LCA and Responsible Innovation of Nanotechnology

by

Benjamin Wender

A Thesis Presented in Partial Fulfillment
of the Requirements for the Degree
Master of Science

Approved April 2013 by the
Graduate Supervisory Committee:

Thomas Seager, Chair
Matthew Fraser
Peter Crozier
David Guston

ARIZONA STATE UNIVERSITY

May 2013

ABSTRACT

Life cycle assessment (LCA) is a powerful framework for environmental decision making because the broad boundaries called for prevent shifting of burden from one life-cycle phase to another. Numerous experts and policy setting organizations call for the application of LCA to developing nanotechnologies. Early application of LCA to nanotechnology may identify environmentally problematic processes and supply chain components before large investments contribute to technology lock in, and thereby promote integration of environmental concerns into technology development and scale-up (enviro-technical integration). However, application of LCA to nanotechnology is problematic due to limitations in LCA methods (e.g., reliance on data from existing industries at scale, ambiguity regarding proper boundary selection), and because social drivers of technology development and environmental preservation are not identified in LCA. This thesis proposes two methodological advances that augment current capabilities of LCA by incorporating knowledge from technical and social domains. Specifically, this thesis advances the capacity for LCA to yield enviro-technical integration through inclusion of scenario development, thermodynamic modeling, and use-phase performance bounding to overcome the paucity of data describing emerging nanotechnologies. With regard to socio-technical integration, this thesis demonstrates that social values are implicit in LCA, and explores the extent to which these values impact LCA practice and results. There are numerous paths of entry through which social values are contained in LCA, for example functional unit selection, impact category selection, and system boundary definition – decisions which embody particular values and determine LCA results. Explicit identification of how social values are embedded in LCA promotes integration of social and environmental concerns into technology development (socio-enviro-technical integration), and may contribute to the development of socially-responsive and environmentally preferable nanotechnologies. In this way, tailoring LCA to promote socio-enviro-technical integration is a tangible and meaningful step towards responsible innovation processes.

ACKNOWLEDGMENTS

Funding for this work was provided in part by the National Science Foundation (NSF) and Department of Energy (DOE) Quantum Energy and Sustainable Solar Technology Engineering Research Center at Arizona State University (NSF CA EEC-1041895), and in part by the Center for Nanotechnology in Society (CNS) at Arizona State University (NSF NSEC 0531194 & NSF 0937591). Any opinions, findings, conclusions, and recommendations expressed in this material are those of the authors and do not necessarily reflect those of NSF or DOE. The authors would like to thank the students and faculty of the Sustainable Energy and Environmental Decision Science (SEEDS) studio at ASU.

TABLE OF CONTENTS

CHAPTER 1

LCA AND RESPONSIBLE INNOVATION OF NANOTECHNOLOGY

Introduction

Until recently, the social implications and environmental impacts of developing technologies were neither explored nor regulated until after commercialization. Thus, technological innovation has been disconnected from technology assessment and regulation (Dewick, Green et al. 2004; von Gleich, Steinfeldt et al. 2008). This tradition has positioned environmental and social governance as retrospective and reactive (Davies 2009). However, there is a growing realization that intervention at the nascent stages of technology development may be more effective, as it provides a pathway for integration of environmental and social concerns into innovation processes. Therefore, there is a critical need to transcend retrospective models of technology assessment and regulation by applying life cycle assessment (LCA) to technologies at these early stages (Fleischer and Grunwald 2008; Meyer, Curran et al. 2011) such that the broader impacts of emerging technologies can be explored in modeling scenarios before significant investments in infrastructure create technological lock-in or result in stranded costs.

I. Calls for Life Cycle Assessment of Nanotechnology

LCA is increasingly recognized as a powerful framework to understand the environmental impacts of processes, technologies, and products (Curran 2004; Bauer, Buchgeister et al. 2008; Eason 2011; Curran 2012) because it accounts for shifting of environmental burdens from one life-cycle phase to another. For example, efforts to promote corn-derived ethanol as a low-carbon substitute for fossil fuels may result in increased eutrophication in the hypoxic zone of the Gulf of Mexico, an environmental tradeoff identified through LCA (Miller, Landis et al. 2006). Accordingly, a number of experts, including the United States Environmental Protection Agency (USEPA) and

Woodrow Wilson Institute for Scholars have called for the application of LCA to nanotechnology (Klopffer 2007; Şengül, Theis et al. 2008; EPA 2009). Most recently, the National Nanotechnology Initiative (NNI) and the National Research Council (NRC) suggest LCA as the proper framework for understanding the systemic environmental implications of emerging nanotechnologies (NNI 2011; NRC 2012). Application of LCA at the nascent stages of nanotechnology development promotes identification of serious environmental consequences *before* they pose a threat to human and environmental health (Theis, Bakshi et al. 2011; Upadhyayula, Meyer et al. 2012). Once identified, threats posed by emerging technologies may be mitigated through integration of environmental concerns into technical research agenda – called enviro-technical integration. However, LCA of nano-enabled products, and any resulting enviro-technical integration, faces significant barriers and following these recommendations is presently impracticable.

II. Barriers to LCA of Nanotechnology

Existing LCA frameworks rely on detailed inventory data collected at scale, making them retrospective and insufficient for the high uncertainty characteristic of rapidly developing technologies (Wiek, Lang et al. 2008; Meyer, Curran et al. 2009). Specific sources of uncertainty include:

1. Uncertainty regarding the human and ecological health impacts of nanomaterials (Oberdörster, Oberdörster et al. 2005; Wiesner, Lowry et al. 2006; Oberdörster, Stone et al. 2007; Stefani, Paula et al. 2011; Wiesner and Bottero 2011),
2. Uncertainty in extrapolating laboratory-scale inventory data to commercial scales (Gutowski, Branham et al. 2009; Seager and Linkov 2009; Gutowski, Liow et al. 2010), and

3. Selecting a functional unit relevant to the use phase of a nanomaterial that captures the potential benefits of engineered nanomaterials (Matheys, Autenboer et al. 2007; Wender and Seager 2011).

Among these drivers of uncertainty, the potential ecotoxicity of individual nanomaterials (item 1 above) has received relatively the most attention (e.g., Mitka (2012). For example, a recent review of LCA of nanotechnologies Gavankar, Suh et al. (2012) calls for full impact assessment of engineered nanomaterials based upon early toxicology studies, and similarly Philbrick (2010) calls for the incorporation of risk assessment into governance strategies through an extensive review of *in vitro* and *in vivo* screening studies. However, exclusive focus on the potential human and ecological toxicity of engineered nanomaterials overlooks the environmental burden resulting from manufacturing and upstream processes, which are significant for engineered nanostructures (Şengül, Theis et al. 2008). For example, recent analysis of the manufacturing pathways for single wall carbon nanotubes (SWCNTs) suggests that the majority of environmental burden in their life cycle is a result of electricity consumption during the manufacturing phase (Healy, Dahlben et al. 2008), and that these impacts outweigh downstream, direct-exposure impacts (Eckelman, Mauter et al. 2012). Specifically, these analyses call attention to high-purity inputs, large electricity consumption, and low product yields of SWCNT manufacturing processes (Ganter, Seager et al. 2009; Gutowski, Liow et al. 2010).

Nonetheless, cradle-to-gate analyses do not assemble the LCA relative to a functional unit descriptive of the use-phase, and thus do not connect reported inventory data with potential improvements in the use-phase. While some analyses do overcome use-phase uncertainty (Lloyd and Lave 2003; Lloyd, Lave et al. 2005; Reijnders 2010; Walser, Demou et al. 2011), these do not incorporate ongoing human health and toxicology research (Aditi, Helen et al. 2008; Krishnan, Boyd et al. 2008; Plata, Hart et al. 2009). Similarly, the environmental impacts of end-of-life recycling and processing of nanoproducts (Olapiriyakul and Caudill 2008; Ostertag and Hüsing 2008) are typically explored independent of research into exposure pathways (Köhler, Som et al. 2008; Maynard 2009), which in turn is uninformed by research into social and market acceptance of nano-enabled technologies (Scheufele, Corley et al. 2007; Siegrist, Cousin et al. 2007; Siegrist, Keller et al. 2007; Siegrist, Wiek et al. 2007; Scheufele, Brossard et al. 2009). Table 1 (taken from Theis et al, 2011) organizes the existing science, and shows how the fragmented efforts that inform different aspects of nano-LCA have yet to be integrated in a comprehensive whole.

Table 1: Relation of Nanostructured Material and Product Research Needs to LCA

	LIFE-CYCLE STAGE			
	Acquisition	**Purification & Manufacture**	**Use**	**End-of-life Disposition**
Material abundance & acquisition	scarcity & criticality of materials	by-product & waste minimization	risk assessment for emissions inventory & characterization, including source term characterization, fate & transport, exposure and dose-response assessment	
Bioavailability & Toxicity				
Synthesis pathways	energy & material intensity			
Life-cycle characteristics		technology comparison	cost, functionality & efficiency	persistence, mobility, bioaccumulation
Social context	geopolitical sensitivities	worker safety	market acceptance	disposal & take-back regulations

More importantly, Table 1 suggests that LCA of nanotechnologies requires knowledge from multiple fields of study, as different research questions and investigative methods are required at each life cycle stage. Thus LCA of nanotechnology cannot proceed without parallel research in prerequisite specialty areas, and must incorporate social science, materials science, and environmental science in order to be applicable across *all* of Table 1.

III. Social Dimensions of Technology Development

Technology and society continually shape one another – a model called ‘co-production’ in Science, Technology, and Society (STS) literature. Society shapes which technologies are developed (e.g., through government funding mechanisms), and individuals in society are the end users of technological innovations. Similarly, technology remakes society through incremental and disruptive innovations, which provide solutions and simultaneously create new problems for society – prompting the development of the next round of technological innovations (Jasanoff 1996). Early explorations of the complex relationship between society and technology took a historical and descriptive approach (e.g., Hughes (1989). Similarly, Abernathy and Townsend (1975) made substantive efforts to map governance forces enabling and constraining the adoption and diffusion of technology by describing the interconnected forces that contribute to socio-technical transformations. While these efforts provide a foundation for understanding the co-production of science and technology, they fall short of intervening in technology development processes.

Recognition of the dynamic relationship between science and society underlies technology assessment efforts, which seek to guide scientific and technological innovation towards explicitly stated and socially desirable outcomes. Guston and Sarewitz (2002) moved away from historically descriptive studies and theorized a new approach called real-time technology assessment (RTTA), with the intent to influence contemporary decision makers and engage directly with scientists and technology developers. Three critical components of RTTA are:

1. *Foresight* constructs plausible futures with explicit incorporation of values, and builds capacity to address both positive and negative potential socio-technical outcomes (Selin 2007; Selin and Hudson 2010).
2. *Engagement* between scientists, engineers, the lay public, and policy-makers through workshops, conferences, and public events is intended to make people aware of what others are doing, and to shape knowledge development, technological innovation, and acknowledge values that impact the creation of, and reactions to, novel nanotechnologies (Karinen and Guston 2010; Chittenden 2011).
3. *Integration* connects social and natural scientists through activities such as patent and publication analysis, surveys of scientists and citizens, and infusion of humanists into nanoscale science and engineering laboratories (Fisher 2006; Barben, Fisher et al. 2008). More recent work reconciles emerging nanotechnology solutions with complex problem constellations depicting sustainability challenges formulated by expert elicitation of social and environmental researchers (Wiek In press).

Together these activities contribute to the development of socially robust technologies through explicit identification and integration of societal values into innovation processes.

A Theory of Anticipatory LCA

Combining RTTA techniques and advances in LCA, this thesis augments LCA capabilities for promoting integration of environmental and social concerns into technology development – henceforth referred to as socio-enviro-techno integration. Existing approaches to LCA (i.e., as codified in ISO 14040) rely heavily on inventory and performance data collected from mature at-scale industries, and are ineffective at socio-enviro-technical integration because they are *retrospective*. Growing recognition of the need consider environmental impacts of rapidly developing technologies, for example biofuels and nanotechnology, has led to the development of *prospective* LCA, which explore potential environmental tradeoffs that may result from a decision or technology. While this orients analyses towards the future, many prospective LCAs are narrowly focused and fall short of intervening in technology development, partially because they fail to identify and tailor analyses to salient decision makers and impacted segments of society, and communicate findings to technology developers. This thesis theorizes *anticipatory* LCA as a forward looking technology assessment framework that draws upon expertise from environmental, social, and technological domains, to explicitly identify social values embodied in LCA and engage relevant stakeholders and actors in technology innovation activities. Specific tools incorporated from prospective LCA and RTTA are presented in Figure 1.

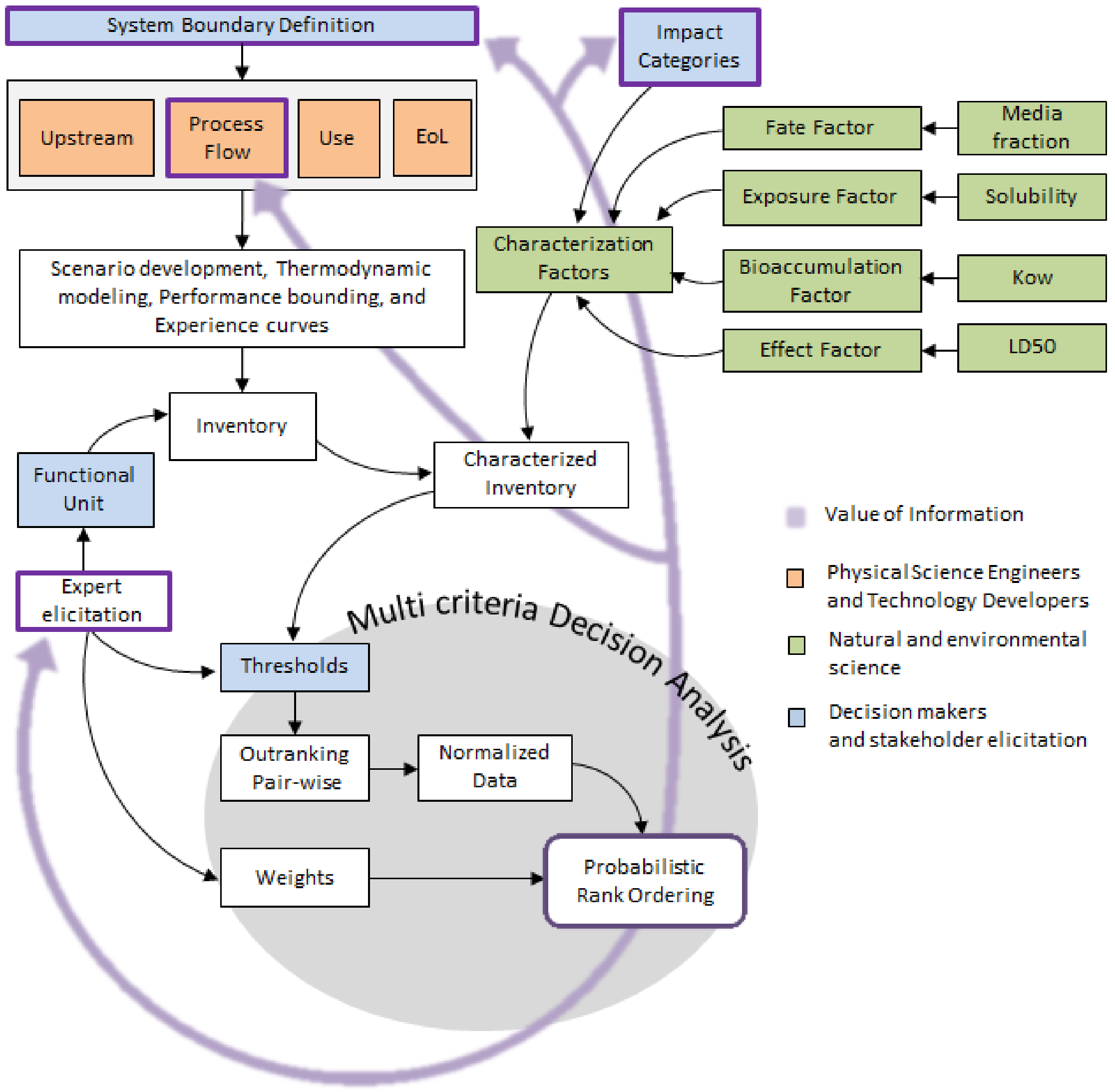

Figure 1: Anticipatory LCA Framework and knowledge feedback to technology developers, environmental researchers, stakeholders, and decision makers.

Figure 1 calls attention to the role of stakeholder and expert elicitation in system boundary definition, functional unit selection, and impact category definition. More importantly, Figure 1 distinguishes anticipatory LCA from prospective analyses through identification of relevant actors (e.g., technology developers – orange boxes, environmental researchers – green boxes) in innovation processes, and communication of results through knowledge feedback (purple arrows). This thesis argues that application of anticipatory LCA to technologies in their nascent stages will enable socio-enviro-technical integration, potentially redirecting technology development trajectories towards both socially and environmentally preferable outcomes.

Methods – Components of Anticipatory LCA

Promoting socio-enviro-technical integration through anticipatory LCA advances the science in two ways:

1. Identification of implicit social values inherent in LCA frameworks and exploration of how these shape LCA practice and results, and
2. Methodological improvements to LCA frameworks that build capacity for foresight in LCA and promote its application to rapidly emerging technologies, where data is scarce and uncertainty high.

I. Enabling socio-technical integration through anticipatory LCA

Although ISO guidelines consider only valuation stages (i.e., normalization and weighting) as subjective, this thesis argues that all stages of LCA – including goal and scope definition, inventory collection, impact assessment, and interpretation, are decision points for LCA practitioners that have social motivations and implications. Specific paths of entry through which social values are implicitly incorporated into LCA, although these are rarely made explicit, are explored in more detail in Table 2.

Table 2: Implicit incorporation of social values in LCA

LCA Component	Demonstration of Social Values Embodied
Functional Unit (FU)	The functional unit that any LCA is assembled relative to reflects a societal valuation of the service provided. For example, a commonly used FU in LCA of transportation services is km/hr, which reflects a social value of mobility and time. Similarly, the functional unit defines which social values are not reflected in the LCA – in the transport example, an FU of km/hr does not account for the number of people being transported. Changing the FU to passenger-km reflects a social value of mobility for many people, with no valuation of time. Changing the FU will yield different results – a bus (slow) will likely have large impacts compared to a car (fast) when assembled relative to km/hr, whereas the bus (many people) will be preferable if measured in passenger-km.
System Boundaries	System boundary definition determines the processes and activities considered and those excluded. For example, a cradle-to-gate assessment of semiconductor manufacturing may include mining, benefaction, and manufacturing processes, which emphasizes values surrounding manufacturing efficiency and calls attention to decisions made by manufacturing firms. Conversely, an assessment of end-of-life disposal of computers may consider only post-use transportation and recycling activities, which places emphasis on material re-use. These boundaries emphasize decisions and impacts of recyclers, both formal and informal.
Impact Categories	Selection of impact categories reflects social value of some environmental impacts or compartments more than others. For example, the prevalence of global warming potential in published LCAs emphasizes social concerns about global warming.

Failure to identify and make explicit the social values embodied in LCA is problematic, as it may introduce bias into the LCA and overlook values held by relevant stakeholders impacted by the technology. Furthermore, explicit identification of social biases allows LCA practitioners to explore how alternative formulations (e.g., different functional units, changing system boundaries) impact LCA results and the corresponding potential for enviro-socio-technical integration.

II. Incorporation of RTTA methods to broaden social values embodied in LCA

After explicitly identifying the role of social values in LCA, incorporation of the real-time technology assessment (RTTA) methods of foresight, engagement, and integration can be applied to broaden the range of societal outcomes considered and to integrate knowledge of differing values into LCA and technology development, as discussed in Table 3.

Table 3: Incorporation of RTTA Methods into Anticipatory LCA

RTTA Component	Inclusion in Anticipatory LCA	Changes to LCA and Results
Foresight	Scenario development and thermodynamic modeling Analogous experience curves (discussed in detail below)	Generation of alternative inventories Explore sensitivity of LCA results to improvements in specific processes or life-cycle stages
Engagement	Stakeholders identification and value elicitation Influence mapping	Selection of alternative functional units and system boundaries Explore sensitivity of LCA results based on explicit social values of different stakeholders
Integration	Knowledge feedback Socio-enviro-technical integration	Results and associated sensitivities communicated back to technology developers and stakeholders Identification of alternative research strategies

Using RTTA methods to formulate alternative inventories, functional units, and system boundaries promotes a transparent understanding of how values shape LCA practices and results. Furthermore, the results and associated sensitivity may call attention to socially or environmentally preferable research agenda, which can be communicated to technology developers and policy makers. Thus, though explicit identification of the role of social values in LCA and incorporation of RTTA methods, anticipatory LCA may promote integration of social considerations into innovation processes.

III. Enabling enviro-technical integration through anticipatory LCA

Anticipatory LCA seeks to integrate environmental concerns into technology development through early identification and communication of environmentally problematic processes and supply chain components. Application of ISO-codified LCA frameworks to nano- and other emerging technologies is problematic due to paucity of data and high uncertainty regarding potential improvements in nanomanufacturing processes and use-phase performance. Anticipatory LCA overcomes these barriers through a combination of thermodynamic modeling, scenario development, and use-phase performance bounding, explained in more detail below.

1. Combining laboratory-scale material and energy inventories with scenario development to explore potential changes in laboratory or pilot-scale thermodynamic degree of perfection. Those processes that are far from thermodynamic perfection might be expected to improve more quickly than those that are already approaching practical thermodynamic limitations (Gutowski et al, 2010; Gutowski et al, 2009).
2. Calculating upper and lower boundaries to use phase performance based on theoretical limits and existing laboratory measurements coupled with thermodynamic modeling of use and manufacturing phases. Together these may

identify lifecycle phases with the most potential for environmental improvement (Wender and Seager, 2011).

3. Analogous experience curve modeling. It is well understood that high technology industries improve cost, material, and energetic efficiencies as total production knowledge accumulates. Analysis of experience curve patterns from more mature industries (e.g., aluminum, silicon) may result in estimates of the efficiency gains that accrue as emerging technologies are scaled up (McDonald and Schrattenholzer 2001).

In situations of high uncertainty (e.g., nano-enabled energy technologies) this analysis can be used to develop scenarios of environmental burden, and can call attention to environmentally problematic processes and technologies. Furthermore, by providing estimates of manufacturing and use-phase efficiency respectively, these analyses can lead to prioritization of research needs that will result in the most meaningful environmental improvements. For example, an environmental agenda might call attention to research needs in manufacturing, rather than in product use-phase performance. Model results are ultimately incorporated into existing LCA tools (e.g., Simapro and EIO databases) to broaden system boundaries and account for supply chain impacts.

In the following case study we apply these components of anticipatory LCA to single wall carbon nanotube (SWCNT) manufacturing, compare the rapid improvements in SWCNT manufacturing to analogous material processing industries, and discuss the use of SWCNTs as an active anode material for advanced lithium ion batteries.

Case Study – Single Wall Carbon Nanotubes for Lithium ion Batteries

A major thrust of battery research is to increase the energy storage density of rechargeable batteries. This is motivated in part by consumer preference for lightweight electronics, but is increasingly environmentally relevant as electric and hybrid electric vehicles are implemented on larger scales. Recently, the energy density of batteries has increased dramatically—from lead acid batteries with a mass-based energy density up to 50 Wh/kg to lithium polymer batteries approaching 250 Wh/kg. Lithium ion batteries have emerged as the preferred chemistry because of their comparatively high energy densities per unit mass (Wilburn 2008). Further improvements will depend upon increasingly sophisticated materials and manufacturing techniques. Engineered nanomaterials are appealing because of their large surface area and superior electrical properties. Specifically, single wall carbon nanotubes (SWCNTs) can store lithium ions in interstitial spaces, collect charge carriers, and conduct charge to external circuits (Landi, Ganter et al. 2008; Landi, Cress et al. 2011). SWCNT battery anodes could eliminate the need for charge collecting metal foil, thus reducing battery weight and increasing energy storage density. The potential gains in use phase performance in SWCNT-enabled lithium ion batteries could justify increased energy investments in SWCNT manufacturing. However, there is no data available describing commercial scale manufacturing of SWCNT anodes, and only preliminary laboratory-scale data describing their use phase performance potential. Thus, the systemic environmental consequences of SWCNT-enabled lithium ion batteries are inherently unclear, and necessitate anticipatory LCA methods to quantitatively explore energy tradeoffs between the manufacturing and use phases, and how these may change with increased scale. Specifically, the aforementioned analyses can provide insights into future developments in nano-manufacturing processes (e.g., potential sources of efficiency gains) coupled with comprehensive use-phase modeling (e.g., from present capabilities to thermodynamic limits) to evaluate the promise of future nanotechnologies from cradle-to-use. Ultimately, these results can be incorporated into existing LCA tools to broaden system boundaries and include potential supply chain impacts of future technologies.

I. SWCNT Manufacturing from an Environmental Perspective

SWCNTs can be synthesized through at least four different pathways: chemical vapor deposition (CVD), high pressure carbon monoxide (HiPCO), arc discharge, and laser vaporization. Early environmental assessments have called attention to the massive electricity consumption, high-purity input materials requirements, and low synthesis yields common to these processes (Healy, Dahlben et al. 2008; Ganter, Seager et al. 2009; Canis, Linkov et al. 2010). The majority of environmental impact is attributable to electricity consumption during SWCNT synthesis and to a lesser extent purification processes, while the most significant impact categories are climate change, airborne inorganics, and acidification. HiPCO demonstrates the comparatively lower environmental burdens because it is a continuous flow process with recycled exhaust gasses, and thus has potential for scale-up to produce kilogram quantities of SWCNT (Aditi, Helen et al. 2008).

II. Mechanisms of the HiPCO Process

The HiPCO process is a specialized form of chemical vapor deposition through which SWCNTs are produced at a high rate (.45 g/h) from a carbon monoxide (CO) feedstock (Bronikowski, Willis et al. 2001; Pavel 2004). Catalytic iron nanoparticles, formed *in situ* by the thermal decomposition of $Fe(CO)_5$ and aggregation of gas-phase Fe atoms, provide preferential sites for CO disproportionation, shown below in reaction (1). The formation of solid carbon from CO gas in disproportionation, promotes formation of SWCNT on the surface of the catalyst via the *Yarmulke* mechanism (Hafner, Bronikowski et al. 1998; Moisala, Nasibulin et al. 2006). Briefly, a hemispherical carbon cap forms on appropriately sized particles, and the cap is pushed away from the catalytic particle by the addition of carbon atoms until the particle becomes too large and overcoats with amorphous carbon, or too small and evaporates (Bladh, Falk et al. 2000).

$$2CO\ (g) \leftrightarrow CNT\ (s) + CO_2\ (g) \qquad (1)$$

Δb° 275.1 [kJ/mol-CO] 469.62 [kJ/mol-C] 19.87 [kJ/mol-CO_2]

Listed below reaction (1) are the standard exergies of formation of the reactants and products. Overall, the reaction releases 60.7 kJ/mol-C (or 5.06 kJ/g-SWCNT) at standard conditions (Szargut and Morris 1987; Gutowski, Liow et al. 2010) and consequently is spontaneous. However, the reaction rate is significant only at temperatures above 550 degrees C (Renshaw, Roscoe et al. 1970) and increases with pressure, thus the HiPCO process requires high temperature (900-1100 C) and pressure (30-50 atm) conditions. Reaching and maintaining these conditions requires significant exergy inputs, currently orders of magnitude greater than energy released in CO disproportionation.

III. Degree of Perfection of the HiPCO Process

The degree of perfection provides a measure of the second law efficiency of manufacturing processes, and is defined as the ratio of the chemical exergy of the product(s) at standard conditions to the sum of all exergy input (Szargut, Morris et al. 1988). Assuming the kinetic and potential exergy of the CO gas stream is negligible, the degree of perfection can be estimated as,

$$DoP = \frac{b_{ch,SWCNT}}{b_{ph,in}+b_{ch,in}} \qquad (2)$$

where the standard chemical exergy of SWCNT ($b_{ch,\ SWCNT}$) is 469.62 kJ/mol-SWCNT. Assuming ideal gas behavior, the minimum physical exergy (b_{ph}) required to heat and pressurize CO from standard conditions (25 C, 1 atm) to those at which SWCNT synthesis occurs (~1100 C, ~30 atm) is given by (3), (Szargut et al, 1988).

$$b_{ph} = c_p\left[(T - T_0) - T_0 ln\frac{T}{T_0}\right] + RT_0 ln\frac{P}{P_0} \quad [\frac{kJ}{mol\ CO}] \qquad (3)$$

The total input exergy is then given by the sum of physical inputs and the standard exergy of CO feedstock multiplied by the mole ratio of CO to SWCNT (given by the inverse of the reaction yield), which results in the total exergy input per mole of SWCNT produced. When the HiPCO process was first reported in 1999, inputs were greater than 600,000 grams of CO per gram of SWCNT (Nikolaev et al, 1999), and by patent application in 2004 CO inputs had fallen to tens of thousands of grams (Smalley 2004), which drives the observed improvements. The ideal (although never attainable) manufacturing process has a degree of perfection of one with lesser values indicating increased potential for efficiency gains. Presently, the degree of perfection for the HiPCO process is on the order of 10^{-3} to 10^{-4} which indicates significant room for improvement. By comparison, electric induction melting processes have a degree of perfection on the order of 10^{-1} (~.7), and are thereby approaching their second law limit.

IV. Analogous Experience Curve Modeling

It is well understood that the thermodynamic and economic efficiency of material manufacturing processes improve with increased experience and scale (Haupin 1986; Smil 2008; Gutowski, Branham et al. 2009). For example, the electricity demands of aluminum production via the Hall-Heroult process have asymptotically decreased towards the thermodynamic limit over 120 years. Likewise, the gross energy consumption of blast furnaces used for pig iron production decreased by orders of magnitude from early production values. The rapid gains in manufacturing efficiency early in process development, as shown in Figure 2 top, illustrate the challenge of environmental assessment of emerging technologies – early on LCA is trying to hit a moving target. Analogous to aluminum and pig iron production, SWCNT manufacturing may greatly improve in energetic efficiency with increases in scale and experience, scenarios for which are shown in Figure 2 bottom.

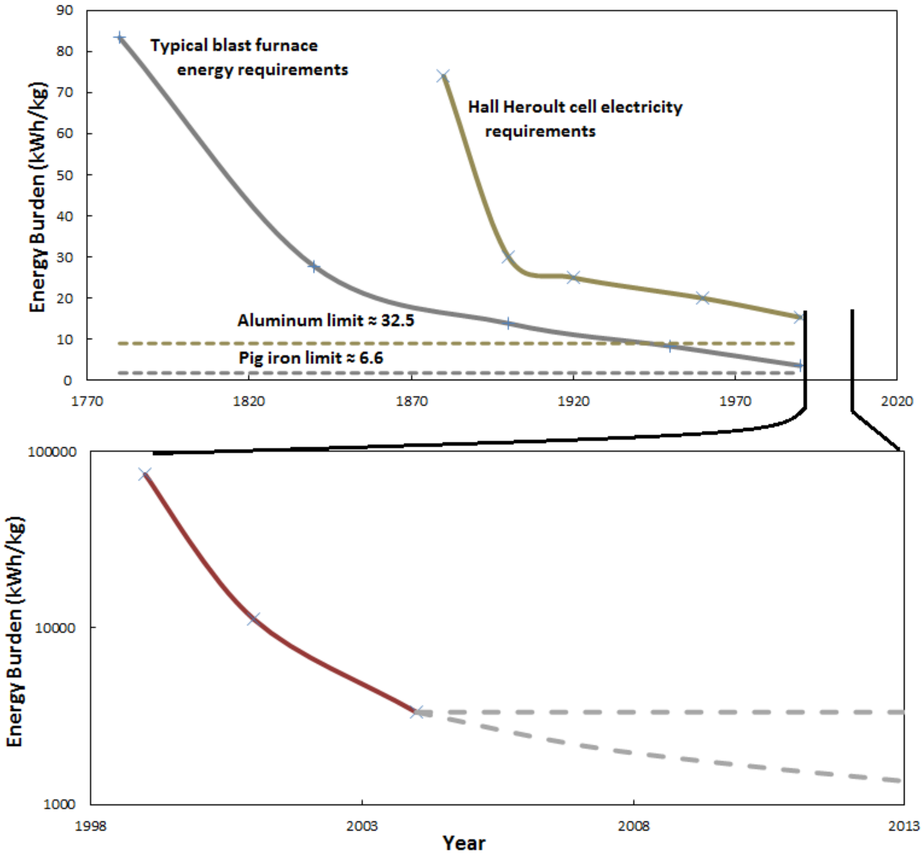

Figure 2: Historic Reductions in Aluminum and Pig Iron Process Energy and Analogous Improvements in the HiPCO Process

There are several historical examples of advances in material processing that subsequently enabled the development and growth of transformational industries. For example, improvements in aluminum processing enabled the aerospace industry and advances in pig iron production contributed significantly to the industrial revolution. Yet the improvements in aluminum and pig iron production accrued over centuries, whereas the HiPCO process was discovered less than 15 years ago. If carbon nanotubes are to have equally transformative effects as aluminum and steel industries, there is a critical need to identify sources of efficiency improvements *early* such that reductions occur rapidly. The next section will reveal that anticipatory LCA of SWCNT manufacturing and application in advanced batteries may call attention of research agenda that accelerate process improvement.

V. Use Phase Performance Bounding of SWCNT Anode Lithium ion Batteries

Half-cell testing of SWCNT anodes reveals a reversible capacity of 400 mAh/gSWCNT, compared to a theoretical limiting capacity of 1100 mAh/gSWCNT (Landi, 2008). Both values represent a significant improvement over traditional lithium ion battery anodes (made of mesoporus carbon beads) which provide a reusable capacity around 150 mAh/gC. The specific energy density of the battery is computed as the product of specific capacity and cell voltage, nominally 3.6 volts for $LiCoO_2$-carbon battery cells (Linden 1984). Assuming complementary advances in cathode technology and optimized battery geometry, SWCNT-enabled lithium ion batteries might store between 1.44 and 3.96 Wh/gSWCNT. Using these two limiting cases to provide upper and lower boundaries on battery performance, we convert the cradle-to-gate exergy consumption of SWCNT manufacturing (e.g., energy or material invested per gram of SWCNT produced) into a functional unit representative of battery performance, specifically kWh storage capacity. Specifically, dividing the exergy input per gram of SWCNT produced via the HiPCO process by the two limiting-case conversion factors above provides a range of energy requirements per kWh storage capacity as shown in Figure 3.

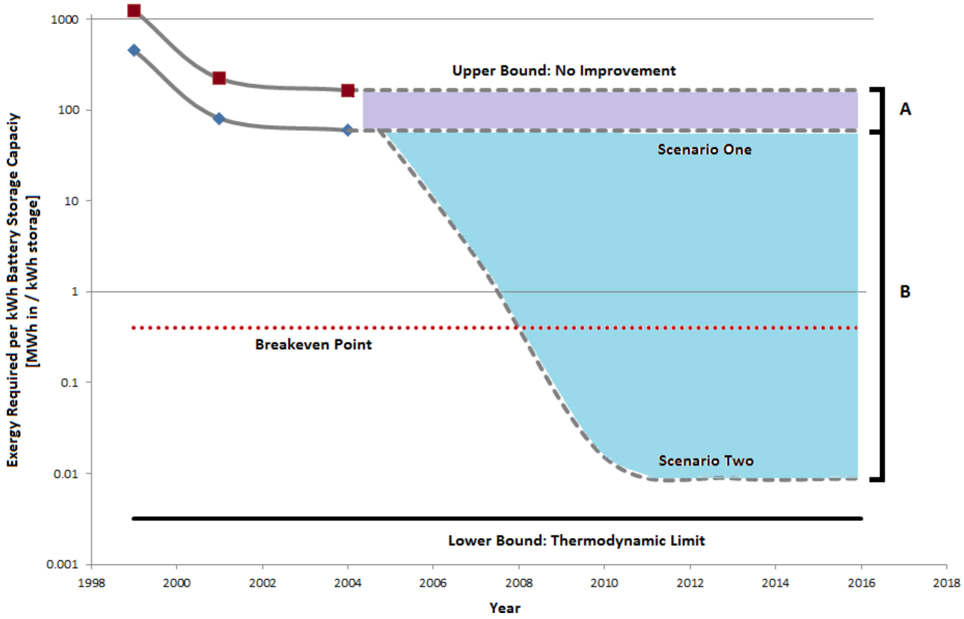

Figure 3: Cradle-to-use exergy consumption of SWCNT anode lithium ion batteries and two scenarios of future improvement

Anticipating future developments in SWCNT manufacturing and battery performance is carried out in the absence of empirical evidence (data points), and thus scenarios are represented as dashed lines in Figure 3. The analysis takes for a starting point presently reported values, with no future improvements (shown as the *upper bound: no improvement* in Figure 3). We construct two future-oriented scenarios, which represent improvements in manufacturing efficiency *or* functional performance. The range of possibilities is constrained by the second law of thermodynamics, in this case representing improvements in both functionality *and* manufacturing efficiency (shown as the *lower bound: thermodynamic limit* in Figure 3). The breakeven point represents the value at which SWCNT anodes are competitive with estimates for commercially-produced lithium ion batteries, available on the market today (Samaras and Meisterling 2008).

Between the two limiting boundaries (i.e., the Upper: no improvement, and Lower: thermodynamic limit) we present two scenarios:

- Scenario One represents the theoretical limit of SWCNT anode performance, but no improvement in SWCNT manufacturing, and
- Scenario Two represents thermodynamically ideal SWCNT manufacturing, but no improvement in anode performance.

Thus, Region A (shaded purple in Figure 3) represents all possible embodied exergy values if anode functionality alone is improved. Conversely, Region B (shaded blue) represents all possible embodied exergy values if there are manufacturing efficiency improvements alone, and no functionality gains. Region B spans approximately four orders of magnitude – that is SWCNT manufacturing is far from its thermodynamic ideal, indicating considerable room for efficiency improvement in SWCNT manufacturing via the HiPCO process. Conversely, Region A spans approximately one order of magnitude, which indicates that present functionalities are near (relative to manufacturing) their thermodynamic limit. Thus, research into improving SWCNT anode *functionality alone* will not reach the breakeven point, and thereby will not provide a net energy benefit compared to commercially available lithium ion batteries (i.e., without SWCNT anodes).

Conclusion

Research and development of nano-enabled energy technologies is inherently uncertain, and the tools necessary to conduct environmental assessment, specifically LCA, under such uncertainty have lagged behind nanotechnology development. Paradoxically, current approaches to LCA are least able to inform environmental understanding in the early stages of technology development, when LCA could most reduce the eventual systemic environmental burdens of the technology. This necessitates the development of *anticipatory* LCA methods, which employ thermodynamic analysis as a guidepost for understanding both the limits of manufacturing improvements and use phases performance, thereby replacing a complete lack of data with potential scenarios. Ultimately, an anticipatory analysis may contribute to reorientation of laboratory research agenda towards pathways with decreased environmental burden. This chapter presented an example demonstrating the limits of a research agenda that focuses on improving use-phase performance of SWCNT-enabled lithium ion batteries alone, which is less valuable than research into lowering energy requirements of SWCNT manufacturing processes.

REFERENCES

Abernathy, W. J. and P. L. Townsend (1975). "Technology, productivity and process change." Technological Forecasting and Social Change 7(4): 379-396.

Aditi, S., H. L. Helen, et al. (2008). Environmental Impact Assessment for Potential Continuous Processes for the Production of Carbon Nanotubes, Science Publications.

Barben, D., E. Fisher, et al. (2008). "38 Anticipatory Governance of Nanotechnoiogy: Foresight, Engagement, and Integration."

Bauer, C., J. Buchgeister, et al. (2008). "Towards a framework for life cycle thinking in the assessment of nanotechnology." Journal of Cleaner Production 16(8-9): 910-926.

Bladh, K., L. K. L. Falk, et al. (2000). "On the iron-catalysed growth of single-walled carbon nanotubes and encapsulated metal particles in the gas phase." Applied Physics A: Materials Science & Processing 70(3): 317-322.

Bronikowski, M. J., P. A. Willis, et al. (2001). Gas-phase production of carbon single-walled nanotubes from carbon monoxide via the HiPco process: A parametric study, AVS.

Canis, L., I. Linkov, et al. (2010). "Application of stochastic multiattribute analysis to assessment of single walled carbon nanotube synthesis processes." Environmental Science & Technology.

Chittenden, D. (2011). "Commentary: Roles, opportunities, and challenges—science museums engaging the public in emerging science and technology." Journal of Nanoparticle Research 13(4): 1549-1556.

Curran, M. A. (2004). "The status of life-cycle assessment as an environmental management tool." Environmental Progress 23(4): 277-283.

Curran, M. A. (2012). Life Cycle Assessment Handbook: A Guide for Environmentally Sustainable Products, Wiley-Scrivener.

Davies, J. C. (2009). Oversight of Next Generation Nanotechnology, Woodrow Wilson International Center for Scholars.

Dewick, P., K. Green, et al. (2004). "Technological change, industry structure and the environment." Futures 36(3): 267-293.

Eason, T., Meyer, D.E., Curran, M.A., and Upadhyayula, V.K.K. (2011). Guidance to Facilitate Decisions for Sustainable Nanotechnology. National Risk Management Research Laboratory, U.S. Environmental Protection Agency.

Eckelman, M. J., M. S. Mauter, et al. (2012). "New Perspectives on Nanomaterial Aquatic Ecotoxicity: Production Impacts Exceed Direct Exposure Impacts for Carbon Nanotoubes." Environmental Science & Technology 46(5): 2902-2910.

EPA (2009). Nanomaterials Research Strategy. Washington DC, Office of Research and Development.

Fisher, E. (2006). Midstream modulation: Integrating societal considerations into and during nanotechnology research and development: A case study in implementing United States federal legislation, ProQuest.

Fleischer, T. and A. Grunwald (2008). "Making nanotechnology developments sustainable. A role for technology assessment?" Journal of Cleaner Production 16(8-9): 889-898.

Ganter, M. J., T. P. Seager, et al. (2009). A life-cycle energy analysis of single wall carbon nanotubes produced through laser vaporization. Sustainable Systems and Technology, 2009. ISSST '09. IEEE International Symposium on.

Gavankar, S., S. Suh, et al. (2012). "Life cycle assessment at nanoscale: review and recommendations." International Journal of Life Cycle Assessment 17(3): 295-303.

Guston, D. H. and D. Sarewitz (2002). "Real-time technology assessment." Technology in Society 24(1-2): 93-109.

Gutowski, T. G., M. S. Branham, et al. (2009). "Thermodynamic Analysis of Resources Used in Manufacturing Processes." Environmental Science & Technology 43(5): 1584-1590.

Gutowski, T. G., J. Y. H. Liow, et al. (2010). Minimum exergy requirements for the manufacturing of carbon nanotubes. Sustainable Systems and Technology (ISSST), 2010 IEEE International Symposium on.

Hafner, J. H., M. J. Bronikowski, et al. (1998). "Catalytic growth of single-wall carbon nanotubes from metal particles." Chemical Physics Letters 296(1–2): 195-202.

Haupin, W. (1986). History of electrical energy consumption by Hall-Heroult cells.

Healy, M. L., L. J. Dahlben, et al. (2008). "Environmental Assessment of Single-Walled Carbon Nanotube Processes." Journal of Industrial Ecology 12(3): 376-393.

Hughes, T. (1989). American Genesis: A Century of Invention and Technological Enthusiasm, 1870-1970. . New York Penguin Books.

Jasanoff, S. (1996). "Beyond Epistemology: Relativism and Engagement in the Politics of Science." Social studies of science 26(2): 393-418.

Karinen, R. and D. H. Guston (2010). Toward Anticipatory Governance: The Experience with Nanotechnology

Governing Future Technologies. M. Kaiser, S. Maasen, M. Kurath and C. Rehmann-Sutter, Springer Netherlands. 27: 217-232.

Klopffer, W., Curran, M.A., Frankl, P., Heijung, R., Kohler, A., and Olsen, S.I. (2007). Nanotechnology and life cycle assessment: A systems approach to nanotechnology and the environment, Woodrow Wilson International Center for Scholars.

Köhler, A. R., C. Som, et al. (2008). "Studying the potential release of carbon nanotubes throughout the application life cycle." Journal of Cleaner Production 16(8–9): 927-937.

Krishnan, N., S. Boyd, et al. (2008). "A Hybrid Life Cycle Inventory of Nano-Scale Semiconductor Manufacturing." Environmental Science & Technology 42(8): 3069-3075.

Landi, B. J., C. D. Cress, et al. (2011). "High energy density lithium-ion batteries with carbon nanotube anodes." Journal of Materials Research 25(08): 1636-1644.

Landi, B. J., M. J. Ganter, et al. (2008). "Lithium Ion Capacity of Single Wall Carbon Nanotube Paper Electrodes." The Journal of Physical Chemistry C 112(19): 7509-7515.

Linden, D. (1984). Handbook of batteries and fuel cells.

Lloyd, S. M. and L. B. Lave (2003). "Life Cycle Economic and Environmental Implications of Using Nanocomposites in Automobiles." Environmental Science & Technology 37(15): 3458-3466.

Lloyd, S. M., L. B. Lave, et al. (2005). "Life Cycle Benefits of Using Nanotechnology To Stabilize Platinum-Group Metal Particles in Automotive Catalysts." Environmental Science & Technology 39(5): 1384-1392.

Matheys, J., W. Autenboer, et al. (2007). "Influence of functional unit on the life cycle assessment of traction batteries." The International Journal of Life Cycle Assessment 12(3): 191-196.

Maynard, A. D. (2009). "Commentary: Oversight of Engineered Nanomaterials in the Workplace." The Journal of Law, Medicine & Ethics 37(4): 651-658.

McDonald, A. and L. Schrattenholzer (2001). "Learning rates for energy technologies." Energy Policy 29(4): 255-261.

Meyer, D., M. Curran, et al. (2011). "An examination of silver nanoparticles in socks using screening-level life cycle assessment." Journal of Nanoparticle Research 13(1): 147-156.

Meyer, D. E., M. A. Curran, et al. (2009). "An Examination of Existing Data for the Industrial Manufacture and Use of Nanocomponents and Their Role in the Life Cycle Impact of Nanoproducts." Environmental Science & Technology 43(5): 1256-1263.

Miller, S. A., A. E. Landis, et al. (2006). "Use of Monte Carlo Analysis to Characterize Nitrogen Fluxes in Agroecosystems." Environmental Science & Technology 40(7): 2324-2332.

Mitka, M. (2012). "Committee Calls for Framework to Assess the Safety of Nanotechnology Materials." JAMA: The Journal of the American Medical Association 307(11): 1123-1124.

Moisala, A., A. G. Nasibulin, et al. (2006). "Single-walled carbon nanotube synthesis using ferrocene and iron pentacarbonyl in a laminar flow reactor." Chemical Engineering Science 61(13): 4393-4402.

NNI (2011). Environmental, Health, and Safety Research Strategy. National Nanotechnology Initiative.

NRC, N. R. C. (2012). A Research Strategy for Environmental, Health, and Safety Aspects of Engineered Nanomaterials, The National Academies Press.

Oberdörster, G., E. Oberdörster, et al. (2005). "Nanotoxicology: An Emerging Discipline Evolving from Studies of Ultrafine Particles." Environmental Health Perspectives 113(7): 823-839.

Oberdörster, G., V. Stone, et al. (2007). "Toxicology of nanoparticles: A historical perspective." Nanotoxicology 1(1): 2-25.

Olapiriyakul, S. and R. J. Caudill (2008). A framework for risk management and end-of-life (EOL) analysis for nanotechnology products: A case study in lithium-ion batteries. Electronics and the Environment, 2008. ISEE 2008. IEEE International Symposium on.

Ostertag, K. and B. Hüsing (2008). "Identification of starting points for exposure assessment in the post-use phase of nanomaterial-containing products." Journal of Cleaner Production 16(8-9): 938-948.

Pavel, N. (2004). "Gas-Phase Production of Single-Walled Carbon Nanotubes from Carbon Monoxide: A Review of the HiPco Process." Journal of Nanoscience and Nanotechnology 4(4): 307-316.

Philbrick, M. (2010). "An Anticipatory Governance Approach to Carbon Nanotubes." Risk Analysis 30(11): 1708-1722.

Plata, D. L., A. J. Hart, et al. (2009). "Early evaluation of potential environmental impacts of carbon nanotube synthesis by chemical vapor deposition." Environmental Science & Technology 43(21): 8367-8373.

Reijnders, L. (2010). "Design issues for improved environmental performance of dye-sensitized and organic nanoparticulate solar cells." Journal of Cleaner Production 18(4): 307-312.

Renshaw, G. D., C. Roscoe, et al. (1970). "Disproportionation of CO: I. Over iron and silicon-iron single crystals." Journal of Catalysis 18(2): 164-183.

Samaras, C. and K. Meisterling (2008). "Life Cycle Assessment of Greenhouse Gas Emissions from Plug-in Hybrid Vehicles: Implications for Policy." Environmental Science & Technology 42(9): 3170-3176.

Scheufele, D. A., D. Brossard, et al. (2009). "Are scientists really out of touch." The Scientist.

Scheufele, D. A., E. A. Corley, et al. (2007). "Scientists worry about some risks more than the public." Nature Nanotechnology 2(12): 732-734.

Seager, T. and I. Linkov (2009). "Uncertainty in life cycle assessment of nanomaterials." Nanomaterials: Risks and Benefits: 423-436.

Selin, C. (2007). "Expectations and the Emergence of Nanotechnology." Science, Technology & Human Values 32(2): 196-220.

Selin, C. and R. Hudson (2010). "Envisioning nanotechnology: New media and future-oriented stakeholder dialogue." Technology in Society 32(3): 173-182.

Şengül, H., T. L. Theis, et al. (2008). "Toward Sustainable Nanoproducts." Journal of Industrial Ecology 12(3): 329-359.

Siegrist, M., M. E. Cousin, et al. (2007). "Public acceptance of nanotechnology foods and food packaging: The influence of affect and trust." Appetite 49(2): 459-466.

Siegrist, M., C. Keller, et al. (2007). "Laypeople's and experts' perception of nanotechnology hazards." Risk Analysis 27(1): 59-69.

Siegrist, M., A. Wiek, et al. (2007). "Risks and nanotechnology: the public is more concerned than experts and industry." Nature Nanotechnology 2(2): 67-67.

Smalley, R. E. K. A. S., Daniel T. Colbert, Pavel Nikolaev, Michael J. Bronikowski, Robert K. Bradley, Frank Rohmund (2004). Single-Wall Carbon Nanotubes from High Pressure CO. US.

Smil, V. (2008). Energy in nature and society: general energetics of complex systems, MIT Press.

Stefani, D., A. J. Paula, et al. (2011). "Structural and proactive safety aspects of oxidation debris from multiwalled carbon nanotubes." J Hazard Mater 189(1-2): 391-396.

Szargut, J. and D. R. Morris (1987). "Cumulative exergy consumption and cumulative degree of perfection of chemical processes." International Journal of Energy Research 11(2): 245-261.

Szargut, J., D. R. Morris, et al. (1988). Energy analysis of thermal, chemical, and metallurgical processes.

Theis, T. L., B. R. Bakshi, et al. (2011). "A life cycle framework for the investigation of environmentally benign nanoparticles and products." physica status solidi (RRL) – Rapid Research Letters 5(9): 312-317.

Upadhyayula, V. K. K., D. E. Meyer, et al. (2012). "Life cycle assessment as a tool to enhance the environmental performance of carbon nanotube products: a review." Journal of Cleaner Production 26(0): 37-47.

von Gleich, A., M. Steinfeldt, et al. (2008). "A suggested three-tiered approach to assessing the implications of nanotechnology and influencing its development." Journal of Cleaner Production 16(8-9): 899-909.

Walser, T., E. Demou, et al. (2011). "Prospective environmental life cycle assessment of nanosilver T-shirts." Environ Sci Technol 45(10): 4570-4578.

Wender, B. A. and T. P. Seager (2011). Towards prospective life cycle assessment: Single wall carbon nanotubes for lithium-ion batteries. Sustainable Systems and Technology (ISSST), 2011 IEEE International Symposium on.

Wiek, A., D. J. Lang, et al. (2008). "Qualitative system analysis as a means for sustainable governance of emerging technologies: the case of nanotechnology." Journal of Cleaner Production 16(8-9): 988-999.

Wiek, A., Rider W. Foley and David H. Guston (In press). "Nanotechnology for Sustainability - What does Nanotechnology Offer to Solve Complex Sustainability Problems." " Journal of Nanoparticle Research.

Wiesner, M. R. and J.-Y. Bottero (2011). "A risk forecasting process for nanostructured materials, and nanomanufacturing." Comptes Rendus Physique 12(7): 659-668.

Wiesner, M. R., G. V. Lowry, et al. (2006). "Assessing the Risks of Manufactured Nanomaterials." Environmental Science & Technology 40(14): 4336-4345.

Wilburn, D. R. (2008). Material use in the United States -- Selected case studies for cadmium, cobalt, lithium, and nickel in rechargeable batteries. Scientific Investigations Report 2008-5141, U.S. Geological Survey.