water; however, rain and snow are now usually contaminated with various pollutants that we have added to the atmosphere. It is still desirable to collect rainwater and use it for a variety of purposes. Water reclamation is necessary to achieve sustainability. Diverse yet similar solutions are necessary for various countries. It is important to remember that reclamation can provide sustainable solutions to water availability and quality problems.

References

1. Ahuja, S. *Handbook of Water Purity and Quality*; Elsevier: Amsterdam, 2009.
2. Ahuja, S. *Arsenic Contamination of Groundwater; Mechanism, Analysis, and Remediation*; Wiley: New York, 2008.

3. Ahuja, S.; Hristovski, K. *Novel Solutions to Water Pollution*; American Chemical Society: Washington, DC, 2013.
4. Ahuja, S. *Monitoring Water Quality: Pollution Assessment, Analysis, and Remediation*; Elsevier: Waltham, MA, 2013.
5. Ahuja, S. *Comprehensive Water Quality and Purification Volumes 1-4*; Elsevier: Kidlington, Oxford, 2014; see Chapter 2 in Vol. 4.
6. Brundtland, G. H. *Our Common Future, The World Commission on Environment and Development*; United Nations: 1987.
7. Ahuja, S. Assuring Water Purity by Monitoring Water Contaminants from Arsenic to Zinc. Presented at American Chemical Society Meeting, Atlanta, GA, March 26−30, 2006.
8. EPA. *National Water Quality Inventory: Report to Congress*, 2004 Reporting Cycle.
9. EPA. Basic Information about Regulated Drinking Water Contaminants and Indicators [online]. Last updated on May 29, 2013.
10. McEwen, C. S.; Fedorka-Cray, P. *Clin. Infect. Dis*. **2002**, *34* (Suppl. 3), S93.
11. *Chem. Eng. News*; August 7, 1978.
12. *Chem. Eng. News*; Sept. 25, 1978.
13. Ahuja, S. *CHEMTECH* **1980**, *11*, 702.
14. Ahuja, S. *Ultratrace Analysis of Pharmaceuticals and Other Compounds of Interest*; Wiley: New York, 1986.
15. Ahuja, S. *Trace and Ultratrace Analysis by HPLC*; Wiley: New York, 1992.
16. McNeil, E. E.; Otson, R.; Miles, W. F.; Rahabalee, F. J. M. *J. Chromatogr.* **1977**, *132*, 277.
17. U.S. EPA. Current Drinking Water Regulations. http://water.epa.gov/lawsregs/rulesregs/sdwa/currentregulations.cfm (retrieved July 1, 2015).
18. Ahuja, S. Water Sustainability and Reclamation. Presented at American Chemical Society Meeting, San Diego, March 25−29, 2012.
19. Ahuja, S. *Water Reclamation and Sustainability*; Elsevier: Amsterdam, 2014.
20. *Chem. Eng. News*; November 17, 2008; p 42.
21. Newman, C. *National Geographic*; May 1, 2005.
22. *Star News*; Wilmington, NC, August 18, 2003.

Chapter 9

Sustainability: GEOC's Perspective

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At the 2014 spring national meeting of the American Chemical Society, the symposium Sustain-Mix: Sustainability Across the Society was convened by the Division of Chemical Education. Members of the executive board of the Division of Geochemistry prepared a presentation addressing sustainability from a geochemistry perspective. The group identified four grand challenges: 1) Understanding Earth-atmospheric processes, climate change and ocean acidification, 2) Understanding natural and anthropogenic impacts on water quality, 3) Sustainable mining for critical elements, and 4) Preventing soil degradation due to intensive agriculture.

Introduction

Environmental sustainability requires practices that meet current needs without causing long lasting damage to the environment as well as without compromising the ability of future generations to meet their needs. Recently, a number of researchers have questioned whether sustainability is even achievable. For example, Benson and Craig (*1*) implore scientists to abandon the concept of sustainability, describing the consequences of human activities, which include

In Teaching and Learning about Sustainability; Levy, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

extensive loss of biodiversity (e.g. (*2*)), global warming, and depletion of critical resources, as irreversible (*1*). Indeed, evidence is mounting that long lasting damage to the environment has occurred, damage that may have already compromised the ability of future generations to meet their needs. Thus, a shift of focus from achieving sustainability to resilience, which must include redesigning human systems to realize harmony between human activities and our natural environment, is warranted.

Critical issues of sustainability faced by the world's population include food, water, climate, and energy. Access to safe and healthful food varies greatly around the world, with some populations facing starvation and malnutrition and others malnutrition despite food surpluses (e.g. (*3*) and references contained therein). Current food production methods are energy intensive and often cause substantial soil degradation and contamination of surface and near surface waters with agrochemicals. Safe water supplies are essential to maintaining health and well being, and many communities do not have adequate access to drinking water, much less drinking water free of toxic substances. Climate change is manifested in rising sea levels, increased frequency of extreme weather events such as destructive storms, flooding, and prolonged droughts (*4*). These changes compromise the habitability of currently populated areas. Finally, access to a safe and abundant energy supply requires development of methods to produce usable energy that do not further damage the environment. The majority of currently produced energy comes from fossil sources; oil, gas, and coal comprise 81.7 % of energy sources worldwide (*5*). Burning fossil fuels results in substantial releases of CO_2, as well as emissions of other greenhouse gases and toxic compounds.

At the heart of these sustainability issues are scientific questions relevant to the scientific discipline of geochemistry. Geochemistry combines geology and chemistry in order to better understand the fundamental processes governing the distribution and cycling of the elements in the Earth's crust, atmosphere, and oceans. It is a field of chemistry that addresses the behavior of geologic materials, as well as the interactions of anthropogenic materials within geo-, hydro-, and bio-spheres. This work is crucial for energy, climate, and environmental applications. Geochemistry focuses on planetary composition, chemical reactions that govern the fate of a wide variety of chemical species (i.e., solids, liquids, and gases), and the cycling of chemical species and energy in time and space. Chemists in this field focus their efforts on studying rocks and minerals, hydrospheres, biospheres, atmospheres, and even anthrospheres—i.e., environments directly impacted or modified by human activities. Geochemists strive to understand changes in elemental fluxes as a result of climate change, planet formation and evolution as well as how minerals are deposited and altered and how impacts of human activities are changing Earth. Furthermore, geochemists are seeking ways to minimize, and even mitigate, negative human impacts on Earth. Finally, the field of geochemistry extends beyond Earth to other planets.

Interests of scientists in this field cross length scales over many orders of magnitude, ranging all the way from the planetary scale down to the molecular scale. At the smallest length scale, one can examine individual molecules and ions in a wide range of environments, nanoparticles of a wide variety of solid materials, and even pores within solid matrices. Similarly, geochemists study processes that range temporally from very fast (femptoseconds to weeks) to very slow (millennia and beyond). Emphasis is placed on understanding these processes individually, and their interplay across the large range of length- and time-scales, with an important goal of improving fundamental understanding and prediction and management of environmental risk.

The Grand Challenges

Members of the 2014 executive board of the Division of Geochemistry of the American Chemical Society identified four grand challenges related to sustainability:

1. Earth-atmospheric processes, including climate change and ocean acidification;
2. natural and anthropogenic impacts on water quality;
3. mining for critical elements; and
4. preventing soil degradation due to intensive agriculture.

This chapter will detail these challenges, emphasizing the connection between energy and climate systems, interplay between water quality and chemical fate and transport, mining and its impacts, and soil degradation owing to significant natural and anthropogenic activities.

Energy and Climate

Energy is a pressing issue facing the world's population and, as of 2012, the global energy demand was estimated to exceed 17 terawatts. The demand for energy only continues to grow, as evidenced by the total emissions of CO_2 from nonrenewable sources - oil, gas, and coal - doubling over the last ca. forty years (*5*). According to the International Energy Outlook report of 2013, renewable energy sources, such as solar, wind, geothermal, only comprised about 11% of the energy consumption worldwide (*6*). There are three approaches to reducing the environmental harm resulting from energy consumption. The first is to simply reduce energy consumption itself, but with the growing world population combined with greater availability to modern technology, this seems unlikely to prove realistic. The second approach is to increase the efficiency of energy use. We are already seeing dramatic improvements in efficiency due to technological advances. The third approach is reduce the net carbon footprint of energy production by increasing the contribution from renewable energy sources, reducing the amount of CO_2 emitted per unit energy produced (e.g. shifting from coal to gas), and deploying carbon capture and sequestration technologies.

Using the definition of risk as a "function of the hazard and the exposure (*7*)," one can examine the generation of usable energy, especially fossil fuel-based energy production, which is accompanied by a large amount of emitted CO_2. Although CO_2 is not toxic in the range of concentrations encountered on Earth, it has a dramatic effect on Earth's climate. With the current CO_2 release rate, the world's exposure is ever growing, which is leading to severe consequences. The data collected using the Vostok ice core as well as those data gathered at the Mauna Loa Observatory in Hawaii demonstrates vacillating CO_2 levels over the millennia (Figure 1). Data quantifying the CO_2 concentration in the atmosphere over ca. one-half million years before 1957 demonstrate no excursions above 300 ppm CO_2 despite fluctuations from lows of about 180 ppm CO_2 and highs of approximately 300 ppm (*8*). Just this year (2015), the monthly average of the concentration of CO_2 in the Earth's atmosphere has exceeded 400 parts per million CO_2, and the average rate of increase over the last nearly sixty years is almost 2 ppm CO_2 per year (*9*). No evidence in the geologic record for excursions that are consistent with this level of CO_2 has been found.

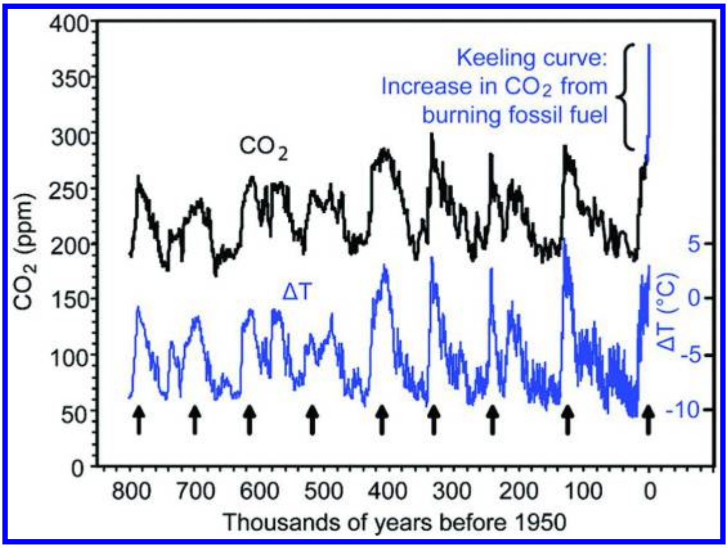

Figure 1. Atmospheric CO_2 concentration and temperature from 800,000 years before present. These data were derived from the Vostok Antarctic ice cores. The Keeling curve is the steep segment from 1957 until 2008 in this graph, and those CO_2 data were obtained at the Mauna Loa observatory located in Hawaii, U.S.A. The ice core data were obtained from reference number (10). Reproduced with permission from reference number (11). Copyright 2010 American Chemical Society.

A major consequence of the increase in CO_2 level is global warming. Solar radiation reaches Earth's surface, and the balance between re-radiated heat that escapes or is trapped is a function of the gas composition of the atmosphere. With increased concentrations of greenhouse gases, such as methane (CH_4) and CO_2, more heat is trapped in Earth's atmosphere. As a consequence, the planet warms. Consequences of this warming have come in different forms, such as melting glaciers and ice caps, rising sea levels, exacerbated weather extremes (e.g., stronger and more frequent storms and longer droughts), desertification, and thawing permafrost. Recently, large craters formed in Siberia, and the photographs are shocking (*12*). The latest hypothesis is that the craters formed as a consequence of ice cores, which are called pingos, melting due to unusually warm temperatures in Siberia. The result of this melting was collapse, leading to the formation of craters, and scientists believe the collapses were accompanied by large releases of natural gas. While different metrics are used for predicting the global warming impact of each individual greenhouse gas (e.g. reference (*13*)), we do know that CH_4 absorbs more strongly in the infrared than CO_2 and, therefore, has the potential to accelerate warming, despite its substantially lower concentration as compared to CO_2. Increased releases of methane from thawing permafrost could result in substantitive, additional acceleration in global warming.

Nearly one-third of the CO_2 released into the atmosphere by human activities dissolves into surface waters, including oceans, lakes, and rivers. Dissolved CO_2 results in an increase in carbonic acid concentration, which drives pH down and decreases the concentration of the carbonate ion. Indeed, the pH of the world's oceans has decreased by 0.1 pH unit (26% increase in hydrogen ion concentration) since the beginning of the industrial era (*14*). The consequences of ocean acidification directly and strongly impact organisms that make calcium carbonate shells due to the decrease in carbonate ion concentration (*15*).

Increase in the oceanic water temperature has also been recorded (*14*). The most significant warming is observed for the upper 75 m, which have warmed at a rate of 0.11-0.13 °C per decade (since 1971 to 2010). Warmer water holds less dissolved oxygen, and decreased oxygen levels have been recorded since 1960 (*14*). Dissolved oxygen levels exhibit large regional variations, as well as variations with ocean depth. However, overall decreased dissolved oxygen concentration has the potential to strongly impact local oceanic ecosystems. This means that ocean warming and acidification have far reaching effects on fish, other kinds of aquatic life, and even on the world population's food supply.

To reduce or mitigate anthropogenic CO_2 emission to the atmosphere and thus limit further global warming (e.g. (*16*) and references contained therein), multiple efforts have been considered (Figure 2). First, carbon capture and geologic CO_2 storage (GCS) have been proposed as a viable option. If CO_2 is captured at point sources (e.g. fossil fuel based power plants) and stored in deep underground geologic reservoirs, that CO_2 would not enter the atmosphere, which could make the goal of maintaining the current +2 degree Celsius excursion in global temperature (*14*) realistic. Geologic formations proposed for long term (over 1000 years) storage for CO_2 include sandstone reservoirs overlaid with low-permeability caprock. Understanding mineral dissolution and precipitation triggered by the injection of large volumes of CO_2 is critical to these efforts (*17–20*). Similarly, CO_2 is expected to dissolve and acidify groundwater, potentially causing mineral dissolution and development of fractures (e.g. (*21*) and references therein). Every action that leads to reduced emissions will only contribute to minimizing the acceleration in global warming. Because safer GCS design and operation requires vast knowledge from geochemistry, hydrogeology, geomechanics, and engineering, interdisciplinary collaborations are essential.

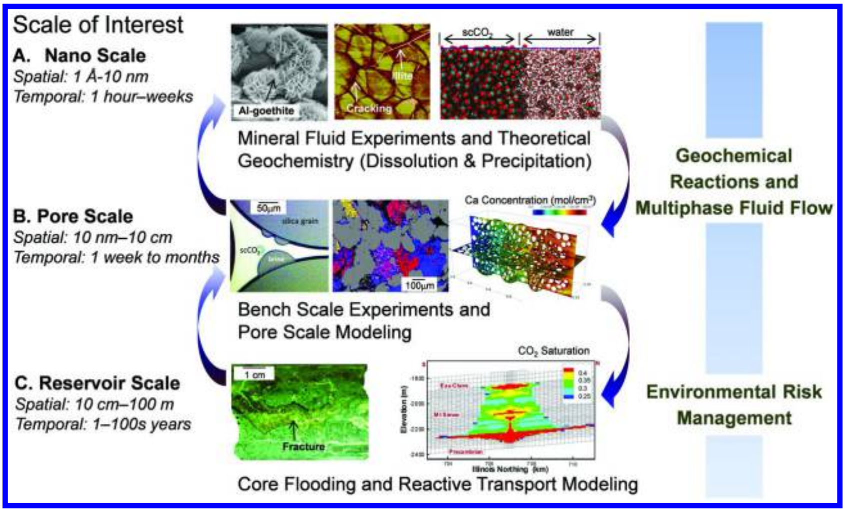

Figure 2. Schematic showing multiscale spatio-temporal nature of CO_2 storage. Reproduced with permission from reference (17). Copyright 2013 American Chemical Society.

Nuclear power and renewable energy also result in less overall CO_2 emissions. While nuclear power does not contribute substantively to CO_2 emissions, its use is controversial (*22*). Considering the risk equation, there is a huge hazard associated with nuclear power, and it is absolutely essential for the exposure piece of this equation to be extremely small, as close to zero as possible. Unfortunately, we do not have a history of preventing release of radioactive materials and unacceptable exposures, and unforeseen events, such as earthquakes, can cause even the most advanced technology to fail to prevent the release of radionuclides. Recent nuclear disasters (e.g., the Fukushima Daiichi nuclear disaster of 2011 (*23*)) as well as extensive radioactive waste from both nuclear energy and military applications (e.g., see report by DOE (*24*)) demonstrate that radioactive materials are a major environmental concern. Furthermore, attempts to contain such materials have met with varied success. For example, in the Ural Mountains, Lake Karachay was used as a storage lake. After partially drying out, radioactive dust was blown out during a dust storm, resulting in the exposure of hundreds of thousands of people to radioactive materials (*25*). In the United States, extensive contamination of local groundwater by nuclear waste materials is found in Hanford, Washington, an important site heavily contaminated by nuclear waste from military applications (*26*). While nuclear power does have a lot to offer in terms of CO_2 emissions-free energy production, the hazards associated with its implementa-tion and waste products are large indeed.

The link between global warming and our current fossil-fuel based energy technology has been well established. Global warming is an interdisciplinary problem that requires a broad range of scientific and engineering solutions. Advances in energy generation, conservation, storage, and efficient use will come from fundamental science and engineering through the development of new technologies. This will allow producing energy efficient devices capable to meet the needs and demands of their users. Advances in how usable energy is generated and stored will come from fundamental science and engineering through developments in, for example, materials used in photovoltaic devices, energy storage devices, and beyond. The development of carbon sequestration technologies could lead to a substantial reduction in the continued increase of CO_2 concentration in Earth's atmosphere. Thus, a combination of CO_2 capture and storage, energy conservation, and production of more energy efficient devices could lead to substantive progress.

Fate and Transport of Chemicals and Water Quality

Returning to the four grand challenges identified earlier, access to safe drinking water is a critical issue facing many people worldwide. The hydrologic cycle describes how water moves continuously between the atmosphere and Earth's surface, as well as how water moves at and below Earth's surface. Water interacts with diverse types of materials—soils, sediments, rocks, plant matter, and more—and those interactions are closely linked to water quality. Geochemists quantify elemental fluxes between reservoirs and often draw schematics of elemental cycling to visually convey the biogeochemical mechanisms that regulate the fate and transport of chemical species. In addition, geochemists think about the cycling of crucial nutrients, such as phosphorus and nitrogen, for which we can draw very similar schematics. Anthropogenic activities result in dramatic changes in the cycling of these very important species.

Chemical transformations at the solid-liquid interface control elemental fate and transport, and this is vital in nutrient and contaminant cycling (*27–29*). Key chemical reactions include dissolution and precipitation, redox (reduction and oxidation) reactions, adsorption, and phase transformations. The reactivity of the solid's surface depends very strongly on the chemical speciation of the reactive sites and local molecular environment. The local molecular environment, in turn, is a function of the bulk solution chemistry in which the mineral surface resides. Changes in temperature, pressure, pH, ionic strength (i.e., salinity), redox condition, natural organic matter composition and concentration will be accompanied by changes in the reactivity of the solid surface.

The solid-liquid interface is also central to understanding the fate and transport of anthropogenic materials released to the environment. A particularly timely example is engineered nanoparticles (*30*, *31*). Detecting and quantifying engineered nanoparticles in the environment is especially challenging because natural nanoparticles are abundant at and near Earth's surface. Examples of engineered nanoparticles include metal oxide nanoparticles used in cosmetics (e.g., titanium dioxide in sunscreen), carbon nanotubes used in sports equipment, and more (*31*). How these engineered nanoparticles move through the environment, how they are transformed, and how they participate in chemical reactions—whether they can be sequestered away from our water sources, whether they dissolve and then release contaminants into our water sources—involves a wide variety of fundamental processes. For example, engineered CeO_2

nanoparticles have been used for catalytic converters in diesel engine cars to minimize particulate carbon and NO_x emission for environmental concerns. However, their usage and production can increase the unexpected environmental and safety and health impacts. Furthermore, during their transport in the environment or water treatment processes, these particles can undergo redox surface reactions with surrounding elements to form new hybrid nanoparticles whose properties and behavior are not fully understood (*32*). These mixtures of natural and engineered nanoparticles and their hybrid nanoparticles can introduce new concerns.

Groundwater is a critical source of fresh water. Around 20% of drinking water is withdrawn from groundwater sources in the United State and trace contaminants— pesticides, herbicides, pharmaceuticals, personal care products, explosives, radioactive species—are commonly found in our drinking water supplies (*33*). Avoiding materials that have overall lifetimes that far exceed their useful lifetimes (e.g., plastic pollution that can contain leachable and toxic molecules) or compounds that resist degradation in the environment (e.g., highly oxidized molecules designed for long-term stability) will reduce hard-to-remediate pollution.

To respond to water shortage problems of overdrafting groundwater and recent significant drought events, managed aquifer recharge (MAR) has been implemented. "Reclaimed" wastewater, which has been treated beyond conventional wastewater treatment, is a common source for the MAR. However, recent reports about MAR field sites have shown that reclaimed water recharge can trigger unfavorable soil–water interactions, resulting in, for example, arsenic release from aquifer materials by altering the geochemistry of the system. Arsenic mobilization as a result of artificial aquifer recharge has also been reported globally (e.g., Australia, Germany, China, the Netherlands, United States of America (*34*)). Protecting our drinking water supply requires close attention to the fate and transport of a wide range of both natural and anthropogenic species.

Mining, Environmental Impact, and New Approaches

The supply of critical elements for technology and other valuable elements is crucial to the global economy. In particular, mining for critical elements (precious metals, and rare-earth elements) involves extraction from natural, solid materials, and even seawater. Technological advances are designed to render sources with lower elemental abundances economical for the extraction of scarce elements. Throughout history, mining has caused substantial damage to water quality and ecosystems (e.g. (*35*)).

For example, acid mine drainage, or the outflow of acidic waters from mines, forms when sulfide minerals from mine tailings are oxidized to sulfate by exposure to air and precipitation. Acid mine drainage can contaminate surface waters and water supplies by leaching into local ground water. The pH of acid mine drainage can drop to well below zero. With such low pHs, heavy metals become soluble and can be transported long distances. Contamination of local waters as a result of acid mine drainage is a critical issue.

New technological approaches using abundant rather than rare elements can serve to minimize the necessity and limit the impacts of extensive mining. Such technological advances can also lead to improved resource security as well as lower cost of products. In considering the less abundant elements, such as indium, substantially more material must be mined in order to yield usable amounts of the element in question. If we attempt to calculate an E-factor, which is equivalent to the amount of waste generated per mass of product, values on the order of 10^6 and higher are not uncommon.

Using nature as a guide and taking a benign-by-design approach, solar cells constructed using absorber materials that are more analogous to natural, non-toxic minerals like kesterite ($Cu_2(Zn,Fe)SnS_4$ (*36*, *37*) and perovskite ($CaTiO_3$) could represent major improvements. The best efficiency for solar cells constructed using selenized Cu_2ZnSnS_4 has only just exceeded 12%, which is not nearly sufficient for broad implementation in commercial and private settings. Researchers have improved the efficiency of perovskite cells to 20.1% (commercial solar cells have *ca.* 17% efficiency) and replaced the toxic lead with the more benign tin (*38*).

Focusing materials development using elements residing in the first row transition metals series rather than working with naturally scarce elements like indium, cadmium, and tellurium pushes these technologies closer to benign-by-design. The major challenge is improving efficiency to the point that the energy density is sufficient to make the solar panels implementable and affordable by the general populace. Furthermore, a cradle to cradle approach that emphasizes recyclability in product design could serve to further avoid the negative consequences of mining.

Further, treating current waste as a resource could prevent the need for more mining. For example, mobile phones contain small amounts of precious and naturally scarce elements like gold and indium. Thus, devices that have entered the waste stream could become viable sources for these elements (*39*, *40*). In fact, designing with such recyclability in mind could result in dramatic reductions in new environmental damage due to mining (*41*).

At the same time, the use of earth abundant elements is not enough. Crystalline silicon-based solar panels serves as an example. Silicon is the second most abundant element in the Earth's crust, and it is fairly easy to obtain silicon-rich materials. However, the purification of silicon from mined materials such as sand to high purity crystalline silicon is an energy-intensive process. For example, the production of silicon solar panels is currently accompanied by extensive CO_2 emissions. Advances that enable the production of efficient solar cells using silicon that contains substantial impurities (*42*) represents an important step towards more sustainable energy production using silicon-based solar cells. Critical is achieving sufficient efficiency so as to enable wide spread deployment.

As technology and materials advance, the benign-by-design approach can solve many issues and provide ways to make objects that are intentionally nontoxic or at least less toxic, at all stages of the objects' lives. Avoiding naturally scarce elements like ruthenium, rhodium, cadmium, and palladium and favoring the rock-forming elements like iron, aluminum, and silicon, translates to less environmental damage due to mining. Designing products with recycling and repurposing in mind could result in substantive reductions in pollution and environmental damage. One critical goal is to achieve high performance, or the new products and compounds will simply not be adopted by private citizens, agriculture, or industry.

Soil Degradation

The final of the four grand challenges is preventing soil degradation due to intensive agriculture as well as other human impacts. Soil degradation has multiple causes and is manifested in contamination, loss of productivity (nutrient depletion), or loss of the actual soil material (erosion) when natural plant coverage is disturbed (*43*). Chemical degradation of soil results in nutrient and organic matter loss, salinization, acidification, and pollution. For example, soils in the proximity to urban areas are contaminated due to runoff from asphalt roads and toxic compounds settling from automotive emissions. As presented by Tilman et al., approximately 17 percent of vegetated land in Europe experienced human-induced soil degradation (*43*, *44*). Soil degradation contributes to compromised food security, ecosystem resilience, water quality, as well as climate change and more.

Summary

Environmental sustainability requires practices that meet current needs without causing long lasting damage to the environment or compromising the ability of future generations to meet their needs. At the heart of these sustainability issues are scientific questions concerning the fundamental processes governing the distribution and cycling of the elements in the Earth's crust, atmosphere, and oceans, topics relevant to the geochemistry community. Our grand challenges are: (1) addressing earth-atmospheric processes, including climate change and ocean acidification; (2) understanding how natural and anthropogenically perturbed elemental cycles impact water quality; (3) developing sustainable mining for critical elements, while limiting the use of rare elements and replacing them with Earth-abundant and nontoxic materials; and (4) preventing soil degradation due to intensive agriculture and human activities. Geochemists, by definition, are interdisciplinary scientists, employing a broad range of techniques to study heterogeneous materials over length scales from the molecular to the planetary. Such an interdisciplinary approach is essential to addressing the ever growing environmental damage to Earth.

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References

1. Benson, M. H.; Craig, R. K. *Soc. Nat. Resour.* **2014**, *27* (7), 777–782.
2. Kolbert, E. *The sixth extinction: An Unnatural History*; Henry Holt and Company: New York, 2014.
3. Levinson, F. J.; Bassett, L. Malnutrition is still a major contributor to child deaths, but cost-effective interventions can reduce global impacts; Population Reference Bureau: 2007. http://www.popline.org/node/193614 (accessed October 10, 2015).
4. Trenberth, K. E. *Clim. Change* **2012**, *115*, 283–290.
5. International Energy Agency. Key World Energy Statistics. 2014. www.iea.org/publications/freepublications/publication/keyworld2014.pdf (accessed October 10, 2015).
6. U.S. Energy Information Administration. International Energy Outlook. 2013; p 300.
7. Anastas, P. T.; Warner, J. C. *Green chemistry: Theory and practice*; Oxford University Press: New York, 2000; p 152.
8. Barnola, J. M.; Raynaud, D.; Lorius, C.; Barkov, N. I. Historical CO_2 record from the vostok ice core. In *Trends: A Compendium of Data on Global Change. Carbon Dioxide Information Analysis Center*; Oak Ridge National Laboratory, U.S. Department of Energy: Oak Ridge, TN, U.S.A., 2003.
9. Tans, P.; Keeling, R. Trends in atmospheric carbon dioxide - Mauna Loa. 2015. http://www.esrl.noaa.gov/gmd/ccgg/trends/ (accessed October 10, 2015).
10. Moskvitch, K. *Nature News* **2014**, 511.
11. Shine, K. P.; Fuglestvedt, J. S.; Hailemariam, K.; Stuber, N. *Clim. Change* **2005**, *68* (3), 281–302.
12. Luthi, D.; Le Floch, M.; Bereiter, B.; Blunier, T.; Barnola, J. M.; Siegenthaler, U.; Raynaud, D.; Jouzel, J.; Fischer, H.; Kawamura, K.; Stocker, T. F. *Nature* **2008**, *453* (7193), 379–382.
13. Harris, D. C. *Anal. Chem.* **2010**, *82* (19), 7865–7870.
14. IPCC. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, 2013. http://www.ipcc.ch/report/ar5/wg1/ (accessed October 10, 2015).
15. Feely, R. A.; Sabine, C. L.; Lee, K.; Berelson, W.; Kleypas, J.; Fabry, V. J.; Millero, F. J. *Science* **2004**, *305* (5682), 362–366.
16. Princiotta, F. T.; Loughlin, D. H. *J. Air Waste Manage. Assoc.* **2014**, *64* (9), 979–994.

17. Jun, Y. S.; Giammar, D. E.; Werth, C. J. *Environ. Sci. Technol.* **2013**, *47* (1), 3–8.
18. Li, Q.; Lim, Y. M.; Flores, K. M.; Kranjc, K.; Jun, Y. S. *Environ. Sci. Technol.* **2015**, *49* (10), 6335–6343.
19. Shao, H.; Ray, J. R.; Jun, Y.-S. *Environ. Sci. Technol.* **2010**, *44* (15), 5999–6005.
20. Yang, Y.; Min, Y.; Jun, Y. S. *Environ. Sci. Technol.* **2013**, *47* (1), 150–158.
21. Depaolo, D.; Cole, D. R.; Navrotsky, A.; Bourg, I. C. Geochemistry of Geologic CO_2 Sequestration. *Reviews in Mineralogy and Geochemistry*; Mineralogical Society of America: 2013; Vol. 77.
22. Ewing, R. C. The Nuclear Fuel Cycle: A Role For Mineralogy and Geochemistry. *Elements* **2006**, *2*, 331–334.
23. Ewing, R. C.; Murakami, T. *Elements* **2012**, *8* (3), 181–182.
24. U.S. Department of Energy. Strategy for the management and disposal of used nuclear fuel and high-level radioactive waste; 2013. http://energy.gov/sites/prod/files/; Strategy for the Management and Disposal of Used Nuclear Fuel and High Level Radioactive Waste.pdf (accessed October 10, 2015).
25. Goldman, M. *Environ. Health Perspect.* **1997** (Suppl 6), 1385–1391.
26. U.S. Department of Energy. Cleanup Progress at Hanford; 2015. http://www.hanford.gov/news.cfm/DOE/Cleanup_Progress_at_Hanford-05-2015.pdf (accessed October 10, 2015).
27. Stumm, W.; Morgan, J. *Aquatic chemistry, chemical equilibra and rates in natural waters*; Environmental Science and Technology Series; Wiley-Interscience: 1996.
28. Putnis, A. *Science* **2014**, *343* (6178), 1441–1442.
29. Putnis, C. V.; Ruiz-Agudo, E. *Elements* **2013**, *9* (3), 177–182.
30. Environmental Protection Agency. Emerging contaminants – nanomaterials; 2010. http://www.epa.gov/region09/mediacenter/nano-ucla/emerging_contaminant_nanomaterials.pdf (accessed October 10, 2015).
31. Mueller, N. C.; Nowack, B. *Environ. Sci. Technol.* **2008**, *42* (12), 4447–4453.
32. Liu, X.; Ray, J. R.; Neil, C. W.; Li, Q.; Jun, Y. S. *Environ. Sci. Technol.* **2015**, *49* (9), 5476–5483.
33. Brezonik, P. L.; Arnold, W. A. *Water chemistry: An introduction to the chemistry of natural and engineered systems*; Oxford University Press: New York, 2011.
34. Neil, C. W.; Yang, Y. J.; Schupp, D.; Jun, Y.-S. *Environ. Sci. Technol.* **2014**, *48* (8), 4395–4405.
35. Lottermoser, B. G. *Mine wastes. Characterization, treatment and environmental impacts*; Springer: 2010.
36. Mitzi, D. B.; Gunawan, O.; Todorov, T. K.; Wang, K.; Guha, S. *Sol. Energy Mater. Sol.* **2011**, *95* (6), 1421–1436.
37. Todorov, T. K.; Reuter, K. B.; Mitzi, D. B. *Adv. Mater.* **2010**, *22* (20), E156–E159.
38. Hao, F.; Stoumpos, C. C.; Cao, D. H.; Chang, R. P.; Kanatzidis, M. G. *Nat. Photonics* **2014**, *8* (6), 489–494.
39. Cui, J.; Zhang, L. *J. Hazardous Mater.* **2008**, *158* (2−3), 228–256.

40. Li, J.; Lu, H.; Guo, J.; Xu, Z.; Zhou, Y. *Environ. Sci. Technol.* **2007**, *41* (6), 1995–2000.
41. Hagelueken, C.; Corti, C. W. *Gold Bulletin* **2010**, *43* (3), 209–220.
42. Istratov, A. A.; Buonassisi, T.; Pickett, M. D.; Heuer, M.; Weber, E. R. *Mater. Sci. Eng. B* **2006**, *134* (2−3), 282–286.
43. Oldeman, L. R. In *Soil Resilience and Sustainable Land Use*; Greenland, D. J., Szabolcs, I., Eds.; CABI: Wallingford, U.K., 1994; p 9.
44. Tilman, D.; Cassman, K. G.; Matson, P. A.; Naylor, R.; Polasky, S. *Nature* **2002**, *418* (6898), 671–677.

Chapter 10

Sustainability Using Solar Energy: Present and Future

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Currently, the world is facing energy and environmental challenges that could possibly be met using renewable energy primarily from solar flux. The present chapter outlines the potential of solar energy for alleviating current and future energy demands. We review the environmental consequences of using fossil fuels to power the world followed by comparing the various forms of renewable energy. A detailed presentation of the present state of research for various forms of alternative energy is included with potential avenues for further improvements to these renewable technologies. The five types of renewable energy that include hydroelectric, geothermal, tidal, wind, and solar is discussed herein briefly with emphasis placed on solar energy.

Introduction

Increasing energy demand results in severe stress on the current energy infrastructure, and it damages the health of the world's environment. In order to initiate sustainable development and to overcome these energy issues, long term potential actions need to be taken soon. Figure 1 illustrates the different energy sources that are used in the United States (*1*).

In Teaching and Learning about Sustainability; Levy, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

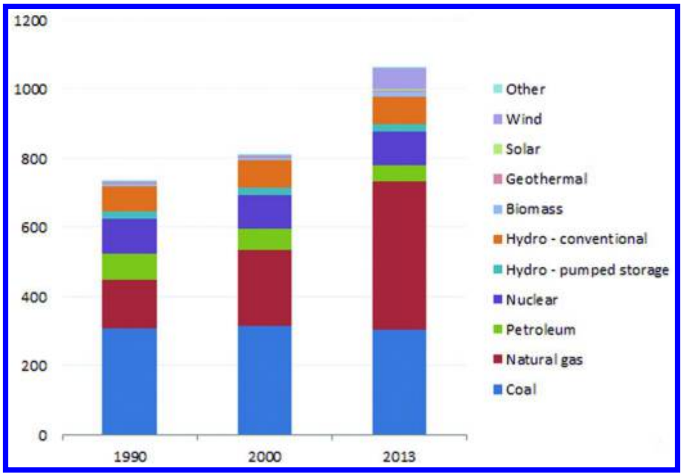

Figure 1. U.S. primary energy consumption by source. Reproduced with permission from reference (1). Copyright 2014 U.S. EIA.

Although non-renewable energy sources mostly fulfil the current energy requirements, these sources lead to several environmental challenges, such as air pollution (CO_2 levels and acid rain), soil erosion and contamination, and water pollution (heavy metals, etc.). Thus, there is a vast necessity to utilize renewable energy resources, as these appear to be the most effective solutions that can provide healthy, sustainable development. In particular, solar energy has the largest potential to eliminate the need for using carbon based fuels, because more solar flux strikes the earth's surface in one hour than that is needed for an entire year. The major challenges in harvesting this renewable energy are related to the design of efficient devices for converting the solar photons to heat, electricity, and fuels and the infrastructure needed to support this.

The enormity of the challenge in transitioning from a fossil fuel to renewable energy can be understood from the concept of *Cubic Mile of Oil* (CMO) (*2*). Currently, the world uses about 3 CMO, and the projected demand is between 6 to 9 CMO by 2050. Of the 3 CMO used, only a fraction, 0.005 is from solar and wind energy. To meet the burgeoning demands of the world by 2050, significant improvements in solar energy capture and storage, and new technologies that are scalable need to be developed.

Much research work has been completed to prevent the recombination of the photo-generated charge-carriers to improve the solar energy efficiency, but additional sustained research is needed for wide spread deployment. In addition, understanding the mechanisms for solar energy conversion will provide future avenues to design highly efficient solar harvesting structures. The previous methods in designing solar conversion involved starting with a known structure and making analogs of the material, but other equally important material design methods include the inverse design approach. In the inverse material design approach, first-principles theoretical calculations and combinatorial studies are carried out to model desired properties to identify new materials that have not been explored previously. A combination of inverse material design and advanced surface probe techniques offer the potential of revolutionizing the future of solar energy conversion devices. Finally, the last major obstacle for renewable energy has been developing a storage medium, which is the game changer for wind power and other forms of alternative energy.

Types of Energy

The types of energy can be primarily classified into conventional and renewable. Conventional (non-renewable) energy is comprised of fossil fuels and nuclear energy. Fossil fuels can be broken down into coal, natural gas, and oil. Among them, coal, a sedimentary organic rock mostly containing carbonaceous materials, is the largest produced source, particularly in United States. The U.S. Energy Information Administration (EIA) reports that about 39% of electricity is generated from coal. In addition, many industries use coal to make their products, such as plastics, tar, synthetic fibers, fertilizers, and medicines. Natural gas, another non-renewable energy source, is mainly produced from the underground decomposition of organic matter (*i.e.*, dead plants and animals). Apart from the usage for electricity production, natural gas is used as a major fuel source to heat buildings and is employed in several industries. In their October 2014 report, the EIA stated that 31% of natural gas was used for the electric power production, and 28% was used for industrial purposes. Crude oil is a non-renewable fuel that is naturally in liquid form, and it is mainly used to make liquid petroleum products such as gasoline, diesel fuel, and heating oil. Nuclear fission is also non-renewable, because the needed uranium will be depleted over time.

These non-renewable energy sources are considered the primary energy sources as depicted in the Figure 2. Today's global energy economy faces an increasing energy demand.

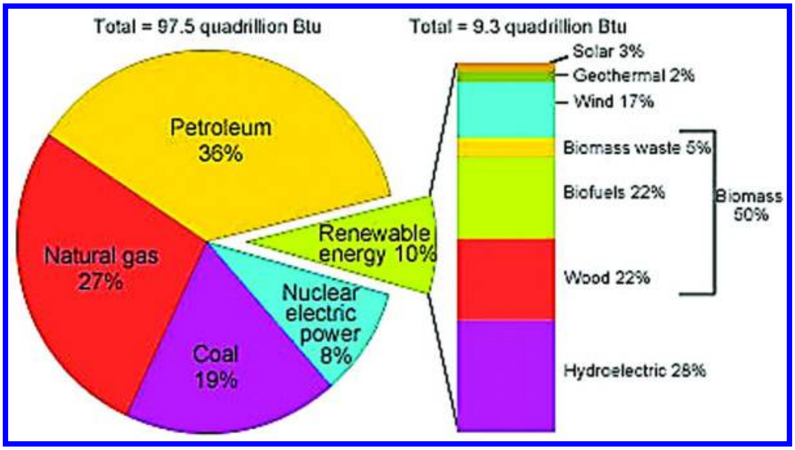

Figure 2. U.S. primary energy consumption by source. Reproduced with permission from reference (1). Copyright 2014 U.S. EIA.

Much of the energy sources are non-renewable. In addition, environmental issues, such as global warming, ozone depletion, air pollution, acid precipitation, forest devastation, and the emission of radioactive substances are also caused by the usage of non-renewable energy (*3*). Thus, there is a need to intensify the usage of renewable energy sources to sustain the world's future economy. Renewable energy sources, including hydroelectricity, geothermal, tidal, wind, and solar energy, have the potential to replace our need for using conventional fuels. Although renewable energy reduces greenhouse gas emissions, the use of renewable sources can be limited due to their restricted availability from the lack of an adequate energy storage medium. The following section will discuss the different renewable energy sources and their applications.

Renewable Energy

Hydropower

Hydropower is one of the oldest and largest renewable energy sources that has been used for the generation of electricity in United State since 1880. Mobile water is a powerful source of renewable energy that can provide fast and flexible electricity (*4*, *5*). About 6-7% of total U.S. electricity generation and of all of the renewable energy produced, 52% within the renewable sector was obtained by using hydropower. Further, Ardizzon *et al.*, reported in a recent review that 3500 TWh of hydropower electricity production was achieved worldwide in 2010, and it represented 16.3% of world's electricity. Figure 3 graphically depicts the large amount of electricity generated using hydropower. Even though, the share of electricity generated from hydropower is relatively small, it may be considered as a renewable and green source of energy (*6*). In addition, hydropower encourages price stability, reduces hazards to the environment, and contributes to the storage of fresh water for drinking and irrigation. However, these environmental issues have impacted the environment and social surroundings *via* affecting the landscape and the biodiversity of the ecosystem. The environmental issues has perhaps led to a decrease in the production of hydroelectric power in the early 21st century (*6*). The decreased hydropower use can be seen in Figure 3 with other renewable energy sources; other sources show increase while hydropower generation has declined, especially in 2013 (*7*).

Geothermal

Geothermal energy is defined as the thermal energy stored at an accessible depth in the earth's crust and mantle (*8*). A temperature gradient causes a continuous, upward conduction and convection of heat energy. This is remnant from the earth's formation or has been produced through radiogenic decay of certain elemental isotopes, mainly potassium, uranium, and thorium (*8*). Geothermal energy use is generally divided into direct use – for heating and industrial purposes – and electrical power generation (*9*). Sources can be liquid-dominated (which mainly produces superheated water, often called brine) or vapor-dominated (producing steam). There are four categories of geothermal energy deposits: hydrothermal, hot dry rock, magma, and geopressured, as shown in Figure 4 (*8*).

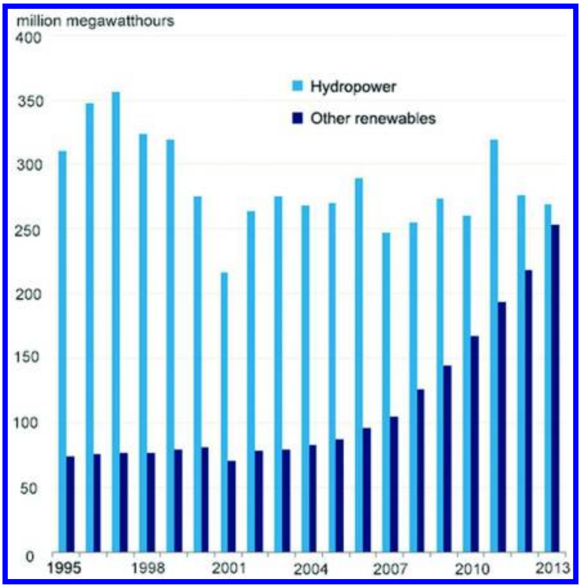

Figure 3. Hydropower and other renewable electricity generation, 1995-2013. Reproduced with permission from reference (7). Copyright 2014 U.S. EIA.

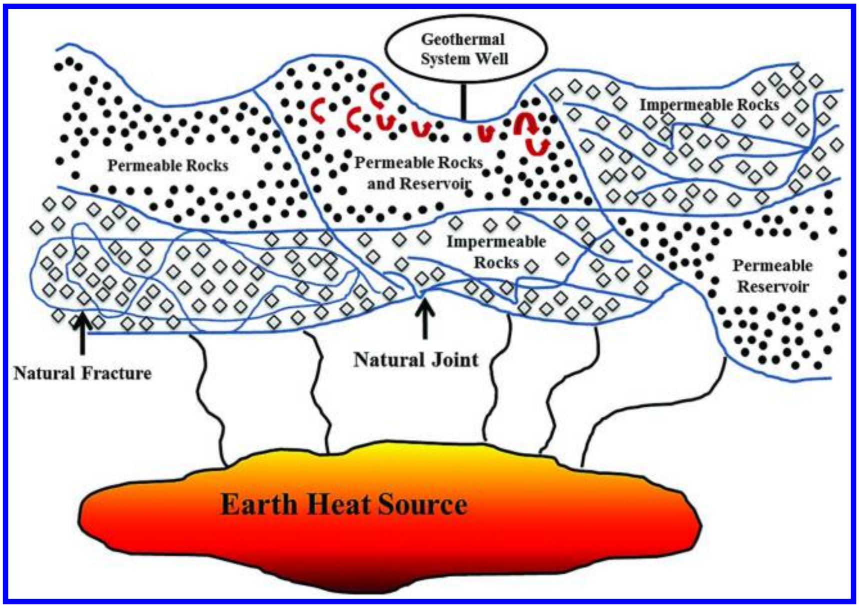

Figure 4. The figure shows the needed geological formation for geothermal energy production.

Geothermal energy has many advantages over traditional fossil fuels. Geothermal power is largely immune to fuel cost fluctuations and relies on an invariable source of energy, unlike wind, solar, or tidal power. Its renewability is good, as any projected amount of heat energy extracted is negligible when compared to the earth's total heat content. Also, geothermal energy plants are simple and adaptable, and land use and waste products are very modest (*8*). However, geothermal power does not come without drawbacks. Extraction of heat energy requires pumps, and these pumps require energy, possibly obtained from a polluting source. In addition, the capital cost of drilling, logging, and completing geothermal wells is high compared to that of oil or gas drilling, especially if the rock is hard, the formations are fractured, and the temperature of operation are high (*9*). The drilling may also be noisy; wells newly drilled or during maintenance have a noise level of 90–122 dB (75–90 dB through silencers). By comparison, a jet takeoff is 125 dB at 60 m, and the pain threshold is 120 dB at 2000–4000 Hz (*10*).

While geothermal energy does not rely on variable sources, it is still limited by depth and quality of source; the geothermal system in question must be at an accessible depth by conventional drilling methods and have sufficient reservoir productivity (*8*). Furthermore, local and regional geologic and tectonic plate phenomena play a major role in determining location, fluid chemistry, and temperature of the resource (*8*). Many geothermal reservoirs are located at unstable areas in the earth's crust, and geothermal electric power plants are generally built, therefore, in regions of high tectonic plate activity. When large volumes of fluid are removed from these already unstable regions in the earth's crust, seismic activity increases due to super-hydrostatic fluid pressures, causing an increased number of plate shifts and earthquakes in those areas (*8*). Water reinjection, a process by which the fluid from the crust is re-injected into the reservoir after the heat is extracted, may also induce increased seismic activity due to decreasing rock stress, loosening vertical faults, and triggering the release of accumulated tectonic stress (*10*). Also, while the total heat content of the earth far surpasses any extracted amount, production must be monitored to avoid local depletion of certain regions (*8*).

One must also take into account a major environmental impact of pollution of air and bodies of water. For instance, the steam extracted from a geothermal resource has concentrations of non-condensable gases (CO_2, H_2S, NH_3, CH_4, N_2, and H_2) that range from 1 to 50g/kg of steam (*10*). The vapor may also contain traces of mercury, boron, antimony, arsenic, and radon, which all negatively affect soil, vegetation, and aquatic life (*10*). Though the liquid containing these toxic elements is injected back into the reservoir, much steam escapes into the atmosphere.

Geothermal power plants are not as efficient as would be necessary to be completely sustainable. The fluid loses heat as it travels up toward the surface; the amount lost depends on the length of pipe (depth of reservoir), the specific pipe insulator, and the ambient temperature. Heat is also lost in the mechanics of the turbine and in the cooling of the steam using pumps and fans. And finally, the overall conversion efficiency of geothermal power plants is affected by plant design, size, gas content, parasitic load, ambient conditions, and many other variables; furthermore, the laws of thermodynamics limit the efficiency of heat engines in extracting useful energy (*11*).

Tidal Power

Tidal power, or tidal energy, is a form of hydropower that converts the oceanic energy of tides into useful forms of power, generally electricity. It is a form of oceanic energy, along with wave, current, thermal gradient, and salinity gradient (*12*). The forces that cause Earth's tides are periodic variations in the gravitational attraction of Earth's moon and, to a lesser extent, sun. A strong attraction causes a swelling of the ocean's water level, increasing sea level temporarily in the form of high tide. Because both the rotation and orbit of the earth are consistent, tides occur on a regular and unfailing schedule. Coastline geography and changes in the sea floor can affect tides on a local level, though. A tidal stream generator converts the kinetic energy of the tidal flows into electricity by the turning of a turbine, much like a wind turbine, and Figure 5 shows the shape of a tidal turbine.

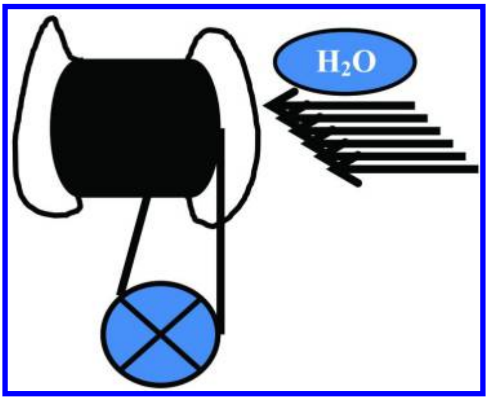

Figure 5. Representation of a tidal turbine with the blue color representing water and the circle marked X as the turbine blade.

Tidal power production has many advantages over not just fossil fuel energy, but also other forms of renewable energy. In addition to producing zero carbon emissions, tidal energy, unlike solar or wind energy, is consistent and fairly steady (*13*). Unlike solar or wind energy, it is not affected by weather patterns and therefore has the large advantage of predictability (*12*). Greater tidal variation and higher tidal current velocities when they do occur, can considerably increase the potential of a site for tidal electricity production. Moreover, the potential and kinetic energy stored in the ocean is of a very large magnitude and is for all practical purposes, inexhaustible (*14*).

Traditionally, tidal energy production suffers from high costs and limited availability of appropriate harvest sites. In addition, effects on marine life can be extensive (*15*, *16*). Noise produced during placement and caused by movement of sediment is augmented because these devices are in the water, and the acoustic output can be greater than those created with offshore wind energy. Marine life that echolocate to communicate and navigate in the marine environment could be particularly affected. Degrading water quality and disrupting sediment processes, from small traces of sediment build up near the device to major adverse effects on ecosystems and processes occurring near shore, are also issues with the generators. Moreover, the power turbines have the opportunity to inadvertently kill swimming sea life with the rotating blades. Simply installing a barrage may change the shoreline within the bay or estuary, affecting a large ecosystem that depends on tidal flats. Mechanical fluids, such as lubricants, can leak out of the devices as well, which may be harmful to the marine life nearby. Proper maintenance can minimize the amount of harmful chemicals that may enter the environment. The energy transfer from the offshore turbines to the onshore electrical grid also poses a challenge. Laying dedicated umbilical cables is neither an economical nor reliable solution, as this necessitates the establishment of local subsea electric grid systems (SEGS). This receives power from the multiple turbines in the farm, synthesizes it to the required power levels, and transmits it to the shore power network using a single power take-off umbilical. SEGS breakdowns lead to power production losses, and system retrieval for repair and maintenance is costly and time consuming – and therefore, these systems need to be robust (*13*). In addition, salt water causes corrosion in metal parts. It can be difficult to maintain tidal stream generators due to their size and depth in the water (*15*, *16*). The use of corrosion-resistant materials such as stainless steels, high-nickel alloys, copper-nickel alloys, nickel-copper alloys, and titanium can greatly reduce, or eliminate, corrosion damage.

Wind Power

Wind power is gleaned from air flow using wind turbines or sails to produce mechanical or electrical power, as shown in Figure 6 (*17*). Wind turbines (WTs) are unmanned, remote power plants (*18*) that are arranged into "wind farms" consisting of hundreds of individual WTs connected to the electric power transmission network that can be onshore or offshore. WTs broadly fall into two categories: horizontal axis wind turbines and vertical axis wind turbines (*19*). Due to its better aerodynamic performances compared with the vertical axis wind turbines, the horizontal axis wind turbines are most commonly used in large-scale offshore wind farms (*19*).

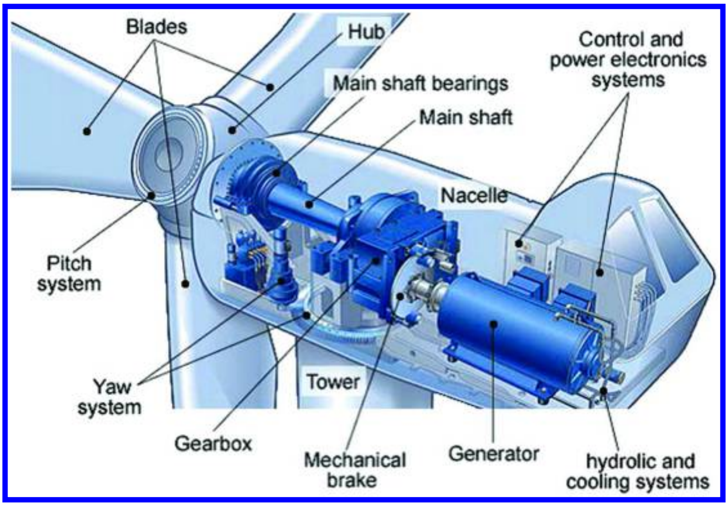

Figure 6. Components that comprise a commercial scale wind turbine. Reproduced with permission from reference (18). Copyright 2014 MDPI.

The use of wind energy has expanded in recent years (*20*). It is extremely clean compared to other forms of conventional energy production, with little to no carbon emissions. Offshore wind power systems in particular have relevant advantages over onshore wind farms, due to the easier transport of the components and lower visual impact and noise (*20*). In addition, offshore winds tend to flow at higher speeds than onshore winds, which permit the turbine to generate more electricity, as the energy produced from the wind is proportional to the cube of the wind speed. Also, unlike onshore winds, offshore winds can be stronger in the afternoon, aligning nicely with the time when load demands are highest (*19*). There are also many indirect advantages of wind energy. For example, the U.S. wind industry generates tens of thousands of jobs and billions of dollars of economic activity. In addition, wind projects provide local taxes and strengthen the economy of rural communities by offering revenue to farmers with wind turbines on their land (*21*).

While wind energy has many advantages, it also has many disadvantages. Wind farms can cover very large areas of land; however, the land that lies in between the turbines can be cultivated for farming purposes and the like. Wind speed varies continuously because of fluctuations in the thermal conditions of air masses (*19*) and, therefore, wind energy can be unpredictable, often requiring supplementation with another energy production form. Unlike conventional power stations, WTs are exposed to extremely variable and harsh weather conditions, such as calm to severe winds, tropical heat, lightning, arctic cold, hail, and snow. Because of the variable environment, WTs experience constantly changing loads, which result in highly inconstant operational conditions that cause deep mechanical stress (*18*). WTs necessitate much maintenance in order to deliver a safe, cost-effective, and reliable power yield with adequate equipment life (*18*). For offshore farms, as the power rating and the distance of the wind farm from the shore increase, the mechanical challenges related to the installation and maintenance of the power generation equipment also grow (*19*).

Solar

Solar energy can be broken down into three main classes: thermal, electricity, and fuels. Solar thermal energy has three aspects that have been developed in previous applications: residential heating, such as home heating (both air and water) and domestic water heating; thermal electricity uses molten salts and thermoelectrics; and solar fuel production of splitting water into hydrogen and the photoreduction of CO_2. We will review solar collectors using thermal energy in this first sub-section. The second sub-section will focus on solar electricity generation, which can be broken down into the first, second, and third generation solar energy harvesting devices. The last sub-section under solar energy utilization is comprised of different avenues for the production of fuels, such as photocatalytic and photoelectrochemical splitting of water, or photocatalytic and photoelectrochemical conversion of carbon dioxide. Finally, concluding remarks will be given for the solar energy section, and future directions needed to propel this technology to replace conventional fuels sources presently used will also be discussed.

Solar Thermal

Residential solar water heating is considered a mature field with further improvements to be made in the increasing of the efficiency and durability of the components that comprise a solar thermal energy harvesting system (*22*, *23*). Solar water heating system types can be broken down into thermosyphon, integrated collector storage, direct circulation, indirect heating, and heated air. The research on thermosyphon systems shows that the storage tank should be in the vertical position for obtaining the highest efficiency. In addition, research has been completed studying different types of heat transfer fluid that is not water, such as petroleum-ether and fluorocarbon refrigerants. The second passive hot water heating system includes integrated collector storage, which uses a tank as the collector for heating the water. Many different aspects have been studied on the integrated collector storage, such as surface glazing, tank insulation, and reflectors within the collector unit. The thermosyphon and integrated collector storage systems are classified as passive, because they do not require pumps to transfer the heated liquid from the collector to the storage tank. The direct circulation water heating system does use pumps for transferring the hot water from the collector to the tank. The other active hot water heating method includes indirect heating. In contrast to the active direct heating system, the indirect heating method employs two loops: a closed loop to the collector and a loop from the storage tank. The last heating system uses air to warm stones that will be used in a heat exchanger for producing hot water. We will briefly discuss the advantages and disadvantages of each of these solar water heating methods in the next sub-section.

Solar water heating systems can be categorized as passive or active, depending on the manner needed to transfer the harvested solar heat (*22*). The passive water heating apparatus includes a thermosyphon and an integrated collector. The major advantage of these two solar water heating technologies is that they have few moving parts, which reduces the initial cost of solar water system. Additionally, the lack of circulation pumps reduces the needed maintenance on the water system and the probability of potential pump failures. The challenges for the thermosyphon system include the larger piping needed to prevent air bubbles from forming, an auxiliary water heater, and the volume of warmed water related to sunshine duration. Many techniques have been studied to increase the thermosyphon efficiency, such as use of other heat transfer fluids, various collector configurations, and tilt-angles. However, these various efforts have led to only modest improvements in the solar efficiency. The integrated collector also functions in a similar manner as the thermosyphon system. The major difference is the storage tank within the solar collector. This solar hot water system also uses the density principle of warm water rinsing. One area that needs further improvement is heat loss management because of the tendency to lose much solar energy in non-sunshine hours of the day. The active solar water heating methods include direct circulation, indirect, and hot air. The benefit of the direct circulation system is higher efficiency from the collectors, because all-glass vacuum tubes are employed that have lower heat loss.

A representative hot-water solar array using vacuum concentrator tubes is shown in Figure 7. The water heated using this solar system can easily reach over 100°C, so measures have to be taken to prevent damage to the collector and other components that comprise the system. The other challenges that face direct circulation water heating include care of the water that needs to be approximately neutral in pH value with the least amount of hardness minerals, such as calcium and magnesium. Otherwise, the circulation pump components can be easily damaged. The indirect solar water heating system uses two loops, a storage tank, and a heat exchanger.

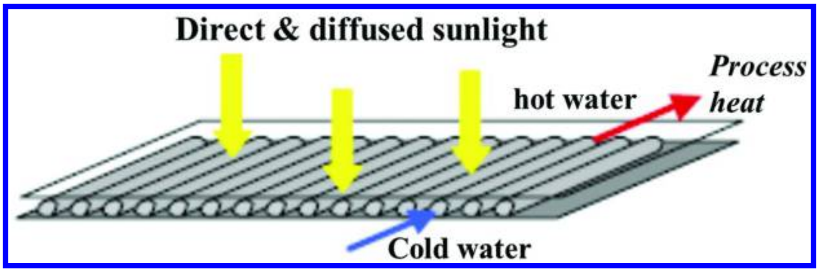

Figure 7. A low temperature solar absorber array used for collecting the light rays as heat. The array shown might be typical in direct water circulation using vacuum concentrator tubes for heating the water from the sunlight. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

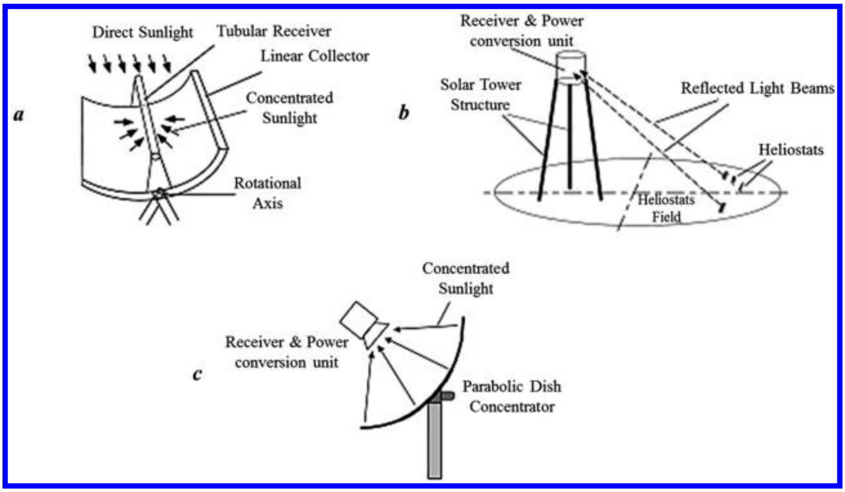

Figure 8. Part (a) shows the parabolic trough used in linear Fresnel collector, and central receiver collector. The trough is designed to track the sunshine throughout the daytime with the central receiver unit in part (b). In part (c) the parabolic dish heat engine focuses the sunlight on one spot for concentrating the heat similar to a central receiver unit in part (b). The parabolic trough can also be employed as array for producing heat fluid for generating steam similar to the hot-water array as in Figure 7. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

The system can be pressurized or non-pressurized with an expansion tank. The manner of operation of the indirect solar water heating is classified as a heat pump, so many of the components need maintenance to prevent failure, similar to the direct circulation solar water heating method.

The active method uses air as the heat transfer fluid to harvest the solar energy. The heated air is passed over stone collectors, which store the energy until needed for heating the water, using a heat exchanger. The major challenge with using air is the low heating capacity, so the amount of heat withdrawal at low temperatures is small. Therefore, an auxiliary heater will be required in colder climates using the solar water heating air extraction method.

The five solar water heating methods have both advantages and drawbacks, yet a hot water system can be devised for any climate that receives solar energy depending on the amount of sunlight and year round temperatures. In the next section, we will focus on solar thermal extraction and the ability to convert the super-heated fluids to produce steam for running an electric turbine.

Solar thermal electricity borrows the idea of water heating used in residential buildings but at much higher operating temperatures. Solar thermal electricity generation can be broken down into four classes: parabolic trough, linear Fresnel, dish heat engine, and central receiver collector, which are depicted in Figure 8. These four different categories represent various configurations of mirror types and arrangements (*24–26*). In addition to mirror type solar thermal electricity generation, there are thermoelectric devices that use the Seebeck effect to produce electricity (*27*).

The major aspects that control the solar efficiency for generating electricity using a concentrator include the geometry of the mirror and number of mirrors that reflect the solar flux to the receiver unit (*24*, *27*). The geometric shape of the mirror influences the amount of solar rays that can strike the absorber. The parabolic trough has a limitation for the size, because solar flux that strikes the trough decreases due to internal reflection. The linear Fresnel mirror arrangement uses curved mirrors to facilitate sunlight to be directed into a linear absorber tube. The linear Fresnel mirror system assumes that the sunshine strikes the mirrors in a straight line manner, which may not be correct for all seasons of year. The dish heat engine flat reflector mirrors that are attached to a parabolic dish with solar flux directed to a central receiver point with an absorber unit. The shortcoming of this solar concentrator is high cost of scale.

Most prototypes developed thus far have been in the range of 1 to 25 kW. The central receiver concentrator collector uses flat panel mirrors that can be positioned in three-dimensions depending on the sunlight angle striking the earth's surface. The ability to position many mirrors in three-dimensions provides the potential to scale-up the utility size electric generator. Using various metal nitrate salts as a heat storage medium gives the ability to provide around the clock electricity production. Therefore, the annual capacity for electricity generation is up to 77%, whereas the capacity factor ranges from 23% to 50% for the parabolic troughs and dish heat engine. The peak efficiency is lower compared to the dish heat engine, but the central receiver unit is within a similar range for net annual efficiency. The status for commercial application of solar concentrator technology varies from mature for parabolic to prototypes using the dish heat engine. The central receiver unit solar concentrator has been commercialized in the last few years. The economic risk for using the central receiver unit falls in the middle between parabolic (low) to high for dish heat engine. The parabolic cost per watt is similar to a central receiver unit. Finally, thermoelectrics can be used to reduce the cost further for generating electricity from waste heat from solar flux, as shown in Figure 9.

Electricity may also be produced using sunlight, and thermoelectric materials using the Seebeck effect. In this type of devices, a p-type and n-type semiconductor is placed between two plates, and produces electrical current upon heating (*25*, *27*). A representative image is shown for using concentrated solar energy to generate electricity in Figure 10. The major challenge for this technology is discovering novel materials that decouple the components that characterize ZT or figure of merit. The S^2T product represents the ability for lattice vibrations to transmit under heating at a given temperature. Decoupling the temperature from the phonons or lattice vibrations has been challenging; however, recent research suggests the possibility of using nanoparticles encapsulated with an appropriate matrix to assist in enhancing the S^2 term without significantly effecting the temperature variable. The use of novel thermoelectric materials has been indicated to potentially produce up to 10% more electricity from waste heat, so future research needs to focus on materials that have large figure of merit and low cost of production (*24*, *25*, *27*). In the final sub-section within the solar thermal section, we will briefly describe the potential of solar concentrator technology to produces fuels, such as hydrogen from water and methanol using water and carbon dioxide.

Solar fuels using concentrator technology are still in their infancy. The major challenge has been developing high temperature reactor components that are able to withstand extreme temperatures for long periods of time (*24*). Figure 11 shows the potential route for producing solar fuels using the thermochemical cycle. High temperatures are needed for splitting water into hydrogen and oxygen for enhanced reaction kinetics; the reactor temperature needs to be 2500 K or higher for dissociating water. The other challenge has been discovery of novel metal oxides that reduce and oxidize without converting to gas phase. The high temperatures produced in concentrators have been tested for upgrading fossil fuels with success in reducing carbon dioxide emissions and higher efficiency (*24*, *28*). Therefore, much research continues on the development of higher temperature ceramics and redox metal oxides that do not form in the gas phase upon subliming. In addition, another approach taken includes developing solid acid metal oxides that are able to dissociate water under milder temperatures (*29*). The results in the solar thermal fuels research point to need for developing novel components and methods for using the solar flux, which will require sustained research effort (*24*, *27*).

The solar electricity section will provide an overview of the types of solar cells that have been studied and potential benefits for using the sunlight to produce electricity from these devices.

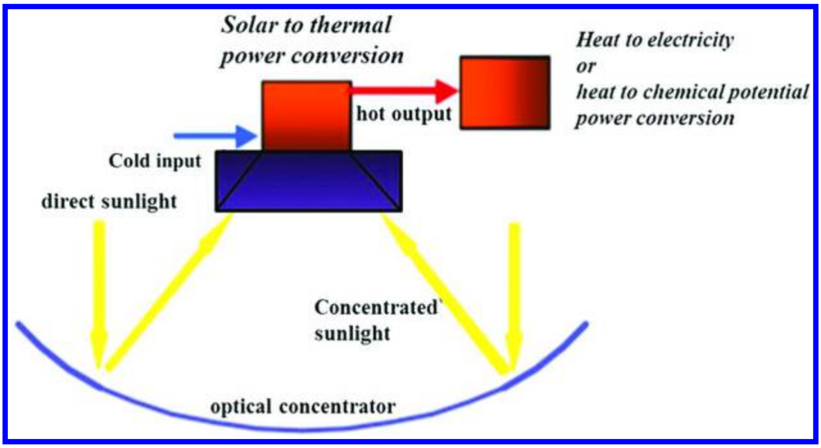

Figure 9. The concentrated sunlight is directed at one area using optics, which rapidly heats the fluid for producing steam to drive an electric turbine. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

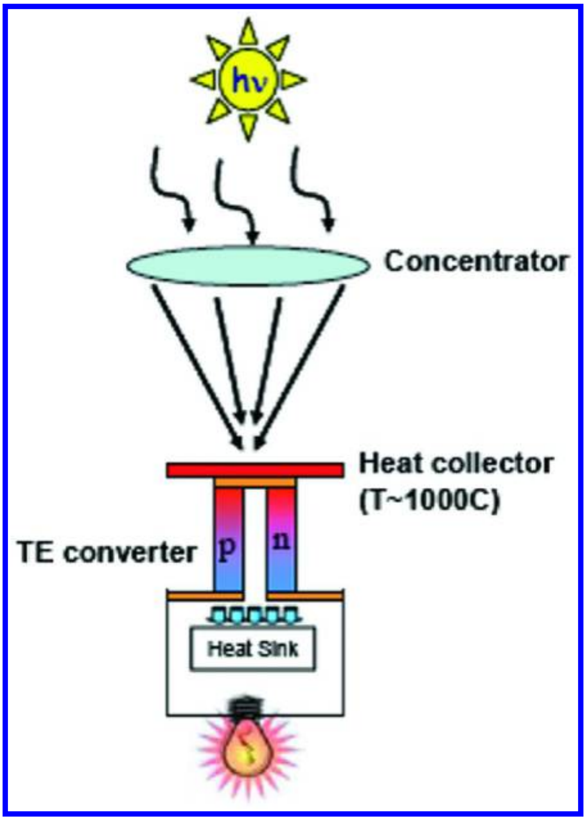

Figure 10. Illustration of a solar-thermoelectric power generator. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

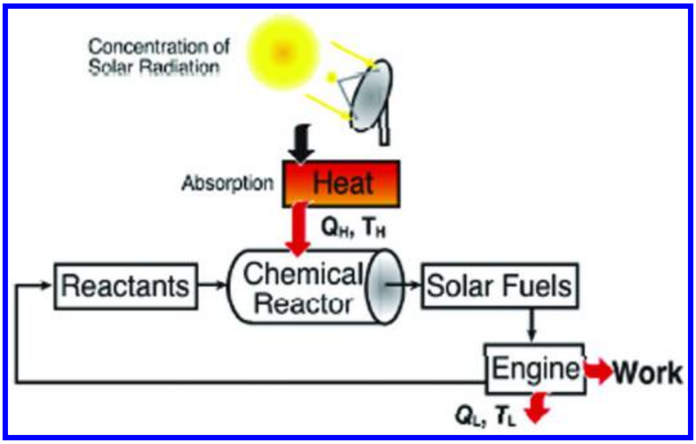

Figure 11. General concept of solar-driven thermochemical cycle. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

Solar Electricity

The solar electricity using photovoltaics can be broken down into first, second, and third generation solar cells. The first generation solar cells use silicon and silicon analogs, such as GaAs, CdTe, and copper indium gallium diselenide (CIGS), to produce electricity (*27*, *30*). The second generation solar cells are comprised of amorphous silicon and were originally developed for space applications. Further research has brought the cost of silicon down to a point where terrestrial applications can be employed here on Earth (*31*). The first generation of solar cells are semiconductors with relatively narrow bandgaps, so they can produce electricity under visible light over the whole visible light spectrum (*27*). The challenges for these p-type semiconductors include the large energy input, toxicity of the resulting materials, and availability of needed elements. The need for highly pure silicon for producing increased efficiency single crystalline materials has further led to research to find alternatives to this semiconductor (*32*). The other major challenge in using silicon based solar cells has been the maximum theoretical efficiency, which is approximately only 32% (*27*, *30*, *32*). A diagram depicting the promotion of light energy to electricity using a first generation silicon solar cell, which shows the energy losses from heat useable photovoltage (qV) with consideration of the p-n band potentials is shown in Figure 12. Therefore, the Si analogs have been developed because of their cost to performance factors. Amorphous silicon has been studied since the 1970s due to the reduced fabrication cost and greater light absorption; however, one drawback is the deterioration of the device after only a few years, with average solar cell efficiency values of 6% to 8% compared with monocrystalline devices of close to 15% or more (*30*). The GaAs, CdTe, and CIGS solar cell devices have great potential for higher solar cell efficiencies than single crystalline silicon photovoltaics, but the mass production has been difficult to scale up from the laboratory. In addition, the low availability of elements that comprise these semiconductors and potential environmental issues have prevented these first generation solar cells from widespread applications in comparison to crystalline Si based solar cells.

The next sub-section will review the third generation that comprises many attempts to reduce materials cost with increased performance: excitonic solar cells, organic photovoltaics, such as p-n junctions (acceptor-donor structures), and organic perovskite photovoltaics.

The excitonic solar cells involve organic semiconductors, dye sensitized, and quantum dot solar cells (*33*). In these, the charge carriers are generated and at the same time separated at a hetero-interface. Figure 13 shows the use of two types of organic materials for producing a heterojunction. In contrast, in bulk semiconductors, the electrons and holes are created throughout the material (*34*, *35*).

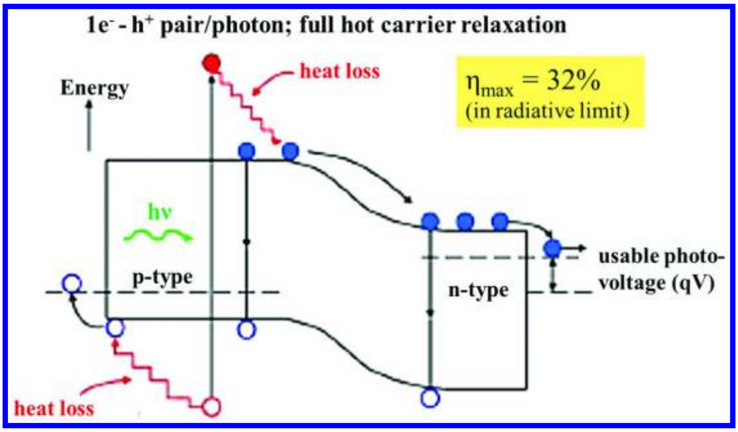

Figure 12. A conventional single p-n junction inorganic photovoltaic cell. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

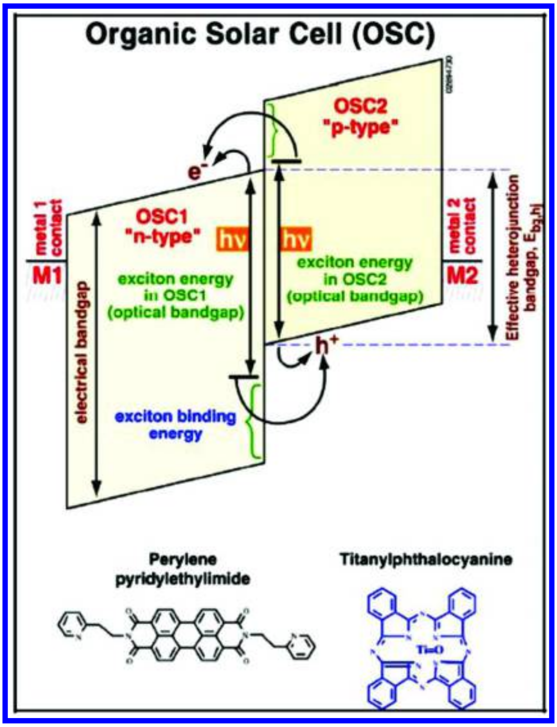

Figure 13. Organic solar cell. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

The organic solar cells have the property of enhanced interfacial charge separation at the heterojunction with no confinement of the exciton pairs. Therefore, the efficiency of charge separation and collection for use in a working device is low compared to one-dimensional polymer/carbon based nanostructures, such as nanotubes, nanorods, graphene, and quantum dots. In dye sensitized solar cells, a dye is adsorbed on a metal oxide, such as TiO_2. A high surface area of the charge transport material (for example, TiO_2), favors large dye uptake, and the complex geometric shape of the titanium dioxide material enhances light scattering followed by greater absorption of the photon flux (*33*). There is an optimal surface area value, because a larger surface area causes greater recombination of the excitons at the interfacial heterojunction region.

The quantum dot excitonic solar cells are semiconductors made of chalcogenides (CdS, CdSe, etc.). These solar cells have materials with particle sizes below the Bohr radius. The quantum confinement effect causes increased bandgap and higher solar cell efficiencies. The hybrid carbon-based organic heterojunctions are more efficient due to their ability to separate exciton pairs effectively. The carbon-based composite solar cells have increased efficiency from the ability to rapidly remove the charge carriers. These carbon-based materials have 1000 times higher conductivity compared to copper metal due to the aromatic-aromatic ring π-π bond delocalization (*36*). Also, the use of the carbon-based materials adds mechanical stability to the organic heterojunction based excitonic solar cells.

In addition to stability, other challenges that need to be overcome in organic photovoltaics include increased charge separation for obtaining larger photovoltages, increasing solar cell efficiency, and creation of mathematical models to better understand the different exciton charge transfer mechanisms (*27*). The opportunities for developing this solar cell could have dramatic outcomes on the photovoltaic industry, because organic solar cells are much less expensive to produce compared to the standard conventional bulk silicon based solar cells, because expensive clean room manufacturing facilities are not required.

Dye-sensitized solar cells could also be a game changer, but the dye, electrolyte, and the host semiconductor material need to be optimized for long-term operation and large-scale deployment. McGehee and co-workers have shown that use of energy relay dyes (ERDs) in dye-sensitized solar cells can increase the solar cell efficiency, but the solubility of the ERDs is another example of the challenges facing DSSCs (*37*). The quantum dot solar cells have the potential to be much less expensive to produce with higher efficiency values possible as third generation material; however, the stability and ability to develop ordered arrays of the quantum dots has been challenging (*38*).

In summary, the efficiency of the excitonic solar cells compared to silicon photovoltaics could be equal or even greater, and the cost of production will be less in the future with the continued research work outlined above (*33*). A big challenge lies in obtaining reasonable efficiencies while scaling up from the laboratory to a high-volume. With the advent of novel processing techniques and identification of newer materials, and device configuration, these challenges can most likely be overcome.

The final sub-section in solar electricity is a hybrid material recently developed made of organic and inorganic components: organic perovskites. The organic perovskites have ABX_3 crystal structure with the center cation species being an organic entity (*39*). The halides – chlorine, bromine, and iodine – are the X component that occupies the faces of the perovskite cube. The eight corners of the cube are lead ions, although other metal ions like tin might be used for the B component or position. The unique quality of this particular solar cell is the use of small, organic molecules for the A positions and inorganic elements for the B positions in the ABX_3 structure.

The ability to use solution phase chemistry opens the door for low cost processing and further increased power conversion efficiency is possible with further optimization. The use of bulky halides coupled with large metal ions provides the opportunity to have absorption and transfer of the charge carriers to the electrodes in order to complete the electric circuit. The reduced electronegativity of the larger iodine atom and the ability of the lead ion to provide vacant valence orbitals leads to the potential for enhanced solar cell efficiency. In addition, the organic species functions as a cation within the perovskite unit cell, so the hybrid perovskite could be thought of as a donor-acceptor structure similar to the other third generation solar cells, such as organic bulk heterojunctions and dye sensitized solar cell devices. This ability to have a large heterojunction interfacial area for efficient charge separation coupled with hole transfer property has led to an explosive growth in this area of solar energy research in only a few years.

Similar challenges lie for organic perovskite solar cells for commercialization like the other third generation photovoltaics. These include developing models that explain and predict the various properties of these novel materials (*40*). Furthermore, other additional challenges abound for these latest third generation solar cells to compete with first generation photovoltaics, and the areas that need focused research and development include identifying alternate ions for the B position in the organic perovskite to replace the lead ions (because of their environmental impact), developing coatings for protections against intense ultraviolet light, durable sealants for preventing moisture entering the solar cell module, and determining methods to scale up the perovskite films for commercial applications. These various challenges will need to be studied and avenues will need to be developed to overcome the commercialization advantage that the first generation Si solar cells have over other later technologies.

The advantages of organic perovskite-based solar cells eventually may lead them to replace existing solar cells based on Si technology, but this will require developing highly stable and durable modules of comparable efficiencies. This may take many years of research and development before entering the marketplace.

The final sub-section highlights the potential that solar fuels could have on the economy and positively impact the environment with little pollution, and we briefly will review the two most common solar fuel research areas: solar water splitting, and solar photoreduction of carbon dioxide.

Solar Fuels

Approximately 45% of the solar rays are in the visible light region, so research endeavors mainly have focused on developing photocatalysts that can absorb the visible portion of the solar spectrum. This research field has been very challenging and progress has been limited. There are many requirements that must be met for complete water splitting to occur in the visible light region (400 to 700 nm). Current research attempts to mimic the photosynthesis process that occurs in plants when CO_2 is converted to carbohydrates using water as the electron source (*38*). The optimal photocatalyst has conduction band and valence band edges with suitable energies for the reduction of protons to hydrogen and oxidation of water to O_2. Figure 14 shows the four types of water splitting that occur (*41*). The challenge has been to locate a family of durable visible light photocatalysts that split water efficiently. Metal oxides are durable for water splitting, but most of them lack the needed bandgap for effective water splitting under solar illumination or have poor efficiencies.

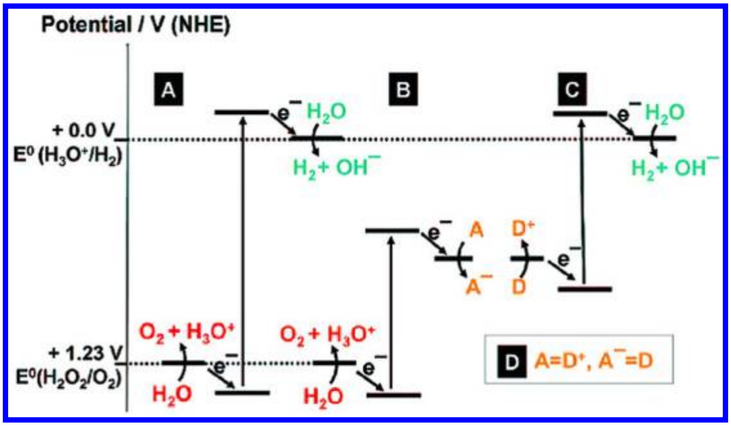

Figure 14. The potential energy diagram is shown for the following cases at pH = 0: (A) ideal semiconductor with both reduction and oxidation occurring simultaneously; (B) semiconductor with an electron acceptor, such as in oxygen evolution; (C) semiconductor with an electron donor, such as in solar hydrogen production; and (D) a two part semiconductor that uses a redox shuttle to transfer electrons from the oxygen evolving unit to the hydrogen evolution unit to produce complete water splitting as in part (A) denoted as z-scheme reaction. Reproduced with permission from reference (41). Copyright 2008 American Chemical Society.

Chalcogenides (such as CdS) have optimal bandgap; however, these materials photocorrode and typically are not stable. Many attempts have been made with few successes, with the exception of a recent publication by Koodali and co-workers that combines TiO_2 and CdS with RuO_2 in a periodic cubic mesoporous silica host material, MCM-48 (*42*). This novel visible light photocatalyst splits water into hydrogen and oxygen gases with a modest apparent quantum yield (AQY) of ~ 1.5% with no photocorrosion occurring.

Approaches have been taken to develop visible light photocatalysts using metal oxides by the combinatorial synthetic methodology. The results of combinatorial type water splitting photocatalysts are just beginning to yield positive outcomes that will likely lead eventually to robust, stable, and highly active water splitting photocatalyst (*43*). In the next sub-section, we will discuss efforts to reduce carbon dioxide to liquid fuels, such as methanol.

The opportunity to convert CO_2 to methanol could potentially be used as feedstock for various chemical productions. However, similar issues arise like with water splitting. These major challenges include developing robust metal clusters that oxidize water and use the electrons to reduce CO_2. Frei and co-workers have had measureable success by incorporating visible light metal oxide clusters within periodic hexagonal mesoporous silica MCM-41 material (*44*). The challenge has been to efficiently transfer the electrons away from one cluster to another, so the photocatalyst does not deactivate with time. The opportunities for converting a pollutant to chemical feedstock appear to be one potential avenue for alleviating carbon dioxide emissions.

Photoelectrochemical conversion of carbon dioxide has merit if a renewable energy source could be used for the electrical current, such as wind or solar energy. The intermittent nature of renewable energy sources has prevented their widespread adoption. Likewise, photoelectrochemical splitting of water could be used to produce hydrogen as chemical energy storage for later use as a fuel for producing electrical power on demand, as needed.

The following sub-section will outline the opportunities and challenges of using photoelectrochemical methods to reduce CO_2 and split water into hydrogen and oxygen. This section will also highlight the broad need for continued funding of basic energy science research to lead to a clean and green environment for future generations here on Earth.

Photoelectrochemical water splitting involves deposition of a semiconducting material on a photoanode where oxidation of water to oxygen occurs (*45*, *46*). At the counter electrode, cathode, reduction of protons produces hydrogen. The challenge has been to discover electrode materials that efficiently absorb visible light.

A big advantage of the photoelectrochemical mode is the fact that the products, hydrogen and oxygen are produced at two separate parts and therefore there is no need to separate them unlike when using a suspension of a photocatalyst. This is especially important when scaling-up since combination of hydrogen and oxygen at large volumes can lead to safety issues. Therefore, various attempts have been completed with the goal of splitting water under visible light in the photoelectrochemical (PEC) mode. The PEC mode decouples the need for one single photocatalyst to have all of the needed attributes for complete water splitting because an external circuit is employed. In addition to light energy, an external electrical bias is needed for the efficient overall water splitting to occur.

The primary advantages of the PEC mode are: (1) the heterojunction required to form can be very simple formed by immersing a semiconductor in a suitable electrolyte solution, (2) an auxiliary electrode can be added to store power,(3) solid-liquid heterojunctions are strain-free in comparison to solid-solid p-n junctions, and (4) there is no need for an electrolyzer. Relatively, large efficiencies of over 15% (electric power) and 10% (hydrogen generation) have been achieved. In summary, overall solar water splitting has great potential with sustained research funding; however, the many challenges of this thermodynamically uphill reaction require durable and cost-effective materials for commercialization.

The final discussion in this section describes the photoelectrochemical reduction of carbon dioxide to fuels, such as methanol. The challenges present with overall water splitting also occur with CO_2 reduction (*47*). The flowchart in Figure 15 shows the many competitive processes that arise when reducing carbon dioxide because of the need to convert water to hydrogen and simultaneously use the electrons to convert CO_2 to reduced product(s).

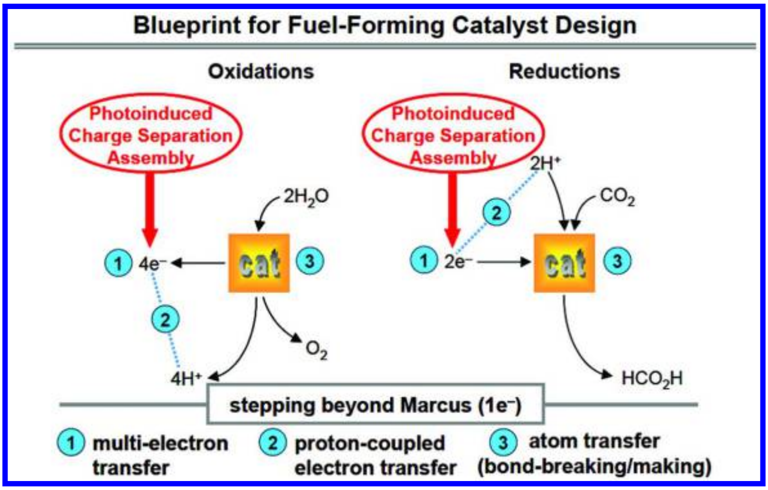

Figure 15. Steps to developing a photocatalyst that splits carbon dioxide and water to form reduced products. Cat refers to Catalyst. Reproduced with permission from reference (27). Copyright 2005 U.S. DOE.

Photoelectrochemical reduction of CO_2 requires a large energy input of 689 kJ per mole (Gibbs free energy) because of the highly stable state of carbon dioxide. Similar to water splitting, several photocatalysts can operate with fair efficiency in the UV spectrum for reducing CO_2 to CO or other products with water or moisture; however, few to no materials exist that can photoreduce CO_2 to CO or other forms in the visible light range.

Other challenges present in CO_2 photoreduction include poor selectivity to the desired reduced product. The potential for splitting CO_2 or photoreducing carbon dioxide appears promising when TiO_2, the most studied semiconductor, is highly dispersed on periodic mesoporous silica hosts, such as small pore MCM-41 and large pore SBA-15 (*48*). The challenges for photocatalytic or photoelectrochemical splitting of carbon dioxide with water will require identification of novel materials that can effectively absorb visible light photons and effectively transport the electrons to form the desired product(s) (*49*). Few studies have used periodic silica hosts for water splitting or carbon dioxide photoreduction with exception of previous work by Koodali, Frei, and co-workers

(*42*, *44*). The mesoporous materials with their periodic array of highly ordered pores offer opportunities because their large pores and high surface area facilitate dispersion of photoactive species. However, much research still needs to be completed in order to understand the various mechanisms that occur in water splitting and carbon dioxide photoreduction (*50*).

For renewable energy to become a major energy source for the world, major funding from governments must continue to grow and sustain the many researchers attempting to address the energy and climate change issues simultaneously (*51*). Our hope is that government leaders will see the value of basic energy research and continue to provide sustained funding in this field of study.

References

1. U.S. Energy Information Administration. Energy in Brief; 2014. http://www.eia.gov/energy_in_brief/article/major_energy_sources_and_users.cfm (accessed Apr. 12, 2015).
2. Crane, H.; Kinderman, E.; Malhotra, R. *Cubic Mile of Oil*, 1st ed.; Oxford University Press: Oxford, U.K., 2010; pp 1−328.
3. Azarpour, A.; Suhaimi, S.; Zahedi, G.; Bahadori, A. *Arabian J. Sci. Eng.* **2013**, *38*, 317–328.
4. U.S. Department of Energy. *Hydro power Project*; DOE/GO-102011-3287; 2011.
5. U.S. Department of Energy. *Water Power for a Clean Energy Future*; DOE/EE-0605; 2014.
6. Ardizzon, G.; Cavazzini, G.; Pavesi, G. *Renewable Sustainable Energy Rev.* **2014**, *31*, 746–761.
7. U.S. Energy Information Administration. Energy in Brief; 2014. http://www.eia.gov/energy_in_brief/article/renewable_electricity.cfm (accessed Apr. 12, 2015).
8. Mock, J. E.; Tester, J. W.; Wright, P. M. *Annu. Rev. Energy Environ.* **1997**, *22*, 305–356.
9. Hammons, T. *J. Electr. Power Compon. Syst.* **2004**, *32*, 529–553.
10. Barbier, E. *Renewable Sustainable Energy Rev.* **2002**, *6*, 3–65.
11. Zarrouk, S. J.; Moon, H. *Geothermics* **2014**, *51*, 142–153.
12. Ng, K.-W.; Lam, W.-H.; Ng, K.-C. *Energies* **2013**, *6*, 1497–1526.
13. Narayanaswamy, V.; Bang-Andreasen, H. *Mar. Technol. Soc. J.* **2013**, *47*, 80–93.
14. Tang, H. S.; Qu, K.; Chen, G. Q.; Kraatz, S.; Aboobaker, N.; Jiang, C. B. *Renewable Sustainable Energy Rev.* **2014**, *39*, 412–425.
15. Vennell, R.; Funke, S. W.; Draper, S.; Stevens, C.; Divett, T. *Renewable Sustainable Energy Rev.* **2015**, *41*, 454–472.
16. Tidal, Pacific Northwest National Laboratory; 2015. http://tethys.pnnl.gov/technology-type/tidal (accessed Feb. 19, 2015).
17. Fthenakis, V.; Kim, H. C. *Renewable Sustainable Energy Rev.* **2009**, *13*, 1465–1474.

18. Tchakoua, P.; Wamkeue, R.; Ouhrouche, M.; Slaoui-Hasnaoui, F.; Tameghe, T.; Ekemb, G. *Energies* **2014**, *7*, 2595–2630.
19. Islam, M. R.; Guo, Y.; Zhu, J. *Renewable Sustainable Energy Rev.* **2014**, *33*, 161–176.
20. Lloberas, J.; Sumper, A.; Sanmarti, M.; Granados, X. *Renewable Sustainable Energy Rev.* **2014**, *38*, 404–414.
21. National Renweable Energy Laboratory. Wind and Water Power; 2012. http://www.nrel.gov/docs/fy12osti/49222.pdf (accessed Feb. 10, 2015).
22. Raisul Islam, M.; Sumathy, K.; Ullah Khan, S. *Renewable Sustainable Energy Rev.* **2013**, *17*, 1–25.
23. Shukla, R.; Sumathy, K.; Erickson, P.; Gong, J. *Renewable Sustainable Energy Rev.* **2013**, *19*, 173–190.
24. Romero, M.; Steinfeld, A. *Energy Environ. Sci.* **2012**, *5*, 9234–9245.
25. Suter, C.; Tomeš, P.; Weidenkaff, A.; Steinfeld, A. *Sol. Energy* **2011**, *85*, 1511–1518.
26. Jamel, M. S.; Abd Rahman, A.; Shamsuddin, A. H. *Renewable Sustainable Energy Rev.* **2013**, *20*, 71–81.
27. *Basic Research Needs for Solar Energy Utilization*; Report of the Basic Energy Sciences Workshop on Solar Energy Utilization; U.S. Department of Energy: Bethesda, 2005.
28. Piatkowski, N.; Wieckert, C.; Weimer, A. W.; Steinfeld, A. *Energy Environ. Sci.* **2011**, *4*, 73–82.
29. Cho, Y. S.; Kim, J. H. *Int. J. Hydrogen Energy* **2011**, *36*, 8192–8202.
30. Surek, T. *J. Cryst. Growth* **2005**, *275*, 292–304.
31. Bye, G.; Ceccaroli, B. *Sol. Energy Mater. Sol. Cells* **2014**, *130*, 634–646.
32. Lewis, N. S.; Nocera, D. G. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 15729–15735.
33. Gregg, B. A. *J. Phys. Chem. B* **2003**, *107*, 4688–4698.
34. Keru, G.; Ndungu, P. G.; Nyamori, V. O. *Int. J. Energy Res.* **2014**, *38*, 1635–1653.
35. Wang, Q. H.; Bellisario, D. O.; Drahushuk, L. W.; Jain, R. M.; Kruss, S.; Landry, M. P.; Mahajan, S. G.; Shimizu, S. F. E.; Ulissi, Z. W.; Strano, M. S. *Chem. Mater.* **2013**, *26*, 172–183.
36. Vomiero, A.; Concina, I.; Comini, E.; Soldano, C.; Ferroni, M.; Faglia, G.; Sberveglieri, G. *Nano Energy* **2012**, *1*, 372–390.
37. Hardin, B. E.; Yum, J.-H.; Hoke, E. T.; Jun, Y. C.; Péchy, P.; Torres, T. s.; Brongersma, M. L.; Nazeeruddin, M. K.; Grätzel, M.; McGehee, M. D. *Nano Lett.* **2010**, *10*, 3077–3083.
38. Ramsurn, H.; Gupta, R. B. *ACS Sustainable Chem. Eng.* **2013**, *1*, 779–797.
39. Park, N.-G. *J. Phys. Chem. Lett.* **2013**, *4*, 2423–2429.
40. Green, M. A.; Ho-Baillie, A.; Snaith, H. J. *Nat. Photonics* **2014**, *8*, 506–514.
41. Osterloh, F. E. *Chem. Mater.* **2008**, *20*, 35–54.
42. Peng, R.; Wu, C.-M.; Baltrusaitis, J.; Dimitrijevic, N. M.; Rajh, T.; Koodali, R. T. *Chem. Commun.* **2013**, *49*, 3221–3223.
43. Liu, X.; Shen, Y.; Yang, R.; Zou, S.; Ji, X.; Shi, L.; Zhang, Y.; Liu, D.; Xiao, L.; Zheng, X.; Li, S.; Fan, J.; Stucky, G. D. *Nano Lett.* **2012**, *12*, 5733–5739.

44. Frei, H. *Chimia* **2009**, *63*, 721–730.
45. Wang, G.; Ling, Y.; Wang, H.; Xihong, L.; Li, Y. *J. Photochem. Photobiol., C* **2014**, *19*, 35–51.
46. Li, Y.; Zhang, J. Z. *Laser Photonics Rev.* **2010**, *4*, 517–528.
47. Izumi, Y. *Coord. Chem. Rev.* **2013**, *257*, 171–186.
48. Kubacka, A.; Fernández-García, M.; Colón, G. *Chem. Rev.* **2012**, *112*, 1555–1614.
49. Corma, A.; Garcia, H. *J. Catal.* **2013**, *308*, 168–175.
50. Tahir, M.; Amin, N. S. *Energy Convers. Manage.* **2013**, *76*, 194–214.
51. McKone, J. R.; Lewis, N. S.; Gray, H. B. *Chem. Mater.* **2014**, *26*, 407–414.

Chapter 11

Power Production that Can Impact Climate Change: Nuclear Fission, Past, Present, and Future

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In the first half of the 19th century, the approximately 1 billion inhabitants of planet Earth derived primary power from "renewable" wood, wind, water, and muscle power. The second half of the 19th and the 20th century was the age of fossil carbon discovery and wide-scale exploitation during which 85-90% of primary power (in the United States) has been provided by coal, petroleum, and natural gas. During this time, the developed world experienced tremendous technological growth. At the beginning of the 21st century, global population passed 7 billion and may exceed 9 billion by 2050. Energy production is still dominated by fossil carbon combustion (85%) globally. Today, the prospects and potential impacts of climate change have spurred consideration of the cost of this fossil energy dominance. Nuclear fission-based electricity entered the mix in the mid 1960s, ultimately increasing its contribution to about 9% of global energy production. This chapter discusses the strengths and limitations of fission-based nuclear energy compared with other low-carbon options.

Global Climate Change and Energy Consumption

Though the geologic record teaches us that climate change has been a fact of existence on planet Earth over the eons of planetary history, we can only guess at the causes of these changes. Reconstruction, analysis and rationalization of the patterns in the fossil record and geology confirm that the climate can (and does)

In Teaching and Learning about Sustainability; Levy, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

change, often with serious consequences for the dominant life forms on the planet. Lacking the ability to travel backward in time, humans will likely never know for certain whether some predecessor dominant life form disappeared from the planet due to its own actions (or lack of actions). As far as the fossil record can tell us, there has never been a more aware species on Earth than humans. Our science and technologies have developed to a stage at which we have been able to manipulate our environment sufficiently to allow the majority of 7 billion widely scattered humans to live in some degree of comfort. Huge quantities of energy and materials have been consumed to achieve this condition.

As a result of our technological advances, we have gained the ability to measure and monitor the consequences of our progress. Though we humans lack the eons-long historic perspective to know for certain that the activities of our 7+ billion neighbors are harmless, we do have the technological ability to monitor changes that are observable and the scientific sophistication to predict the potential impacts of thousands of years of human progress. During the past decade or so, increasingly sophisticated computer models have sought to correlate a century of increasingly complete and accurate climate data to let us know how serious the consequences of advancing civilization (and population) might be. Prediction of the future of such a complex and dynamic system as our planet can really only be made using these computer models. In all honesty, like every computer modeling exercise, the quality of the forecasts that are developed are subject to the limitations of data, its analysis, and interpretation of the effects. However, ignoring credible indicators of potential impacts is never a wise option; the ostrich strategy seldom works out well.

One such indicator of undesirable climate change (focusing on atmospheric science) was the discovery of an “ozone hole” over Antarctica in the 1980s (*1*). Analysis of laboratory studies of the interactions of chlorofluorocarbons with ozone in the atmosphere placed the origins of this phenomenon on the release of CFCs to the atmosphere. Since stringent restrictions have been placed on the release of certain classes of CFCs, recent data seem to indicate a shrinking of the ozone hole. This observation lends credibility to the argument that the activities of 7 billion humans can impact global conditions. The latest correlation of increasing concentrations of CO_2 in the atmosphere and the perception of an increasingly variable global climate would seem to beg for a similar conclusion to be drawn, i.e., that the carbon-consumption patterns of 7 billion Earthlings might ultimately have some undesirable effects. The rise in atmospheric CO_2 undeniably correlates with increased consumption of fossil carbon by a geometrically expanding global population of humans. We cannot say for certain that this consumption has an undesirable effect on the climate (we are arguably overdue for a glaciation event), but it would be ostrich-like to argue that human activities do not impact the climate.

As the computer climate models predict future catastrophes arising from fossil carbon consumption, the discussion turns toward finding alternative means of powering our crowded planet without the need for consuming vast quantities of fossil carbon. Completely replacing 85% of primary power is a daunting challenge. In truth, the prospects for an ice age might well argue for a balanced approach in which the atmospheric CO_2 content is stabilized at some targeted level rather than reducing it to the average of the last millennium (roughly 280 ppm, Table 1). To achieve even the modest goal of stabilizing atmospheric CO_2 at some level, all options for alternative energy production (and conservation), real and imagined, must be considered. Of course, the second law of thermodynamics establishes that no option for creating energy is without consequence, colloquially speaking, there must always be a "tailpipe." In the next section, some cost-benefit analysis for different approaches to power production options will be considered.

Table 1. Atmospheric CO_2 content, 21st century and 800-1800 average (Mauna Loa Observatory). Data from reference (*2*).

Year	*CO_2 (ppm)*
2013	396.48
2012	393.82
2011	391.63
2010	389.85
2009	387.37
2008	385.59
1997	363.71
1959	315.87
800-1800	280 (±10)

The Cost vs. Benefit of Power Production

The most complete statistics available on energy consumption patterns are found in government data bases that emphasize consumption patterns in the United States, hence much of the following discussion will focus on information from the United States. The U.S. Energy Information Administration Monthly Energy Review for April 2013 (*3*) provides the following statistics for 2012: total energy consumption in the United States totaled 95 quadrillion BTUs (Quads) derived 36% from petroleum (mainly for transportation), 27% from natural gas, 18% from coal (mainly electricity), 8% nuclear electricity and 9% renewable. The renewable fraction breaks down as: 2.7% hydroelectric, 4.5% biomass (wood, biofuels, biomass waste), 1.4% wind, 0.3% geothermal, 0.2% solar. Relative to an analysis five years earlier, total energy consumption in the United States decreased by about 1%, the fractions of natural gas and wind have increased, coal has decreased while the petroleum and nuclear fractions remained roughly constant. Global consumption at the same time significantly increased, mainly from advancement of several under-developed economies (China in particular); the increase is almost entirely based on increased consumption of fossil carbon, primarily coal.

Table 2 tabulates the cumulative leaders in CO_2 emissions from approximately the beginning of the industrial revolution to the present. The top five cumulative CO_2 emitters account for nearly 60% of the global total in this historic period. The top three on a per capita basis are United States, Germany and the United Kingdom. These data also are distinguished by the comparatively low per capita CO_2 emissions of France and Japan. For the data describing 2009 (Table 3), the clear shift toward greater energy consumption by China and India are noteworthy, but the largest per capita energy consumers are the United States and Canada, both heavily industrialized with a large geographic area. The 2009 energy production totals by category in China are also interesting: 70% derived from coal, 19% oil, 6% hydroelectric, 4% natural gas, 1% nuclear. China has at least 29 Generation II+ and III light water reactors under construction to help combat a major decline in urban air quality (*4*).

Assuming that there is agreement that CO_2 emissions should decrease to preserve the climate, it is useful to rationally consider which options provide the greatest benefit relative to the cost of the change. There is little disagreement that in the current energy consumption model, fossil fuels are the most cost-effective energy production method for a planet occupied by 7 billion consumers of power. Coal, oil, and natural gas are readily recovered from increasingly diverse environments using relatively inexpensive and well-tested extraction and purification methods. In the long view, it clearly cannot be sustainable to consume a resource (fossil carbon) in a few hundred years that was produced in a timeframe of many millions of years. It is also somewhat ironic to recognize that these fossil carbon resources were created as a byproduct of earth orbiting (at a distance of approximately 93 million miles) a rather large nuclear fusion reactor. Realistically, the long term survival of more than 7 billion residents is difficult to imagine without several replacements for this finite resource. If climate change is truly a serious threat, even if fossil carbon resources are more abundant than we imagine, there is no reason to delay taking action or at least to develop a timetable for taking action.

Considering the IPCC (Intergovernmental Panel on Climate Change) Special Report on Renewable Energy Sources and Climate Change Mitigation (2011) (*7*), nine different primary energy production technologies have been compared (in alphabetical order): biomass, coal, geothermal, hydroelectric, natural gas, nuclear fission, solar photovoltaic, solar thermal, and wind. In Table 4, these methods are ranked with regard to their complete cycle CO_2 emissions potential. It can be seen in this table that on average coal combustion produces a kilogram of CO_2 per kWh_e (kilowatt-hour of electric power). Combined cycle turbine combustion of natural gas produces less than 500 g CO_2/kWh_e, half that of coal, but at least ten times more than any of the non-fossil options. The least emitting option is hydroelectric, while wind, biomass, nuclear fission, and solar thermal are each quite competitive. The nuclear option compared refers to Generation II (commercial power) light water reactors, representing the majority of the current global fleet; Generation II+ and Generation III (advanced) light water reactors are expected to operate with both greater safety margins and higher efficiency than Generation II/II+ reactors. Generation IV (economical, enhanced safety, reduced waste, proliferation resistant) reactors are under development and most are radically different from current light water reactors.

Table 2. Top 10 cumulative CO_2 emitters 1850-2008. Data from Reference (*5*)

Country	*% of world total*	*Metric tonnes CO_2 per person*
United States	28.5	1,132.7
China	9.36	85.4
Russian Federation	7.95	677.2
Germany	6.78	998.9
United Kingdom	5.73	1,127.8
Japan	3.88	367.0
France	2.73	514.9
India	2.52	26.7
Canada	2.17	789.2
Ukraine	2.13	556.4

Table 3. Top 10 CO_2 emitters 2009. Data from Reference (*6*).

Country	*% of global totalannual emissions*	*Tonnes of greenhouse gasesper capita*
People’s Republic of China	23.6	5.13
United States	17.9	16.9
India	5.5	1.37
Russian Federation	5.3	10.8
Japan	3.8	8.6
Germany	2.6	9.2
Islamic Republic of Iran	1.8	7.3
Canada	1.8	15.4
Korea	1.8	10.6
United Kingdom	1.6	7.5

Table 4. Lifecycle Greenhouse Gas Emissions by Electricity Source. IPCC Special Report on Renewable Energy Sources and Climate Change Mitigation (2011) grams of CO_2 emissions per kilowatt-hour electric power produced. Data from reference (*8*).

Technology	*Description*	*50th percentile ($g\ CO_2/kWh_e$)*
Hydroelectric	reservoir	4
Wind	onshore	12
Nuclear	various Generation II reactor types	16
Biomass	various	18
Solar thermal	parabolic trough	22
Geothermal	hot dry rock	45
Solar PV	polycrystalline silicon	46
Natural gas	various combined cycle turbines without scrubbing	469
Coal	various generator types without scrubbing	1001

Table 5. Average Capacity Factors for Electricity Generation, 2014. Data from Reference (*10*).

Fuel type	*Average Capacity Factor (%)*
Nuclear	86.4
Geothermal	68.8
Biomass	61.9 (2012)
Coal (Steam turbine)	60.9
Gas (Combined cycle)	47.8
Hydroelectric	37.5
Wind	33.9
Solar	27.8
Oil (Steam turbine)	12.8
Gas (Steam turbine)	10.0

Another factor that must be considered in the CO_2-emissions-avoidance discussion is the operation cycle for the energy production technology. One of the virtues of tried-and-true coal-fired power plants is their comparatively reliable functionality, widely considered to be in the 60-70% range for availability. In

Table 5, capacity factors (operational time/total time) for ten different electricity generating technologies are listed (data for the year 2012). Nuclear reactor capacity factors have averaged greater than 90% since about 1990; prior to that time the average availability was 65% (*9*). It has been widely quoted that during the "Polar Vortex" intrusion of Arctic air into the contiguous United States (the "lower 48") during the winter of 2013-2014 nuclear power plants operated at about 95% availability in the affected areas, allowing the diversion of natural gas supplies in the pipelines from electricity generation to home heating.

Lawrence Livermore National Lab produces annually a very informative summary Estimated U.S. Energy Use graphic based on information reported by the U.S. Energy Information Administration (EIA) (*11*). In 2013, the estimated U.S. energy use was 97.4 Quads (quadrillion BTUs) originating in the following primary sources: 36.0% petroleum, 27.3% natural gas, 18.5% coal, 8.5% nuclear, 4.6% biomass, 2.6% hydroelectric, 1.6% wind, 0.3% solar, 0.2% geothermal. In the latest two year cycle (2013-2011), this survey indicates that the natural gas fraction has displaced approximately 1.7% of coal usage, while wind and solar combined have increased by 0.6% overall, displacing primarily hydroelectricity, which has declined by a similar amount. Petroleum, biomass, geothermal and nuclear remained flat in that period. More than 90% of coal consumption is in electricity generation, the remainder in the industrial sector; 100% of nuclear power, hydroelectricity and wind generation is also in electricity production. Natural gas contributes to all segments of the economy while biomass splits about 60% industrial, 40% transportation. Transportation consumes about 71% of petroleum, 24% of the remainder is consumed by industry.

In 2013, the total primary power "end user" categories include about 39% in electricity generation (with about 32% efficiency), 12% residential at 65% efficiency), 9% commercial (at 65% efficiency), 25% industrial (at 80% efficiency) and 28% transportation (at 21% efficiency). The system overall efficiency includes a balance of 38.4 Quad in useful energy services out of a total 97.4 Quads for a net 39% efficiency in energy use in the U.S. during 2013. The greatest opportunities for improved efficiency at the end use are seen in transportation and in electricity generation. Transportation costs will always be a challenge in a large country with a highly mobile population. Increased efficiency in the electricity generation might be best achieved by encouraging co-generation in which "waste" heat is employed in some secondary application.

Assets and Liabilities in Primary Power Production

A fundamental feature of each and every approach to primary power production is that there is always an entropic contribution (often several) to consider. As entropy in general impacts overall efficiency, the prior analysis establishes at least the minimal impact of entropy on process efficiency. In 2009, a special issue of Scientific American (*12*) discussed in broad terms various approaches to the primary production of electricity. Drawing from this and other resources, the following analysis of advantages and disadvantages are offered:

Coal

An abundant resource with considerable known reserves in North America and Asia; least expensive overall means of producing electricity 3.0 cents/kWh (2006); capital cost per kWh \$1,534; power plants operate at 70% capacity; costs of generation are stable; mined underground or in open pits; most polluting (CO_2 emissions, heavy metal releases, naturally occurring radioactive materials); mining accidents typically claim hundreds of lives annually around the world; potential for acid rain (HNO_3 and H_2SO_4) and particulate emission with known environmental and health effects; at least 70% of supply used for electricity production.

Natural Gas

Has become an abundant resource with introduction of hydraulic fracturing technology; emits 50% less CO_2 than coal; capital cost per kWh \$717; on-demand option; "Hydrofracking" requires significant amounts of fresh water and generates similar quantities of contaminated water that is reinjected to the subsurface after extraction of gas; many uses contribute to variable supply dynamic and volatility of prices; fracking releases naturally occurring radioactive materials from the subsurface; fracking may also cause earthquakes; minimal physical "mining" required; at least 1% of extracted methane is lost during gas extraction (greenhouse gas).

Wind

No fuel required; produces power only when the wind is blowing; estimated cost to generate electricity 3.4 cents per kWh (2006); no emissions; no water resources required; current technology requires approximately one ton of expensive rare-earth magnets per windmill (high concentration rare earth mineral deposits are comparatively uncommon and the separation of pure samples of suitable metals is difficult); average availability for power production is 10-30% of peak capacity; energy storage options are needed; for electric grid stability complementary generators are needed for times when the wind does not blow; fertile wind areas are sparcely populated hence power must be transported long distances to end users (transmission losses are significant for all foms of electricity generated at a distance from the end user); capital cost for at sea installations comparable per kWh to per kWh nuclear power; predatory birds frequent victims of windmill blades.

Nuclear Fission Reactors

Expensive to build (\$2,475 per kWh); very low fuel costs (3.3 cents per kWh); 90% capacity factor (U.S. average since 1990); for current generation light water reactors; considerable untapped potential for improved utilization; domestic fuel supply that must be mined (underground, open pit, or subsurface leaching); radium-containing ore tailings must be managed responsibly; uranium fuel must undergo isotopic enrichment; used nuclear fuel is highly radioactive requiring eventual disposal in an engineered geologic repository; U.S. standard single-pass operation of a nuclear fuel cycle uses less than 1% of the available energy of the mined uranium; with a closed nuclear fuel cycle (recycle of uranium and plutonium) efficiency of use of fuel supply is doubled and waste volume reduced; possible diversion of used fuel to nuclear weapons or radiological dispersal devices must be avoided; reactor accidents have occurred during 15,000 reactor-years of power plant operations (though only the Chernobyl accident resulted in direct or increased probability of delayed fatalities); decommissioning expense costed into power production expense, but could take decades to complete; alternative fuel cycles can transmute actinides; advanced nuclear power concepts include thorium-based options as alternative to uranium-focused versions.

Hydroelectric

No fuel required; after construction of dam, almost no associated CO_2 emissions; inexpensive source of primary power; land is submerged behind the dam; periodic dredging required; no serious plans for expanding capacity; 200 dams removed in the U.S during the last 10 years; local opposition and demands for restoration of salmon habitats; retired hydroelectric capacity has been replaced almost 1 for 1 (power production basis) by windmills – many windmills are required to replace the power production of a large hydroelectric facility.

Biofuels

Waste wood and paper combustion is carbon neutral; ethanol from corn not very cost effective option for transportation fuels; converting corn to ethanol must be balanced against food supplied for people and livestock; comparatively low energy density fuel.

Solar Thermal/Photovoltaic

Considerable energy available at the surface of the Earth, more at higher elevations; energy extraction materials (polycrystalline silicon) decreasing in price; solar-PV suitable for distributed collection on rooftops, but present electricity grid does not easily integrate distributed source model for electricity delivery; improved storage methods needed; significant potential for improvement; clouds reduce efficiency; must be kept clean to maximize collection efficiency; solar-thermal required large area of dedicated solar arrays; solar thermal installations are reportedly hard on wildlife.

Geothermal

No carbon combustion greenhouse gases; limited suitable locations; installations reported to have average 5-year lifetimes; naturally occurring radioactive materials may be released, corrosive fluids extracted/created.

Ocean Thermal/Wave Energy

Largely experimental; only possible near the coast; ocean water is corrosive.

Projected Cost of Power in 2018

In 2013, the Wall Street Journal published a report based on information from the U.S. Energy Information Adminstration projecting the relative costs of bringing a megawatt-hour of electricity on line by 2018 (Table 6). The analysis was broken down by the comparative cost of fuel/operation and construction. The highest overall cost was $262 for solar thermal installations and $222 for offshore windmills, 80-90% of the cost in each case represented by construction. The third and fourth most expensive options were solar photovoltaic and coal with carbon capture. Coming in at $100 or less were advanced combined cycle natural gas, onshore wind, geothermal, hydroelectric, and conventional coal. Advanced Combustion turbine gas, advanced nuclear and biomass were projected at $100-110. The less that 10% difference between conventional coal and advancd nuclear is particularly revealing.

Table 6. Projected cost of bringing a megawatt hour of electricity on line by 2018 (2011 dollars). Data from Reference (*13*).

Power plant type	*Construction*	*Fuel and operations*	*Total*
Natural gas (Advanced combined cycle)	17	48	66
Wind	70	16	87
Geothermal	76	13	90
Hydroelectric	78	12	90
Conventional coal	66	34	100
Natural gas (Advanced combustion turbine)	30	74	104
Advanced nuclear (GenII+)	83	25	108
Biomass	53	58	111
Advanced coal (with carbon capture)	88	47	136
Solar photovoltaic	130	14	144
Offshore wind	193	28	222
Solar (thermal)	214	47	262

Essential Features of Nuclear Fission-Based Electricity

The world of physical science has made undeniable progress during the past century. Arguably, this surge in knowledge began with the discovery (by Marie and

Pierre Curie and Henri Becquerel) of naturally-occurring radiation and radioactive elements. The spread and expansion of their knowledge combined with the energy-matter insights of Albert Einstein ($E=mc^2$) ultimately drove others to probe the nuclear mysteries of the universe. This quest ultimately led to the development of nuclear energy science and technology including the most destructive weapons ever conceived and a new method of producing power without carbon combustion. In the ongoing discourse on the future of energy production/consumption for a resource-constrained and ecologically-challenged planet, it is often clear that even the scientifically literate public is significantly "underinformed" on the subject of nuclear science and technology. To articulate the case for nuclear fission as a sustainable approach to future energy needs, it is thus appropriate to try to increase the general level of illumination on the subject.

Globally, more than 430 land-based reactors (most of a light water moderation design) produce about 9% of the planet's power. More than 200 nuclear fission powered ships regularly ply the open sea, above and below the surface. On top of this, there are approximately 70 new land based reactors under construction globally, again mostly light water reactors. In China, 24 reactors are in operation providing about 2% of China's power consumption with 25 additional reactors under construction. The current U.S. power reactor fleet includes 32 boiling water reactors and 68 pressurized water reactors. The average age of the U.S. reactor fleet is 32 years; the global average is 25 years. Many U.S. reactors are seeking license extensions to 60 years, but in the past few years five fully functional reactors have been retired from service with more than ten years of authorization to continue operations still on the clock. Most of these early closures were caused by price competitiveness issues arising from energy pricing market factors and government subsidies of competing energy technologies. As has been noted above, significant improvements in availability of U.S.-based reactors have been made (90% fleet average capacity) during the past 20 years. Since 2001, nuclear power plants have achieved lower power production costs than coal, natural gas, and oil.

The Nuclear Fuel Cycle

As currently configured, the nuclear energy fuel cycle is based on uranium as the primary fuel (*14*). The natural abundance of uranium isotopes in the extracted ore is (on average) 99.27% ^{238}U, 0.72% ^{235}U, with a trace of ^{234}U. A nucleus of the ^{235}U fraction will undergo nuclear fission about 80% of the time when it captures a very low kinetic energy (thermalized) neutron; the other 20% of the time it becomes ^{236}U. In contrast, a ^{238}U nucleus does not undergo fission to an appreciable extent when it captures a thermal neutron, instead it becomes ^{239}U; high kinetic energy (fast) neutrons will induce fission of ^{238}U. In conventional reactors, the ^{239}U product nucleus undergoes in relatively rapid succession two β^- decay events to produce ^{239}Pu ($t_{1/2}$ = 24,100 yr.). When ^{239}Pu captures a thermal neutron in a reactor core it undergoes nuclear fission about 75% of the time. These fission reactions of ^{235}U and ^{239}Pu account for most of the energy produced in a nuclear reactor via the conversion of mass into energy ($E=mc^2$). The nuclear fission reaction occurs via about 200 reaction channels to produce measurable amounts of all elements between zinc and erbium, i.e., fission products, and 2-3 excess neutrons per event. These excess neutrons collide with other ^{235}U or ^{239}Pu nuclei to cause further fission reactions resulting in a controlled nuclear chain reaction. The release of the fission energy to the surrounding water heats the water to produce steam which drives a generator to produce the electricity that turns on the lights. Unfortunately, some of these fission products compete for neutrons with U and Pu requiring that about every 18-24 months 1/3 of the reactor "core" must be replaced to make certain that reactor operations remain stable. The fuel elements are secured in a zirconium alloy "can" to minimize the release of fission products and actinides to the reactor coolant pool.

Unfortunately, the 0.72% of ^{235}U that comes out of the ground does not contain enough of this isotope to sustain a nuclear chain reaction in a H_2O cooled and moderated reactor. Natural uranium must undergo isotopic enrichment of ^{235}U to the 3-5% range to establish viable chain reaction conditions in light water reactors. Heavy water reactors, cooled and moderated by D_2O (used primarily in Canada), can sustain a nuclear chain reaction with natural uranium, but generally use slightly enriched (1% ^{235}U) fuel. Uranium isotope enrichment is readily accomplished by several methods based on the easily volatilized compound UF_6. Following isotope enrichment the fuel is converted from UF_6 to UO_2, then the UO_2 pressed into a pellet, canned in zircalloy and stacked in a fuel assembly for insertion into the reactor. As the fuel ages, the 95-97% of ^{238}U present in the fuel produces sufficient ^{239,241}Pu that can favorably impact the energy potential of the fuel.

Open Fuel Cycles

The U.S. nuclear fuel cycle is operated without any recycling of the fuel, the so–called open or single-pass fuel cycle. In this fuel cycle model, uranium fuel rods are resident in the reactor for 18-24 months after which time they are removed and transferred to water-basin fuel storage pools for extended cooling and decay of radioactive byproducts. After some specified time in the storage pool, the fuel rods can be shifted to concrete dry-storage casks for additional cooling and decay. The ultimate pathway in the current (pending) disposal method is based on the direct emplacement of used fuel rod assemblies into a mined geologic repository. After an additional period of cooling in the repository, the underground "drifts" would be backfilled and sealed. There are three principle deficiencies in this model: (1) without recycle of U/Pu less than 1% of the energy potential of the fuel is utilized, (2) the direct-disposed fuel represents a potential U/Pu mine that could be exploited to create nuclear weapons some centuries post deposition, and (3) conservative repository models would require confinement of long-lived actinide elements within the repository boundaries for more than 250,000 years, a feasible outcome, but one difficult to ensure with an acceptable probabililty of success.

A representative composition of fuel exiting a light water reactor at 18 months is about 94% ^{238}U, slightly less than 1% each of ^{235}U and plutonium isotopes (^{238,239,240,241,242}Pu), about 3.5% by mass mixed fission products, and 0.1-0.2% "minor actinides" (Np, Am, Cm). Initially the radiation dose is dominated by the mixed fission products, after a few years dominated by ^{90}Sr and ^{137}Cs. For direct-disposed fuel, nearly a kilogram per ton of ^{241}Am grows in from decaying

^{241}Pu at such a rate as to dominate the dose from about 20 years after discharge to several thousand. Beyond this period, the 24,000 year ^{239}Pu and 2.1×10^6 year ^{237}Np are the most important contributors to dose from used fuel.

Closed Fuel Cycles

Some countries, most notably France, have committed to a single pass recycling option for their commercial nuclear power reactor operations. In the French system (practiced in a similar fashion by the UK, Japan, and Russia), the PUREX process (Plutonium Uranium Redox EXtraction) process is employed to partition dissolved reactor fuel into three fractions 1) uranium (the bulk of the fuel mass), 2) plutonium (about 1% of the fuel mass), and 3) fission products and minor actinides. Fraction 1 is stored for future use (it is effectively slightly enriched in ^{235}U relative to natural U, so could be re-enriched to 3-5% ^{235}U). Fraction 2 is combined with depleted uranium from isotope enrichment to manufacture mixed (Pu-U) oxide fuel (MOX) for recycle in light water reactors. Fraction 3 is vitrified for eventual geologic disposal as waste. This single pass recycling strategy recovers as much as 2% of the energy value of the fuel and reduces the volume of waste going to a repository by a factor of 5-6. The use of PUREX chemistry for this application is controversial in the U.S., as most of the weapons grade plutonium in the combined global arsenals of nuclear weapons was obtained by application of this chemistry; the concern is that separated plutonium could be diverted to weapons of mass destruction.

A more advanced option for operating the nuclear fuel cycle (not currently in operation anywhere in the world) is a fully closed fuel cycle based on repetitive recycling in which some version of PUREX chemistry (or an alternative process) is used to capture for recycle as fuel for fast-spectrum reactors, U, Np, and Pu. This initial separation is complemented by a separate process that enables fast reactor transmutation of Am and Cm. Using fast reactors (more energetic neutrons) can induce fission in ^{238}U, which constitutes the bulk of used fuel. Previous studies of liquid sodium cooled reactors have established that such reactors can be used to both fission ^{238}U and to convert more ^{238}U to ^{239}Pu, which can be transmuted in light water reactors. Sodium cooled fast reactors can be configured to “breed” plutonium, creating more fuel than is burned. Various options for operating such fuel cycles are under investigation.

Fuel Inventory

It has been estimated that known supplies of terrestrial uranium could fuel the current light water reactors for 100-200 years at current use patterns. Full development of fast reactors and full recycle (including the more than 300,000 tons of used fuel in storage) could extend this potential to several thousand years. In the 1960s and 70s, similar fuel cycles based on breeding ^{233}U from natural ^{232}Th were demonstrated. Recently, concerns about providing adequate power to a resource-strained planet has revived interest in this option as well. Terrestrial reserves of thorium are estimated at 3-4 times that of uranium; the largest fraction of uranium is found naturally occurring (about 3 ppb) in ocean water. As thorium isotopes fission only with low efficiency even in fast spectrum reactors, the Th-U reactor concept required the breeding of fissionable material and chemical reprocessing for fissile material recycling.

The Chemistry of Used Nuclear Fuel Recycling

Cumulative understanding of the basic chemistry of conventional reprocessing benefits from a considerable experience gained during many decades of aqueous-based reprocessing for Pu production and used fuel reprocessing. Irradiated fuel is a complex mix of fissionable actinides and fission products representing every group in the periodic table. The best known fuel matrix is a UO_2 ceramic, though metallic, carbide, and nitride fuels have also been investigated. After some years of cooling post discharge from the reactor, the fuel remains moderately radioactive and thermally hot. Conventional aqueous reprocessing begins with oxidative dissolution of the used fuel matrix in 6-8 M HNO_3. Gaseous fission products released from the fuel matrix on fuel dissolution include Xe, Kr, I. The most problematic high yield fission products are (based on their persistent radioactivity) ^{90}Sr, ^{137,135,134}Cs, ^{99}Tc, ^{131}I, and (based on their neutron capture efficiency) the light lanthanides. Actinide recycle is not possible without removal of the strongly neutron absorbing isotopes of Nd, Pm, Sm, Eu, and Gd. The separation of these lanthanides from U, Np, and Pu is readily accomplished using PUREX-like chemistry. The separation of Am and Cm from the lanthandes is more difficult, but possible. Fast reactor fuel concepts can at some level bypass some of these challenges through the use of pyro/electrometallurgical separations.

Nuclear Fuel Security

The remaining fissile material content of used nuclear fuel after discharge from the reactor has always been a concern in the operation of reprocessing systems. The decades of experience in PUREX chemistry and its comparative simplicity establish clearly that synthesis and purification of weapons-usable plutonium is within the grasp of those willing to create suitable facilities or to absorb the considerable radiation dose associated with such chemical processing. The single pass, open fuel cycle concept for nuclear fuel disposal was developed based on the premise that the penetrating radiation dose from the fission products and actinides would constitute a lethal bio-shield to prevent diversion of fissile materials. However, in time this radiation intensity diminishes and the dose-absorption protection effect is seen to be a less dependable deterrent. Concerns about such a diversion of used nuclear fuel to nuclear weapons has gained credence since 9/11/2001. A considerable global research effort aimed at prevention and detection of such a diversion has developed during the past decade. Advocates of a fully closed nuclear fuel cycle have argued that keeping actinides in such a fuel cycle indefinitely significantly reduces the probability of any diversion to weapons of mass destruction.

Geologic Disposal

No matter what approach is taken to the operation of nuclear fuel cycles, there is a global consensus that the final resting place for the radioactive byproducts of fission should be an engineered geologic repository. Research on repository characterization has been carried out in many countries considering different options of crystalline, sedimentary, and volcanic rock formations. Very detailed modeling has been developed to predict migration tendencies from many different repository systems. There is a general agreement that the most important isotopes for intact fuel are those of the long-lived isotopes of Pu, ^{237}Np, ^{99}Tc, ^{131}I, that water intrusion and flow into and away from a repository should be minimized, and that reducing conditions are likely to produce the most stable repository environment. It is also agreed that probabilistic risk assessment can give reasonable long term estimates of repository performance, with the cautionary note that some cosmic/geologic/climatologic events are less predictable. With a degree of confidence, most active repository research indicates a high probability of successful isolation for an adequate length of time; of course, future projections carry by definition an element of uncertainty.

Conclusions

With more than 15,000 reactor-years of experience accumulated globally and about 70 new reactors under construction, it is clear that fission-based electricity will continue to be an important component of the global energy mix at least for the remainder of the 21st century. It is also quite clear that with a global population likely to be at or above 9 billion by 2050, demand for more energy to increase the general quality of life will increase. Concerns about the potential impact of CO_2-induced climate change on that quality of life will remain an important question (or potentially become a well-established fact as the polar ice caps melt) through the century. The larger challenge may well be developing acceptable alternatives to the 85% fossil carbon derived energy inventory should the global climate debate be “settled.” Considering the scientific contrarian view that human activities do not impact climate, it is still important to consider all options for primary power production in the future; perhaps emphasizing those that allow for a reduction in fossil carbon use would be the prudent course.

Nuclear power utilization is increasing globally (most notably in China, where large-scale coal consumption has negatively impacted urban air quality while contributing a significant new source of CO_2 emissions to the global inventory). The means to improve utilization of nuclear fisson-based electricity is at hand, but requires continued advancement toward third and fourth generation reactors, closed nuclear fuel cycles, and improved waste management options. Heightened awareness of the potential danger of nuclear weapons enhances a sense of vigilance in future planning; a fuel cycle based on continuous recycle of actinides arguably offers the most permanent solution to the danger of weapons proliferation. With the fundamental science of nuclear fission based energy comes the challenge of operating complex machines based on highly energetic reactions that occur at a very rapid rate. Such science and technology demands a highly qualified and specialized workforce, including a new generation of dedicated innovators to drive the technology to higher functionality levels. A key component of nuclear fission based power that has not been “credited” in the foregoing discourse is its position as the only energy-from-“combustion” technology that captures all of its combustion residues for controlled disposal.

The balance sheet for fission based power can be summarized in a few sentences. Having accumulated substantial experience in the operation of fission reactors and achieved an average 90% capacity factor (in the United States), it is clear that nuclear fuel cycles based on low-enriched uranium in first and second generation light water (or D_2O) moderated reactors are commercially viable. The three reactor accidents that have occurred were each sobering reminders that nuclear fission is a demanding technology that requires vigilance, wise decision-making, carefully considered engineering design, periodic modernization, and continued research for better approaches. This near-zero CO_2 emission technology employs a comparatively inexpensive fuel (that has no other useful applications) and an underutilized potential that combined represent a component of our present energy balance too important to ignore (or to eliminate). The final component needed is that of education of the general public on the subject of the relative risk of human activities and natural occurrences.

For additional information, the following general references on the subject of nuclear energy and the environment are suggested:

The Making of the Atomic Bomb, Richard Rhodes, Simon and Schuster, New York, 1986.

Power Hungry: The myths of “green” energy and the real fuels of the future, Robert Bryce, Public Affairs, New York, 2010.

Megawatts and Megatons: A turning point in the nuclear age? Richard L. Garwin, Georges Charpak, Alfred Knopf, New York, 2001.

Atomic Awakening: A new look at the history and future of nuclear power, James Mahaffey, Pegasus Books, New York, 2009.

Energy and the Environment, Robert A. Ristinen, Jack J. Kraushaar, John Wiley and Sons, New York, 1999.

Radiochemistry and Nuclear Chemistry, G. R. Choppin, J. O. Liljenzin, J. Rydberg, Butterworth-Heineman, Woburn, MA, 2002.

References

1. The Ozone Hole Inc. (an organization dedicated to protecting the ozone layer, the climate and Earth’s environment). http://www.theozonehole.com/ozoneholehistory.htm. Accessed 3/13/15.
2. CO2Now.org. http://co2now.org/current-co2/co2-now/annual-co2.html. Accessed 3/12/15.
3. U.S. Energy Information Adminstration Monthly Energy Review for April 2013. http://www.eia.gov/totalenergy/data/monthly/previous.cfm. Accessed 5/15/15.

4. Generation I nuclear reactors were the prototype experimental reactors on which commercial power reactors are based; Generation II and II+ reactors are the first power production reactors and reactors with upgraded safety systems; Generation III and III+ reactors are modern designs of light water reactors featuring advanced safety systems and increased efficiency; Generation IV reactors are radically different reactor concepts (e.g., molten salt reactors, gas cooled/graphite moderated reactors, liquid metal cooled fast reactors) in development for future applications of fission-based power.
5. World Resources Institute (WRI). *Climate Analysis Indicators Tool (CAIT): Indicators: GHG Emissions: Cumulative Emissions*; Washington, DC, U.S.A., 2011. WRI, http://cait.wri.org/cait.php (free registration required). Accessed 3/12/15
6. International Energy Agency (IEA). *CO_2 Emissions From Fuel Combustion: Highlights (2011 edition)*; Excel spreadsheet (XLS); Paris, France, 2011. IEA, http://www.iea.org/co2highlights/CO2highlights.xls. Accessed 3/15/15.
7. Intergovernmental Panel on Climate Change. IPCC Special Report on Renewable Energy Resources and Climate Change Mitigation. https://www.ipcc.ch/publications_and_data/publications_and_data_reports.shtml @ https://www.ipcc.ch/report/srren/. Accessed 3/15/15.
8. Intergovernmental Panel on Climate Change. IPCC Special Report on Renewable Energy Resources and Climate Change Mitigation; 2011. http://srren.ipcc-wg3.de/report/IPCC_SRREN_Annex_II.pdf. Accessed 4/10/15. See page 10 Moomaw, W.; Burgherr, P.; Heath, G.; Lenzen, M.; Nyboer, J.; Verbruggen; A. Annex II: Methodology.
9. Nuclear Energy Institute. http://www.nei.org/Knowledge-Center/Nuclear-Statistics/US-Nuclear-Power-Plants/US-Nuclear-Capacity-Factors. Accessed 5/5/15.
10. Nuclear Energy Institute: U.S. Capacity Factors by fuel type; 2014 http://www.nei.org/Knowledge-Center/Nuclear-Statistics/US-Nuclear-Power-Plants/US-Capacity-Factors-by-Fuel-Type.
11. Lawrence Livermore National Laboratory Estimated US Energy Usage graphics https://flowcharts.llnl.gov/.
12. Earth 3.0: A Second Look at Nuclear. *Scientific American*; Special Issue, December, 2008.
13. U.S. Energy Information Administration/Wall Street Journal, 2013.https://www.pinterest.com/pin/98023729362592414/. Accessed 8/4/15.
14. Settle, F. A. Uranium to Electricity: The Chemistry of the Nuclear Fuel Cycle. *J. Chem. Educ*. **2009**, *86*, 316–323.

Chapter 12

Maintaining a Sustainable Scholarly Record

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The increase in published chemical information since the late 1940s has been enormous, approaching exponential rates, but neither the amount of time that chemists have to read the literature nor the budgets of libraries for acquiring it have increased proportionally, resulting in a system of scholarly communication that is fast becoming unsustainable. In order to succeed, the scholarly record must exist, be accessible, and be able to be preserved for the future; the digital medium has made some of these tasks easier and others more challenging. This paper takes a broad-level look at the work done by the chemical information community, which produces the primary literature as well as tools to help chemists locate and use it effectively. We focus on the sustainability issues surrounding the production and use of the literature, particularly initiatives in electronic publishing, good data practices, advances in end-user-enabled searching, and necessary considerations when preserving digital data.

Introduction

The words "sustainability in chemistry" conjure up many images. Men and women in lab coats labor to devise and produce new materials and fuels to conserve our natural resources. They run reactions with extremely high atom economy under conditions that minimize environmental impact. They attempt to bring our carbon emissions, a cause of global climate change, under control and to make healthy food, clean water, and necessary medications available to all who need them.

In Teaching and Learning about Sustainability; Levy, et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 2015.

Other images, however, are *not* evoked by the words “sustainability in chemistry.” A librarian works in her office, flipping through the occasional printed book as her fingers fly across the keys of her computer keyboard, pausing here and there to check her phone or her tablet. A publisher’s scientific advisory board meets with its upper-level management to discuss future directions of their portfolio of journals. Representatives of a major database provider visit bench scientists at a client company, and the resulting discussion of their workflow informs the design of a new tool that streamlines their literature searches and lets them find more material more quickly. Yet these activities are just as important to the sustainable practice of chemistry as efficient, green reactions. A descriptive, well-organized, and accessible body of literature connects current chemists with past research findings, enabling them to benefit from the labor of others. Experiments have a greater chance of success when they are based on past practice, making for a safer laboratory environment, more efficient methods, and less waste. Having seamless and easy access to the literature means less time spent developing routine protocols and more time devoted to making breakthroughs of one’s own, and the chemical information providers and practitioners, the librarians, publishers, vendors, and informaticians, both produce the literature and make sure that it is available at the point of need.

Chemical information, in its most general sense, consists of the primary, secondary, and tertiary publications produced by chemists and information professionals in order to record and access previous advances in the field of chemistry. The job of this literature is twofold: to keep scientists up-to-date on happenings in their fields of research and to save them time by allowing them to build upon the work of others, rather than repeating it. Primary research is published in journals, dissertations, and occasionally in conference proceedings; this literature is organized and made accessible by secondary search tools and is summarized and critiqued in tertiary review articles, monographs (books on a single subject), and large encyclopedic works. The chemical information community consists of all individuals who produce, mine, and provide access to the chemical literature, including (but not limited to) publishers and vendors, informatics researchers, and librarians. The literature succeeds in its job when chemical information professionals and informaticians ensure that the following things happen:

- The scholarly record exists in a useable form.
- Researchers are able to access relevant results in a timely and efficient manner.
- The scholarly record endures.

Nobody would argue that the chemical literature helps scientists communicate with one another to build sustainable research practices. Chemical information is having issues of sustainability itself, however. The increased pace of research, coupled with the many outlets for scientific communication, make it challenging for chemists to remain up-to-date in their fields. We will examine the sustainability issues related to the explosion of chemical literature that began in the mid-twentieth century and begin to discuss the ways in which the chemical information community is addressing these issues to create and maintain a sustainable scholarly record.

The Sustainability Crisis in Scholarly Communication

Long ago, the scholarly meeting was the primary venue for scientists to share information. As the number of scientists grew, not all members were able to attend the meetings, so the societies began producing proceedings documents to distribute to their members, describing what had happened during the meeting. These proceedings evolved into scholarly journals, which now have become the dominant form of communication between scientists and the official vehicle for the scholarly record. The key players in this stage of chemical information are the researchers themselves, who produce the results reported in the literature, and the primary publishers, whose job is to disseminate these results to others.

Sustainability Issues Surrounding the Publication of the Primary Literature

Complications of Interdisciplinary Science and the Proliferation of New Journals

Researchers are responsible for accurately reporting their results, following an established code of ethics, and publishing their findings in a timely manner and in a location that makes sense. This used to be much easier when research areas fell into clear silos. For example, a paper dealt with inorganic chemistry, or it dealt with medicine. Now, however, a research team consisting of materials chemists, synthetic chemists, and medicinal researchers produces a series of papers describing therapeutic methods that rely on organic cages to deliver inorganic nanoparticles to cancer cells. It is much more difficult to choose an appropriate journal for publication, since the study could conceivably interest medical science researchers, organic chemists, inorganic chemists, biochemists, or materials chemists. Increasing trends towards research in this area, indicated by the publication of many similar studies, suggest to a primary publisher that the research community “clearly needs” a journal devoted to this topic, so the publisher creates one, thus presenting researchers with a venue for publishing their research. However, this action also means there is an additional journal of which researchers, who were having enough trouble staying up-to-date with the 20 or so core journals in their fields, must be aware. In addition, purchasing a license to this new journal places an additional burden on library budgets that are already strained to the maximum trying to afford the journals already in existence. Chemistry journals have had the dubious distincition of having the highest average price for some years now; in 2015, they sported an average price per title of $4,871 (*1*). This is a 15.6% increase over last year’s average price of $4215 (*2*), and it is 12.2% higher than the averate price of journals in physics, the next most costly discipline (*1*).

Speed of the Publication Cycle Can Lead to Information Overload

Technological changes resulting in increased speed of research also have resulted in changes to the way in which information is published. Researchers are judged based on the number and quality of papers that they produce; the rise of the h-index in academia is indicative of this. This metric ranks a researcher's publications in order from 1 to *n*, with 1 being the most cited and *n* being the least cited, and graphs the numeric rank of each document against the number of times that it has been cited. The researcher's h-index is the point *h* at which that graph crosses the line x=y; in other words, the researcher has *h* papers that have been cited at least *h* times (*3*).

The correlation between metrics like h-index and academic reputation provides a scientist with incentive to produce a large number of high-quality papers quickly. Because it is the job of the primary publishers to disseminate the researchers' results, journal publishers are trying to publish as many of these papers as possible. These trends in publication practices are clearly illustrated by looking at data from *Chemical Abstracts* over the course of the time that it has been indexing the chemical literature.

If you examine the number of abstracts added to *Chemical Abstracts* between its inception in 1907 and the year 1947, you will see a general upward trend, with dips in publications during the periods of the two World Wars (Figure 1).

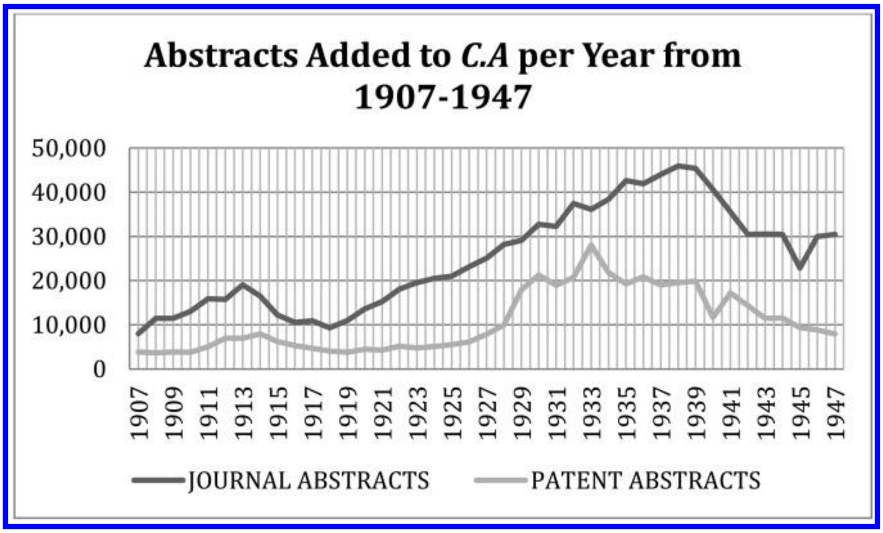

Figure 1. Number of abstracts added to Chemical Abstracts each year, between 1907 and 1947. Data used with permission of CAS, a division of the American Chemical Society (2).

If, however, you add the data from 1948 to 2014, you see some very different and startling trends, particularly in the publication of journal articles and most markedly in the past twenty years. Beginning in the 1960s, the rate of publication has increased so much that the earlier growth looks almost flat by comparison (Figure 2).

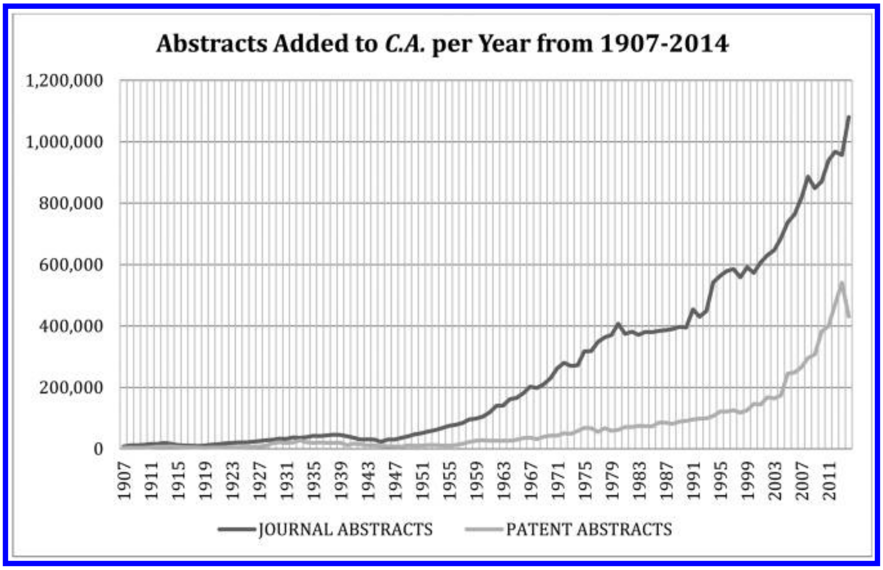

Figure 2. Number of abstracts added to Chemical Abstracts each year, between 1907 and 2014. Data used with permission of CAS, a division of the American Chemical Society (4).

In fact, if you look at the total number of publications in the *Chemical Abstracts* database each year since its inception, you will find that the growth in size of the database is almost exponential. While a chemist searching *Chemical Abstracts* in 1994 would have had to contend with 15,320,394 references, a scientist searching the literature in the beginning of 2015 was wading through over 35,203,797 references, an increase of more than double (*4*) (Figure 3)!

The number of small molecules registered per year shows a similar trend. If one observes the size of the CAS Registry from its inception in 1965 through the end of 2014, one will note that the number of substances has increased exponentially, and, in fact, shows a steeper slope than the exponential curve (Figure 4). In a scant 50 years, the Registry has grown in size from 211,934 small molecules to almost 89 million. In fact, 10,747,330 substances were *added* to the Registry in 2014, 171,459 more than had existed in the *entire* Registry in 1990 (*5*).

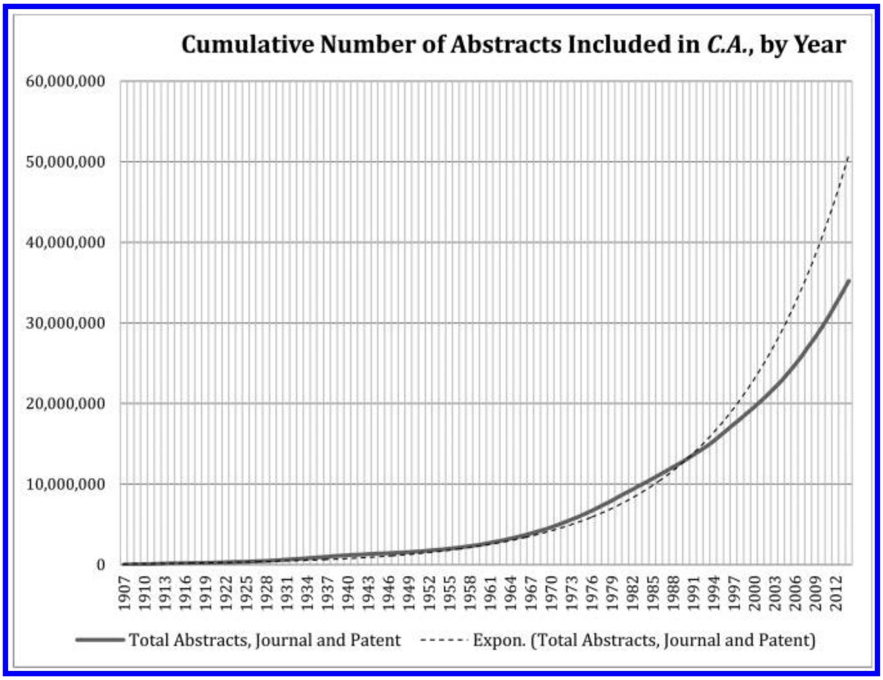

Figure 3. Total number of abstracts of any type that were included in Chemical Abstracts each year since its inception graphed against the exponential curve for the dataset. Data used with permission of CAS, a division of the American Chemical Society (4).

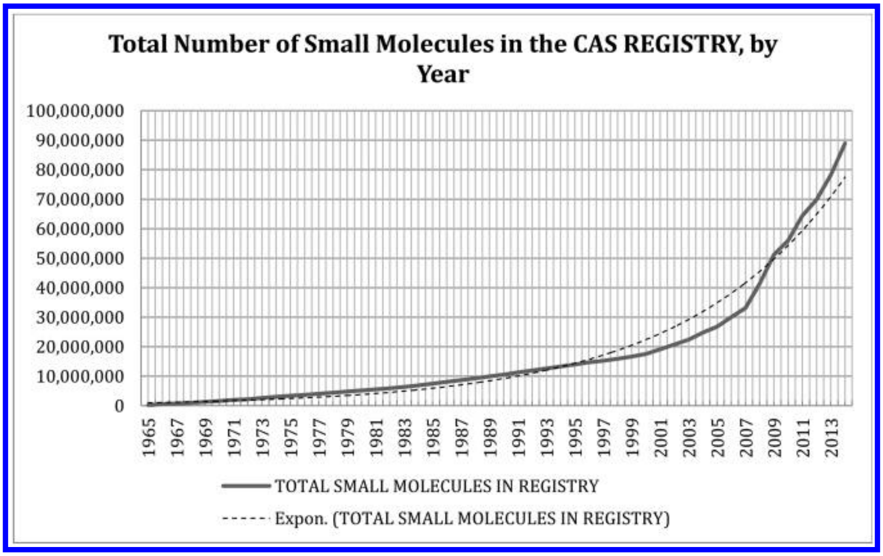

Figure 4. Cumulative number of small molecules in the CAS Registry each year, from 1965 through 2014. Data used with permission of CAS, a division of the American Chemical Society (5).

This introduces the first sustainability problem relevant to chemical information: chemists today have more than twice as many documents available to read as they had in 1994, but they have the same amount time available for reading, and they are not capable of reading twice as quickly. As a result, it is essential that a chemist develops good search strategies to become aware of those papers that are most relevant to their current research program, as well as developing good techniques to evaluate the relevance and reliability of the work retrieved.

The quick timeline for publication, however, causes other problems in creating a sustainable and reliable scholarly record. Ethical issues, such as plagiarism, falsification, and fabrication, can result from the pressure to publish quickly, as can sloppy or incompletely described science. It is frequently very difficult to distinguish ethical breaches from science that has been published prematurely, but the end result is the same in either case: the science is difficult or impossible to reproduce. While the peer review process should remove many of these problematic publications, the need to publish on a short timescale has resulted in major publishers giving busy reviewers a scant 14 days to review a publication, and while most reviewers attempt to do thorough and complete reviews, they also are researchers and frequently teachers, and 14 days may not be sufficient time to do the job well.

Considerations When Taking and Reporting Data

Scientific data have been the subject of much discussion in the chemical information community, ever since the NSF began requiring data management plans as part of their grant application process (*6*). This is a logical extension of the greater "transparency" permitted by digital media; researchers can more easily share data with and reuse data from their peers. This is a good thing from a sustainability perspective, since it allows other researchers to capitalize on the time and money spent taking the data, allowing them to be more efficient and ultimately allowing more science to be done in a shorter time period. Every good thing, however, comes with some drawbacks, and the historic workflows of scientists, as well as the limitations of digital media, present challenges to true reusability of data.

Modified Workflows for Taking Data Are Required

To make their data available and understandable to scientists outside of their specific research project or group, researchers may need to modify their workflows and conventions for taking and reporting the data. When taking data, a chemist must first ensure that they are reproducible and then must provide documentation, annotations, or metadata for the purposes of validation. This can be information about the way in which an experiment was designed, the model and type of instrument used to gather the data, and any conditions that are relevant to the outcome of the experiment. Ideally, the collected data should next undergo some sort of critical validation step. This validation can vary from peer review of a journal article to repetition of the process in another laboratory, as is done with methods published in *Organic Syntheses*, for example (*7*). While external validation is not always possible, it is helpful to have a peer scientist look critically at all published data to make sure that they "make sense."

Conventions for Reporting Data Can Differ from Conventions for Recording Data

When reporting data in a publication, a scientist has a set of considerations that are subtly different from those on which he or she focuses when recording the data during the experimental phase of the project. During the experimental phase, the scientist annotates the data with an eye towards reproducibility; in the publication phase, on the other hand, the data should be annotated for the purpose of discoverability and reuse. In addition to giving a sense of the conditions under which the data were taken, these annotations must clearly articulate the *context* in which the data were taken, carefully attribute any "once removed" data (data reused from another scientist's work) presented, and generally aid a researcher in determining whether or not they will be useful for his or her purposes (*8*).

Producing a Usable Scholarly Record

Advances in Electronic Publishing Make Reading and Writing More Efficient

Since the overall pace of research has increased, the timeline to publication of results needs to decrease accordingly, and electronic publishing initiatives like electronic submission and review have increased the speed of the overall publication process, as well as the speed with which published papers can be disseminated to the general public. In the early 2000s, publishers began to post "pre-paginated" articles on their Web sites. These articles had been through the review and editing process, had been marked up for publication, and were simply awaiting placement in an issue. Different publishers called these documents by different names, among them "As Soon as Publishable", "Advance Articles", and "E-view". Now, results are available even more quickly, with some journals posting "just-accepted" articles as soon as they have been accepted by an editor but before they have been laid out for final publication. Secondary indexing and abstracting services have begun monitoring these pre-paginated and just-accepted articles, including them in their databases, and making them more accessible to scientists.

In addition to making research results available more quickly, many primary publishers have made attempts to streamline the reading process so that researchers can review articles more quickly and maximize the amount of information they consume in the limited time they have available for reading. One of the first of these attempts was the Royal Society of Chemistry's Project Prospect, launched in 2007 that used a combination of semantic programs and manual curation to extract and hyperlink chemicals' names and chemical and biological terminology, using a set ontology, from the text of an article (*9*). This allowed articles to be linked to one another, via pages defining the ontology terms or identifying the substances. The RSC has gradually switched over from the full "Prospecting" of journal articles to automated substance searching through the papers and inserting compound links into ChemSpider, with some additional features available for *MedChemComm* readers, including the ability to directly download structures and QSAR tables (*10*).

In 2009, Elsevier began a project that it called "Article of the Future," using information gained from focus groups and scientist interviews to completely overhaul the presentation of their scientific articles in 2011 and 2012 (*11*). The chemistry "Article of the Future" places the main text of the article in the large central pane of the html version and includes a left sidebar with a hot-linked outline of the article and thumbnails of the figures for easy reference. Readers can click on a section header or figure on the left, and the central pane will zoom to that part of the text. The right sidebar contains "related information," with links to other articles on a similar topic, recommended articles, articles that are known to cite this one, and related book content. In addition, if an author has deposited the underlying data in an external repository and published this information, a link to the repository publisher appears in the right panel (Figure 5).

Many publishers, including the American Chemical Society, choose to include certain reader tools in the entry pages to their journal articles. From the entry page of an article, one can select the type of view (html, pdf, enhanced pdf, etc.) that one wishes of the article, easily link to the supporting information, obtain permission to reuse content, and download the citation to the reference management system of choice. A recent partnership between ACS Publications and Chemical Abstracts Service has led to embedded SciFinder links at the article level of ACS journal articles (Figure 6). Subscribers to SciFinder can click on these links to launch SciFinder searches that retrieve substances or reactions referenced in the publication, cited or citing references, or even other works by the same author. This has the advantage of linking readers to related content from a broad variety of primary publishers without performing manual searches.

Bioorganic & Medicinal Chemistry

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Emerging Approaches for the Design and Synthesis of Innovative Small Molecule Libraries

Stereoselective synthesis of a natural product inspired tetrahydroindolo[2,3-*a*]-quinolizine compound library

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Abstract

A natural product-inspired synthesis of a compound collection embodying the tetrahydroindolo[2,3-*a*]quinolizine scaffold was established with a five step synthesis route. An imino-Diels–Alder reaction between Danishefsky's diene and the iminoesters derived from tryptamines was used as a key reaction. Reductive amination of the ketone function and amide synthesis with the carboxylic acid derived from the ethyl ester, were used to decorate the core scaffold. Thus a compound library of 530 tetrahydroindolo[2,3-*a*]quinolizines was generated and submitted to European lead factory consortium for various biological screenings.

Graphical abstract

Emerging Approaches for the Design and Synthesis of Innovative Small Molecule Libraries
Edited By Adam Nelson and Didier Roche

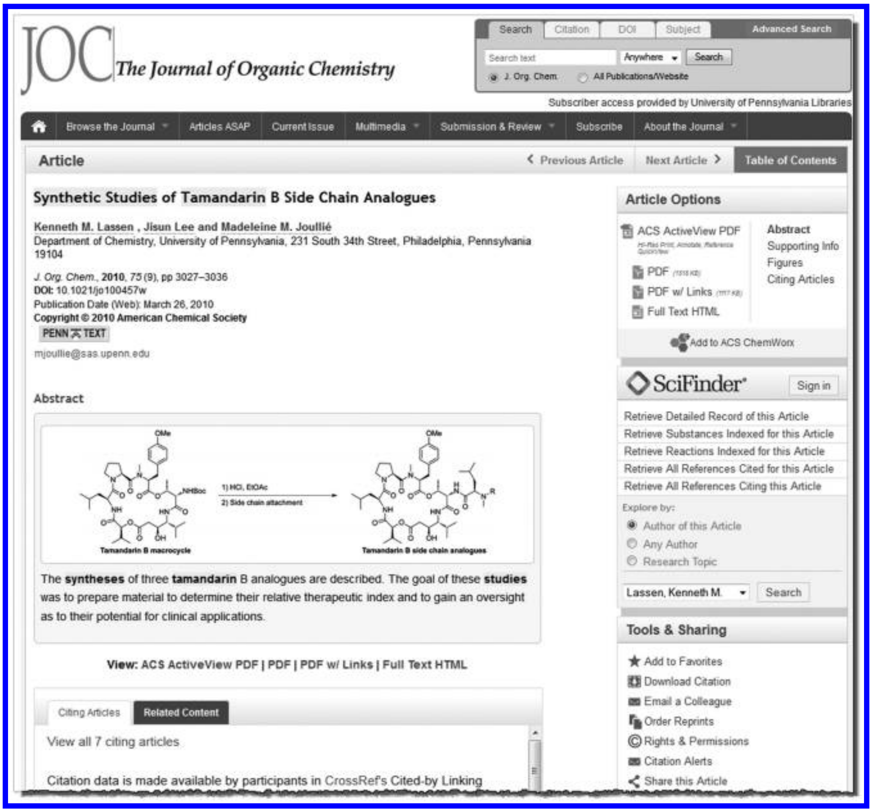
Innovative approaches to the design and synthesis ...
Adam NelsonDidier Roche

Combining two-directional synthesis and tandem re...
Thomas E. Storr, Sarah J. Cully, Michael J. Rawlin...

Design, synthesis and decoration of molecular scaf...
Philip Craven, Anthony Aimon, Mark Dow, Nicolas ...

Figure 5. Elsevier's Article of the Future. Note the hot-linked article outline and figures in the left sidebar, as well as the link to the Cambridge Crystallographic Data Centre, where crystallographic data have been deposited by the authors. Image reproduced with permission from Sankar M. G.; Mantilli L.; Bull J.; Giordanetto F.; Bauer J. O.; Strohmann C,; Waldmann H.; Kumar K. Bioorg. Med. Chem., 2015, 23, 2614. Copyright 2015 Reed Elsevier.

The main problem with many of these new approaches to reading is that, for the most part, they rely on use of the html version of the article. However, a straw poll of two major societal chemistry publishers indicates that between approximately 66% and 90% of chemists prefer to use the standard pdf versions of the articles, rather than html or marked-up pdf (*10*, *12*). Indeed, many scientists are still interested in marking up and filing their papers, and a number of companies have jumped at the opportunity to provide them with digital tools that emulate extremely print-based workflows. Tools like Mendeley (*13*), ACS ChemWorx (*14*), and even EndNote (*15*) have developed technology akin to a digital filing cabinet, allowing researchers to download pdfs of interesting articles directly from the journals' Web sites, file them in folders within the application, read them on screen, and annotate them using typed "sticky notes," highlighting, and even hand-written annotations. A wide variety of applications for tablet computers, including GoodReader® (*16*) and iAnnotate (*17*), also allow readers to use a stylus and hand-write annotations, highlight key passages, and type notes on expandable "sticky notes," although they do not come with built-in reference management capabilities.



Synthetic Studies of Tamandarin B Side Chain Analogues

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Abstract

The **syntheses** of three **tamandarin** B analogues are described. The goal of these **studies** was to prepare material to determine their relative therapeutic index and to gain an oversight as to their potential for clinical applications.

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Explore by:
● Author of this Article
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Lassen, Kenneth M. ▾ Search

Figure 6. The article-level view of an article from The Journal of Organic Chemistry. Note the different options available for viewing, linking to related content in SciFinder, and sharing the reference in the right sidebar. Reprinted with permission from J. Org. Chem., 2010, 75, 3027. Copyright 2010 American Chemical Society.

Providing Timely and Efficient Access to Relevant Literature

Relevant published results must be easily filtered from background noise. The information must be affordable to those who require it. Finally, internal data and results must be organized and easily accessible. The key groups that can improve access to the scholarly record are the secondary publishers and vendors, informatics specialists, and librarians, who all work tirelessly to help researchers answer the following questions.

- What is out there that is relevant to my needs?
- Which pieces of information are the most important?
- How can I access this information

In-House Discovery and Data Reuse

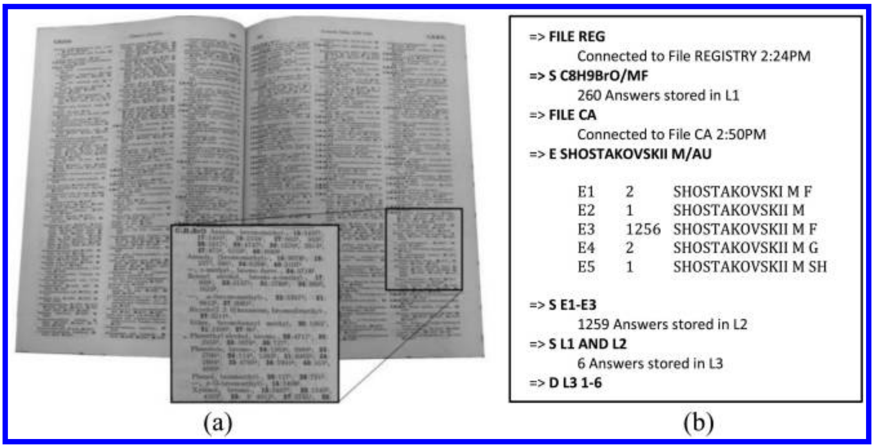
While the laboratory notebook itself is the most primary of all records of research, it turns out that electronic laboratory notebooks (ELNs) can actually serve a dual purpose and effectively "de-silo" the research process. In addition to providing a scientist with a location to record his or her laboratory experiences, ELNs can connect to internal inventory systems and external databases and journals. Researchers can export references from the primary literature to their lab notebook, and ELNs used at a departmental or enterprise level can be made searchable by individuals within the organization. This allows individuals in different groups or departments to discover and reuse relevant data taken by their colleagues, thus saving the organization time and money.

Chemical informatics researchers have been working with companies to construct and organize internal warehouses of data, as well as developing robust systems to query them (*18*). Not only does this also allow information obtained by one group within the company to be utilized by others, it helps members of the original group more easily retrieve past results. Academia has been slower to enter this arena; however, with the advent of the data archiving and sharing requirements of the NSF, NIH, and other funding agencies, academic institutions, particularly libraries and computing groups, are beginning both to create either public or private data repositories that allow researchers to comply with the mandates of their funding agencies.

End-User Searching Revolutionizes Chemical Information Retrieval

While usage statistics indicate that chemists prefer the format of their journal articles to be similar to historic print publications, the same cannot be said for their preferences when it comes to learning about and locating these articles. In the first half of the twentieth century, when scientists only had to contend with 3 to 4 million references in *Chemical Abstracts*, indexing and abstracting tools were provided in printed format. Using these tools was extremely time-consuming for a searcher, as we will see by following the progress of a searcher using *Chemical Abstracts* to attempt to locate all mentions of a specific substance (C_8H_9BrO) by a particular author (M. F. Shostakovskii).

Chemical Abstracts, at the time, was divided into two sections: the abstract volumes, which included the source information (authors, journal, volume, issue, pages, year) and the abstract of the article; and the index volumes, which consisted in part of a subject index (later a general subject index), a patent index, an author index, a formula index, a chemical substance index, and, after 1965, the Registry Handbook. In order to search for all articles in which Shostakovskii used a substance with the formula C_8H_9BrO, a searcher would need to use the formula index to locate all abstracts dealing with the substance in question (Figure 7a) and then use the author index to locate all abstracts by the author. He or she would then construct a final list, consisting of the abstract numbers that appeared on both previous lists, and then laboriously look up every abstract on that list in the appropriate abstract volume, read the abstracts, determine their relevance, and then retrieve the issues of the journals in which interesting article appeared. In order to identify all relevant articles, the chemist would need to repeat search the process for each ten-year period, as well as each single year after the last decennial index. Therefore, a searcher working in 1959 who wanted to perform a comprehensive search would need to repeat the aforementioned process multiple times, using all appropriate decennial indices to cover the literature from 1936, the year of Shostakovskii's first publication, until 1956, as well as two annual indices to cover the literature from 1957 and 1958. This was very time-consuming, but researchers at the time probably had much stronger arm muscles than today's chemists.



```
=> FILE REG
        Connected to File REGISTRY 2:24PM
=> S C8H9BrO/MF
        260 Answers stored in L1
=> FILE CA
        Connected to File CA 2:50PM
=> E SHOSTAKOVSKII M/AU

        E1    2      SHOSTAKOVSKI M F
        E2    1      SHOSTAKOVSKII M
        E3    1256   SHOSTAKOVSKII M F
        E4    2      SHOSTAKOVSKII M G
        E5    1      SHOSTAKOVSKII M SH

=> S E1-E3
        1259 Answers stored in L2
=> S L1 AND L2
        6 Answers stored in L3
=> D L3 1-6
```

Figure 7. (a) An example of looking up a formula in the formula index of a Chemical Abstracts index volume. From here, one would look up the abstract volumes to get the reference to the articles of interest, and then go to the library to determine whether or not the issue of the journal was available. (b) An approximation of the commands used in STN to locate and display abstracts of articles by Shostakovskii that include the substance C_8H_9BrO.

In 1980, Chemical Abstracts Service launched their first online product (*19*). This shortened the researchers' work significantly by automating the retrieval of appropriate index entries and references. Now, a researcher attempting to search for all times that Substance Y appeared in the articles of Author X could perform two searches and ask the system to combine them, identifying only the abstracts of articles that contained both desired pieces of information. This product evolved into the current STN interface to the *Chemical Abstracts* suite of databases, which is heavily used today by information professionals in industry and government libraries. Figure 7b shows a sample search syntax for locating a substance in the Registry file (the database containing all of the substances registered by Chemical Abstracts Service), locating all articles that reference it in the Chemical Abstracts file, and refining to the articles written by a particular author. The final command requests the database to display the article abstracts. From here, a searcher in 1980 would go to the library to determine whether or not printed text was available.

As shown in Figure 7b, learning search syntax for command line-based systems like Chemical Abstracts Online was a major hurdle for seekers of information. In addition, the high cost per search and the cost of viewing individual abstracts encouraged businesses and univerisities to require that such searches be mediated or performed by information professionals. While this improved the efficiency of the searching, it did not necessarily improve the efficiency of the of the chemistry itself, as individual chemists would need to work their searches into another individual's schedule. In addition, the information specialist, while usually a chemist by training, was not the individual working on the project and therefore had limited abilities to filter retrieved results to the most likely to succeed in the lab. This cost additional time, as the bench scientist requested refinements to the search and the information scientist delivered them.

Databases with Ease-of-Use Search Features Put Searching in the Hands of the Bench Chemist

The introduction of end-user-friendly electronic databases with graphic user interfaces is arguably the most important advance in chemical information in the past twenty years. Now, a searcher of *Chemical Abstracts* merely needs to log into SciFinder, perform a substance search for the compound of interest, "Get References," and refine by author to get the work of a single individual. It is relatively easy for a user to get good results from end-user interfaces with no instruction at all. This deceptive "ease of use" presents a danger because no matter what the user inputs, he or she will obtain some answers and will be tempted to think that he or she has seen everything that there is to see. A user still requires formal training or in-depth personal study to learn the nuances of the search system and be able to truly gauge the effectiveness of a query and be sure that he or she is retrieving all relevant information. However, the speed of searching has drastically increased, which is a boon, given the increase in the quantity of information available to be searched. Putting routine searching in the hands of the end-user also frees librarians' and information specialists' time to concentrate on more challenging queries.

Structure-Based Searching for the End-User

Another of the greatest chemical information advances in the past thirty years has been the development of graphical user interfaces to allow end-user chemists to perform their own structure searches. This opened the doors to both increased efficiency in retrieving known molecules and the ability to profile molecules by structural features.

Prior to the introduction of structure searching, the two most descriptive methods of searching for information on a substance were using a molecular formula and a chemical name. The formula, a description of the composition of a substance, will retrieve a desired substance, but brings with it other structural and stereoisomers. Searching for a substance by its name will allow a reader to browse a list of substances with similar names, thus finding related molecules, as well as finding the exact, desired substance. However, the main problem with chemical name as an identifier is that the name being searched needs to be the name represented in the search tool, which is not always the case.

Early methods of structure searching employed a technique known as line notation. Wiswesser Line Notation is a robust method of using codes to indicate functionality and connectivity. For example, in Wiswesser Line Notation, the code 1 stands for a saturated one-carbon chain, and V indicates a carbonyl. Thus, 1V1 indicates the substance acetone, which has a saturated carbon on either side of a carbonyl. The line notations for each substance were placed in the substance's entry in a book or database, and the substance could be located by browsing the index of a printed book or by performing an exact or truncated search of an electronic database.

The major drawback to searching using line notation is obvious: it takes a great deal of time to learn the codes well enough to search fluently. As a result, many chemists were quite relieved when electronic databases began employing graphic user interface (GUI) applications to allow them to draw the structures just as they would in a publication. GUI applications employ connection tables to enable them to work. Each substance in the database is represented structurally and then converted into a series of interconnected nodes, with each node representing one of the atoms in the substance. The connection table defines each node, including its identity (which atom it represents), all the connections that it forms to other nodes, and the types of connections that it forms to those nodes (single bonds, double bonds, etc.) When a user performs a search by drawing a structure into the GUI, the system generates a connection table for it, compares it to all the connection tables in the database, and then retrieves substances whose tables match the query table. This technique also allows for substructure searching, searching for a section of the molecule of interest, because it will search within the connection tables of the database substances and retrieve any that include all of the connections from the query substance, regardless of whether additional connections appear in the table.

New Tools Help Chemists Determine What Is Relevant and Important

Every chemist has had the experience of inputting a search that he or she deemed to be relatively specific, only to retrieve thousands of hits, many of which were completely unrelated to the topic of interest. After viewing the first twenty-five, the researcher feels completely daunted and overwhelmed, and he or she lacks the time and inclination to review all of the retrieved results. Further refining by topic might limit the search too much, excluding information that is relevant because it either contains or lacks specific terms in its abstract and indexing. Fortunately for the modern reader, many tools, from post-processing functions in secondary databases to entire treatises on a relatively narrow field of chemistry, exist to help focus on the most relevant and important pieces of information.

Post-Processing Tools for the Analysis and Visualization of Results

Nowadays, it is almost impossible to find a secondary search tool that does not include post-processing functions. These allow a researcher to narrow a large result set down to a more manageable number by analyzing and refining by author, journal name, year, etc. However, most interesting is the ability to refine using controlled vocabulary, a set of defined terms used by indexers to describe articles similar in topic. Since controlled terms are only applied to articles that focus on the concept described by the term, looking at the controlled vocabulary used with an article can help to determine its relevance. Many secondary databases that use controlled vocabulary give the option of analyzing by controlled terms, or a searcher can return to the search interface and search for the terms of interest, in addition to the keywords previously selected.

Visualization software, including the STN Anavist product, can also help scientists to make sense of large answer sets. This allows one to zero in on key names and phrases, determine gaps in coverage in the existing literature, and produce charts and even two-dimensional graphs of important terms to determine relationships between portions of article and patent records. Digital humanities research has begun employing text mining techniques, which can, among other things, look for the prevelance of terms in a body of literature. While this has not been widely applied to chemistry, it could be of interest in some areas, provided the publishers would permit it.

"More Like This"

Popular Web sites like Amazon include "more like this" features, and databases of scholarly journal articles, as well as some primary publishers, have begun doing the same. Web of Science uses its extensive system of citation networking to recommend articles that have cited the same papers that a retrieved article cites. The thought behind this is that articles that cite similar papers would be of interest to that same reader. This can be a very helpful technique, especially if the terms used in the authors' abstracts are not identical to the search terms that the reader has entered to describe a particular set of concepts, given that Web of Science does not employ a controlled vocabulary. PubMed also has a "related articles" feature, but, instead of relying on a network of citations, it compares the controlled terms used in the hit article to those of other papers in the database and retrieves results that include several of the same controlled terms. While this does not search as far afield from the original article (the best way of searching PubMed or MEDLINE is to employ controlled vocabulary), it is still a useful way of quickly identifying articles that are closely related to a paper of interest.

Social Networking Tools and Curated Compilations

In addition to locating articles that have similar topics or cited references to a useful paper, scientists like knowing what other individuals are reading and what they have found useful. Social networking tools like Twitter, Mendeley, and even Facebook can help a chemist find out about papers that their colleagues are reading, but they are more opinion-based than scholarly, and they do not put the articles into their scientific context. For this, one needs to turn to the tertiary literature.

Tertiary literature, such as review articles, comprehensive sets, compilations, and handbooks, present primary literature in context with other articles and can direct a reader to critically evaluated information. Many of the large comprehensive sets are being produced similarly to electronic databases, making it easy for chemists to perform a search for a topic of interest and retrieve the article or section of the work that includes the requested substances or terms. The two downsides to review sources are that they are dated (additional information has likely been published since the last update of the work) and that one is viewing the literature through the eyes of one individual. While expert curation is one of the draws of the review literature, it can also be dangerous if one does not supplement use of a review source with one's own search of the primary literature, as additional useful information may exist that the author or editor chose, for some reason, to omit.

In addition to the traditional review literature, other resources have emerged in various areas of science to alert researchers to quality information in their areas. The expert opinion series *Faculty of 1000*, now split into two sections *Faculty of 1000 Biology* and *Faculty of 1000 Medicine*, publishes the opinions of reputable researchers who identify and rate articles in their subdisciplines. Thieme's journal *Synfacts* aims to do a similar thing, with researchers writing reviews of recent synthetic articles that include some key reaction schema, a description of the significance of the article, and a commentary section, offering more of the reviewer's perspective on the science.

Digitized Browsing of the Primary Literature

Although digital products have increased productivity in many ways, there are still some timesaving workflows that have been difficult to replicate in the digital medium. Paramount amongst these is the ability to seamlessly browse a journal issue from one article in a title to another. Several primary publishers and a variety of vendors have attempted to address this using mobile apps that allow a researcher to browse the current issues of their favorite periodicals and easily enter and exit articles. The mobile app for *Chemistry World*, the news publication of the Royal Society of Chemistry, allows a reader to swipe from one article to the next and scroll down to read the individual articles. The electronic delivery of *Chemical and Engineering News* to members is designed so that individuals can tap or click the right and left sides of the page to "flip" through an issue or to link to the stories of interest from the interactive table of contents.

BrowZine (*20*) is a mobile app that is not linked to a scholarly publisher. Institutions can subscribe to BrowZine, and their researchers can use the app to create digital bookshelves of journals that they like to monitor. BrowZine will refresh the bookshelf when a new issue becomes available, and researchers can browse its table of contents and navigate directly to the text of the articles without needing additional authentication.

The Scholarly Record Must Endure: Preserving the Literature for Generations to Come

As we have already seen, the chemical literature is expanding rapidly; however, much of it will remain useful for the foreseeable future. Indeed, chemists today are still citing information that was published well over 100 years ago. The problem that we have is that, while we are very good at preserving paper (that's just chemistry, after all!), preserving digital content comes with a whole raft of problems. In addition to the technical problems inherent in preserving digital information, part of the challenge is that we are much less experienced at preserving it than we are at preserving paper. Fortunately for the scholarly record, librarians, primary publishers, and third-party archiving services are working hard to ensure that the papers we write today are accessible for years to come.

There are actually three levels to preserving digital content: first, the individual bits that make up the piece of information to be preserved must be saved; then, software that can convert the bits into usable material must be available; and finally, one must have the appropriate hardware in order to run the software. This means that there are two possible approaches to digital preservation: one could actually preserve the files, software, and hardware used to create the digital information or one could constantly upconvert the information to formats that run easily on the software and hardware du jour. In either case, digital preservation is cost, time, and labor intensive.

When publishing and preserving digital data, a chemist should keep three basic considerations in mind. First, in order to be usable in the future, the data must be able to be located and accessed. One should be sure to keep many copies of internal data, preferably in different locations. When choosing a venue in which to publish, one should look for a site that includes persistent URLs and DOIs to make it easy for others to find and cite the data. Finally, it is extremely important that one attempt to publish data with a reputable source that will not disappear overnight. Third party archiving services, such as LOCKSS (*21*), CLOCKSS (*22*), and Portico (*23*) are good at ensuring that journal articles remain available to subscribers in the event of a publisher collapse or other "trigger event", and we are starting to see some similar policies in place for the archiving of data thanks to the NSF and NIH mandates.

The second consideration is of data integrity. Briefly stated, this means that data must remain uncorrupted. The easiest way of ensuring this is through periodic checks for "bit rot," and data and journal archives need to develop a good method for fixing data that have become corrupted.

The last consideration greatly depends upon the first two: the data must be able to be used at a later date. In addition to being findable and uncorrupted, they must have appropriate annotations and metadata that describe the data format. This is different from the metadata used to describe an experiment that took place; rather than describing the method in which the data were taken, it focuses on information about the nature of the files themselves, including the program used to create them, update information, virus checks, etc. (*8*). Constant automated or manual upconversion can also help to ensure that current software is able to read the information.

Conclusions

To some extent, the community of chemical information scientists works to ensure that the scholarly literature remains available, accessible, and sustainable, but chemists of all types can assist in these endeavors. As chemists, we should attempt to avoid cluttering an already burgeoning literature by publishing when we have something important to say, and telling one full and complete story per paper, avoiding undue fragmentation of research. When picking a publisher, we should try to select one whose policies are consistent with sustainability, thinking about the cost of the journal and its archiving policies, as well as its quality and impact. It is our responsibility to ensure that our data are maintained and annotated appropriately, not only in the lab but also by the party with which we chose to archive or publish them. Despite the tedium, we must be vigilant in documenting everything. We should continue to develop industry standards for the taking and archiving of chemistry data. Finally, when publishers and chemists alike adopt a new technology, we should think critically about issues of persistence and sustainability and, if preserving the information seems challenging, we should concentrate some of our energy into making sure that it can persist in a usable fashion. Remember, the chemical literature does not replace itself; it grows, and we want people using our science 100 years (and more) from now!

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References

1. Bosch, S.; Henderson, K. *Library Journal* **2015**, http://lj.libraryjournal.com/2015/04/publishing/whole-lotta-shakin-goin-on-periodicals-price-survey-2015/ (accessed June 27, 2015).
2. Bosch, S.; Henderson, K. *Library Journal* **2014**, http://lj.libraryjournal.com/2014/04/publishing/steps-down-the-evolutionary-road-periodicals-price-survey-2014/ (accessed June 27, 2015).
3. Hirsch, J. E. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 16569–16572.
4. Data on the number of abstracts added to *Chemical Abstracts* per year since 1907 were supplied by Chemical Abstracts Service, a division of the American Chemical Society, on May 6, 2015, and are used with permission.
5. Data on the number of small molecules added to *Chemical Abstracts* per year since 1965 were supplied by Chemical Abstracts Service, a division of the American Chemical Society, on May 6, 2015, and are used with permission.

6. Chapter II - Proposal Preparation Instructions. http://www.nsf.gov/pubs/policydocs/pappguide/nsf11001/gpg_2.jsp (accessed June 25, 2015).
7. History of Organic Syntheses. http://www.orgsyn.org/history.aspx (accessed June 25, 2015).
8. McEwen, L. R. Cornell University, Ithaca, NY. Personal Communication, August 2014.
9. RSC Prospect FAQ. http://www.rsc.org/Publishing/Journals/ProjectProspect/FAQ.asp (accessed June 25, 2015).
10. Church, R. Royal Society of Chemistry, Cambridge, UK. Personal Communication, June 2015.
11. Aalbersberg, I. J,; Heeman, F.; Koers, H.; Zudilova-Seinstra, E. *Insights* **2012**, *25*, insights.uksg.org/article/download/2048-7754.25.1.33/150/ (accessed June 25, 2015).
12. Wiringi, E. ACS Publications, Washington, DC. Personal Communication, June 2015.
13. Mendeley. https://www.mendeley.com (accessed June 25, 2015).
14. ACS ChemWorx. https://hp.acschemworx.acs.org (accessed June 25, 2015).
15. Thomson Reuters EndNote. http://endnote.com (accessed June 25, 2015).
16. GoodReader. http://www.goodreader.com (accessed June 25, 2015).
17. iAnnotate. http://www.iannotate.com (accessed June 25, 2015).
18. Davis, E. ChenAxon. Personal Communication, August 2014.
19. CAS History. https://www.cas.org/about-cas/cas-history (accessed June 25, 2015).
20. Meet BrowZine™. http://thirdiron.com/browzine/ (accessed June 25, 2015).
21. Lots of Copies Keep Stuff Safe. http://www.lockss.org (accessed June 25, 2015).
22. The CLOCKSS Archive: A Trusted Community-Governed Archive. http://www.clockss.org/clockss/Home (accessed June 25, 2015).
23. Portico. http://www.portico.org/digital-preservation/ (accessed June 25, 2015).

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