Analysis of Nanotechnology from an Industrial Ecology Perspective Part II: Substance Flow Analysis Study of Carbon Nanotubes

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Revised Draft - November 2005

1. Introduction

The "next plastic," the future for electronics, a new energy storage material. Such descriptors have been given to the nanomaterial carbon nanotubes. These carbon atom cylinders with diameters under 100 nanometers are quickly becoming the focus of significant research and production around the world. Many people estimate that we will see high penetration of carbon nanotubes into everyday products in the near future (Cientifica 2004, Hood 2004, Walsh 2005, Karohl 2005b). At the same time, however, many have expressed concern over the potential health risks from exposure to nanotubes (Lam et al. 2004, Steinfeldt et al. 2004, Warheit et al. 2004, the Royal Society 2004). In order to better understand the scope of nanotube production, use, and destiny, particularly in terms of their impacts in the environment and on human health, this paper presents findings from an investigation into the feasibility of performing a substance flow analysis on carbon nanotubes.

A substance flow analysis (SFA) is a study of the flow of specific materials throughout the economy from cradle to grave. This approach has been called "a tool for analyzing the societal metabolism of substances," (Udo de Haes et al. 2000). It examines and attempts to quantify the inputs of a substance or material into production, end-use applications, and ultimately end-of-life phases. Insight into the material inputs and outputs and other detail at one level or stage (e.g., production) may influence findings at other levels (Graedel et al. 2004).

A SFA can be an appropriate tool when the material of interest is linked to a particular impact and thus warrants a more focused analysis on the "stocks and flows" and "concentrations in the environment," (Bringezu et al. 2003). Because of the potential environmental and health impacts of carbon nanotubes (pending their penetration into products and uses), I hypothesized that the SFA approach would help shed light on the uncertain impacts. More specifically, I suspected that information on the quantity of carbon nanotubes produced would better inform understanding on the application of these substances into end uses, and that end-use information would improve the understanding of potential consequences of carbon nanotubes to users and in the environment.

2. Methodology

To perform a SFA on carbon nanotubes, I gathered production and use information from literature (both journals and news sources) and nanotube company websites. Using a list of U.S. nanotube producers from a *Small Times* survey (2004) and other producers identified during my research, I contacted companies to gather information on their nanotube production and the destination of their materials. I requested the following information from these companies on carbon nanotubes:

- 1) Current production
- 2) Raw material inputs and quantities
- 3) End-use applications and destination of materials.

A few companies were unwilling to provide data due to confidential business information; however, many provided data and useful insights. I used available information and developed assumptions to try to characterize production, use, and end-of-life flows of carbon nanotubes based on available information. Despite the difficulty in obtaining quantitative information, the availability of data on carbon nanotubes were actually greater compared than that for other nanomaterials. In my preliminary analysis, there are also appeared to be distinct manufacturer leaders (Mitsubishi, Carbon Nanotechnologies, Inc.), which would aid in the analysis.

The next section provides a brief overview on carbon nanotubes. Section 4 presents the findings on production, use, and end-of-life, and an overview of the SFA findings. The final section (5) offers conclusions and recommendations for further research.

3. Nanotube Overview

There are two types of carbon nanotubes: single-walled and multi-walled. Single-walled carbon nanotubes consist of one graphite sheet tube of carbon atom hexagons (Figure 1), while multi-walled carbon nanotubes are characterized by multiple concentric tubes (Figure 2); both have a diameter of 1 to 100 nanometers, but average at just a few nanometers. The ends of nanotubes are either open or capped with fullerenes. In 1991, Sumio Iijima of NEC Corporation reported the first observations of multi-walled carbon nanotubes, which resembled whiskers or needles of carbon atoms (Iijima 1991).







Source: The Royal Society 2004.

The significant interest in the production, research and development of carbon nanotubes stems from the unique chemical, mechanical, and physical properties inherent in these materials. These desired properties include high tensile strength, high electric and thermal conductivity, lightweight, high surface area per gram, advantages in hydrogen storing and catalyzing, absorbency, and flexibility. The tensile strength of single-walled nanotubes is 100 times greater than that of steel, at only one sixth of steel weight. In terms of thermal conductivity, carbon nanotubes at 1,200-3,000 W/mK exceed that for diamonds at 700-2,000 W/mK. Carbon nanotubes have even been dubbed "the king of nano materials," (NTP 2005). Table 1 presents a comparison of select properties of carbon nanotubes compared to other structural materials.

Material	Elastic/Young's modulus ¹ (GPa)	Strain (%)	Tensile Strength (GPa)	Density (g/cm ³)	Normalized Strength to Weight Ratio
Single-walled carbon nanotube	542 - 1,054	12	~150	1.4	462
Multi-walled carbon nanotube	400 - 1,200	1.5	~150	1.8 - 2.6	15
Steel	~208	9	0.4	7.8	1
Titanium	103	15		4.5	2
Epoxy	3.5		0.05	1.25	
Wood	16		0.08	0.6	

Table 1: Comparison of Properties of Carbon Nanotubes Compared to Other Materials

Source: Zhang 2005a, Colbert 2003.

Because of these properties, many researchers and product developers have been attracted to carbon nanotubes for a broad array of potential applications including composites, displays, sensors, fuel and solar cells, batteries, and pharmaceutical materials. David Karohl of Carbon Nanotechnologies, Inc. predicts that carbon nanotubes will eventually make their way into just about anything that contains plastic (assuming the price comes down) (2005b). Rocky Rawstern, the editor of Nanotechnology Now, provides an optimistic outlook:

"Nanotubes are one of many nanoscale technologies that are set to revolutionize a significant portion of today's industries, help reduce the cost of consumer products, increase our standard of living world-wide, increase our years of optimal health and vitality, and extend our reach into space," (2004b).

4. Carbon Nanotube SFA Findings

The sections that follow present findings on production, use, and end-of-life, and an overview of the SFA findings. Some information on risks at different life stages is also included.

4.1 Production

Production Estimates

Global production capacity of carbon nanotubes is currently at about 100 metric tons per year (Royal Society 2004). Multi-walled nanotubes comprise the majority (over 90 percent) of that production. Production of carbon nanotubes is projected to expand significantly in the next few years. Based on projections shown in Table 2 below, multi-walled nanotube production will nearly triple between 2004 and 2007 and production of single-walled nanotubes will be over ten times greater in 2008 than production in 2004.

¹ Measure of the stiffness or ratio of stress to strain for a material.

		Product	Average rate of growth			
	2004	2005	2006	2007	2008	(metric tons/year)
Multi-walled nanotubes	99			268		84.5
Single-walled nanotubes	9	27			100	21.7

Table 2:	Worldwide	Annual Ca	arbon Na	notube Es	stimated a	and Pro	jected]	Production

Source: Cientifica 2004. Note: Blank cells indicate where projections were not reported.

The Royal Society (2004) also provides generalized estimates of global production of a combined quantity of single-walled nanotubes for nano-electronics and metal oxides for organic light-emitting diodes. They project production of 100 metric tons per year between 2005 and 2010, and at least 1,000 metric tons of production each year between 2011 and 2020. This information is based on data reported in international chemical journals and market research presented at the Business Communications Company (BCC) Conference on *Fine, Ultrafine, and Nano Particles 2001*.

Producers

In 2004, there were 44 nanotube producers around the world (Cientifica 2005) and at least 24 in the United States (Small Times Survey 2004). According to the ETC Group (2002), there were 55 companies producing carbon nanotubes in 2002. *Nanotechnology Now* identified 16 companies worldwide that are making "*commercial* quantities of nanotubes," (Rawstern 2004b). NanoSpace 2002 also indicated that there are 16 major producers. See Appendix A for a list of companies producing nanotubes and their locations. The majority of production currently takes place in the United States and Japan. However, according to a recent report from Cientifica, entitled "Nanotubes for the Energy Market," carbon nanotube production "is shifting from the United States and Japan to Asia Pacific [Korea and China]. By 2010 the major supplier of all types of nanotubes will be Korea," (Cientifica 2005). Industrial-scale production facilities will soon be in operation in Japan, Korea, China, and France (NanoSpace 2002).

Figure 3 displays the number of carbon nanotube producers by geographical region, and Figure 4 maps out the locations of nanotube producers in the United States. The majority of U.S. nanotube production occurs in Texas (i.e., Austin and Houston) and Massachusetts.



Figure 3: Number of Main Carbon Nanotube Producers by Region



Figure 4: Location of Main Carbon Nanotube Producers in the United States

Note: Markers added to U.S. map from www.theodora.com/maps.

Various sources claim that different companies lead in the production of nanotubes. A *Chemical Engineering* article from 2003 notes that Hyperion Catalysis "claims to be the world's only tonnage-scale producer of carbon nanotubes," (Shelley 2003). According to information reported recently in the *Houston Chronicle*, Carbon Nanotechnologies, Inc. is far ahead of its competition, producing about 25 pounds per day, while its 50 competitors' daily production is only in the grams (Roper 2005). However, based on available production data (shown in Table 3), Carbon Nanotech Research Institute (CNRI) located in Tokyo appears to be the largest producer. CNRI is a subsidiary of Mitsui & Co "engaged in the R&D of industrial commercialization technologies for Fullerene tubes and carbon nanotubes that can be applied in next-generation semiconductors, fuel cells and AIDS medication," (CNRI 2005).

Table 3 presents production data reported by companies. The table is generally ordered by magnitude of production.

	Production (metric tons/yr) ^a	
Producer , Location	& Year of Data	Source
Carbon Nanotech Research	40-120 (projected end of 2003)	Rawstern 2004b
Institute (CNRI), Tokyo, Japan	120 (2002)	Miwako 2002
Nanostructured & Amorphous	9.20 (2003)	Rawstern 2004b
Materials (Nanoamor), Houston,	10-15 (projected end of 2004)	
TX		
Shenzhen Nanotech Port Co	over 2.30 (2003)	Rawstern 2004b
(NTP), Shenzhen, China	(based on 10s of kg's MWNTs and	

 Table 3: Nanotube Production Information by Company

	100s of g's SWNTs/day)	
	10 (projected end of 2004)	
Carbon Nanotechnologies, Inc.	4.14 (2005)	Roper 2005
(CNI), Houston, TX		
NanoCyl, Namur, Belgium	1.61 (based on production in April	Decroly 2005
	2005)	
	2.43 (projected end of 2003)	Rawstern 2004b
Hyperion Catalysis, Cambridge,	1.15 (2003)	Rawstern 2004b
MA		
Catalytic Materials LLC,	0.276 (2003)	Rawstern 2004b
Holliston, MA	1.15 (end of 2003)	
Materials and Electrochemical	0.365 (2001)	Amato 2002
Research (MER) Corporation,		
Tucson, AZ		
NanoLedge, Clapiers, France	0.0276 (2003)	Rawstern 2004b
	0.0460 (projected end of 2003)	
Rosseter Holdings Limited,	0.0345 (2003)	Rawstern 2004b
Limassol, Cyprus		
ec systems	0.0360 (end of 2003)	Rawstern 2004b
NanoLab, Inc.,	0.0120 (2005)	Carnahan 2005
Newton, MA	0.0138 (2003)	Rawstern 2004b
	0.230 (projected end of 2003)	
Carbolex, Lexington, Kentucky	0.00805 (2003)	Rawstern 2004b
Nanocarblab (NCL), Moscow,	0.000690 (2003)	Rawstern 2004b
Russian Federation		
SouthWest NanoTechnologies	Competitive amount	Rawstern 2004b
Inc. (SWeNT [™]), Norman, OK		
Luna nanoWorks	confidential	Clark 2005
Nanocraft Inc	proprietary	Pepka 2005

Note: Assumed annual production operations of 5 days per week for 46 weeks per year for daily estimates. ^aProduction estimates given in three significant digits.

Production Methods

Several methods are used to grow carbon nanotubes. The three main techniques include chemical vapor deposition, arc discharge, and laser ablation, as described below (Royal Society 2004, Shelley 2003, Daenen et al. 2003):

- *Chemical vapor deposition (CVD)* involves heating up a precursor carbon gas (e.g., methane, carbon monoxide, or acetylene) with a plasma or a heated coil and reacting it with a metallic oxide surface catalyst, like nickel or iron; can be used to make both single- and multi-walled nanotubes, however the multi-walled tubes are of higher quality; can be scaled up for commercial production.
- *Arc discharge* involves a "plasma-based process" using a high temperature vapor discharge from one solid carbon electrode to make multi-walled nanotubes on another carbon rod; a metal catalyst is added to create single-walled nanotubes.
- *Laser ablation or pulsed-laser vaporization (PLV)* this method, first reported by Richard Smalley at Rice University in 1995, uses a high-powered laser beam (continuously applied or pulsed) to vaporize powdered graphite with a metal catalyst; only creates single-walled nanotubes; produces smaller quantities than the other two methods, but at a higher purity.

The CVD technique is the most commonly used for making nanotubes. The companies CNRI, ec systems, Nanocyl, NanoLab, Nanoamor, and Shenzhen Nanotech use CVD; MER, Nanocarblab, NanoLedge use arc discharge; ILJIN uses both CVD and arc discharge (Rawstern 2004b). The production methods have not yet been mastered and thus nanotubes have yet to be produced in mass quantities.

Some SWNT producers may be "moving away from the older methods (laser, arc, and CVD)" and using "fluidized beds and other high throughput methods, in order to scale production with relatively low costs," as explained by Mike Moradi, Founder and Former Vice President, SouthWest NanoTechnologies, Inc. (Rawstern 2004b).

Production Inputs/Raw Materials

Estimating the quantity of raw materials needed to produce carbon nanotubes throughout the economy would require specific information from all producers. Because most companies are unable or unwilling to provide this information because of proprietary concerns, I used information from a single company to calculate a generalized estimate of total carbon nanotube production inputs. Based on NanoLab's estimates of raw material inputs used in their CVD production process (Carnahan 2005), the production inputs or raw materials used to produce 12 kg of nanotubes per year are the following:

- process gases, such as acetylene, ammonia, methane, hydrogen (consume 1 tank/year for each, containing about 300 cubic feet of gas at atmospheric pressure).
- ceramic catalyst support particles (consume ~ 2 kg/year).
- iron, cobalt, and nickel compounds to catalyze the growth (consume $\sim 1 \text{ kg/year}$).
- acid bath (of either hydrochloric, nitric, hydrofluoric, etc.), if purification is required afterwards (consume ~ 8 liters/year).²

Because NanoLab's inputs are for the CVD production process, the most common and largestscale nanotube growth technique used by companies currently, I used these estimates roughly to approximate the amount of material inputs used globally to produce carbon nanotubes. The estimate of 108 metric tons (or 108,000 kg) of global carbon nanotube production in 2004 (99 metric tons of multi-walled and 9 metric tons of single-walled nanotubes) is 9,000 times greater than NanoLab's annual production of 12 kg. Thus, the inputs presented above were multiplied by 9,000 to give the total production inputs given in the table below.

² Based on this information, producing 1 kg of carbon nanotubes using CVD would require 708 liters (25 ft³) of acetylene, ammonia, methane, hydrogen gases each; 0.17 kg of ceramic catalyst support particles; 0.08 kg of growth catalysts (iron, cobalt, and nickel compounds); and 0.67 liters of acid bath.

Inputs	Quantities
Process gases:	at atmospheric pressure:
Acetylene	76,464,000 L
Ammonia	76,464,000 L
Methane	76,464,000 L
Hydrogen	76,464,000 L
Ceramic catalyst support particles	18,000 kg
Iron, cobalt, and nickel compounds	9,000 kg
Acid bath (e.g., hydrochloric, nitric, hydrofluoric	72,000 L
acid)	

Table 4: Rough Estimates of Global Inputs Required to Produce 108,000 Kilograms ofCarbon Nanotubes Per Year

Note: Estimates assume the CVD method used for all production and that all producers use approximately the same amount of input materials per kg of production.

Qualitative Risk Information

David Carnahan at NanoLab pointed out that welders dealing with nanomaterial chemical inputs, such as those above, face some of the greatest exposure and risk (2005). He explained, "welders...consume a tank a day of oxygen and acetylene each, when they are busy," especially when the oxygen - acetylene ratio is incorrect (2005). They also inhale nanoparticles when welding metals, far more than laboratory personnel are exposed to. In manufacturing facilities, some believe that workers face low risk. Dr. Zvi Yaniv, President, Director, and CEO Applied Nanotech, Editor NanoExpress indicated that "with respect to production facilities, once the carbon nanotubes are in an ink, a polymer or in other solid composite I do not see serious problems," (Rawstern 2004a).

Appendix B presents potential health risks and exposure limits for the CVD process inputs, as reported by the National Institute for Occupational Safety & Health.

4.2 Use

Key applications for carbon nanotubes include conductive composites, batteries, fuel cells, solar cells, field emission displays, biomedical uses, fibers/fabrics, sensors.³ Currently, few products containing carbon nanotubes are commercially available. Most produced nanotube materials are purchased by research institutions and companies that use the substances for research and development of products (Karohl 2005b, Carnahan 2005). See Table 5. The Royal Society (2004) also indicates that although information on the amount of carbon nanotubes available commercially is company confidential, it remains low. Zhang of Shenzhen Nanotech Port Co. indicated that "some of our nanotubes have been used successfully in FED (Field Emission Display), polymers, electrode materials, which are expected to be commercialized in the coming 1-2 years," (2005b). A White Paper by NanoMarkets actually suggests that "despite all the hype, the truth is that nanotechnology is barely penetrating existing markets, and it is, as yet, not creating any new ones," (Lovy 2004). A recent Research and Markets report (2005), however, explains that "the first products are now about to reach the market in the form of non-volatile memory, field emission displays and sensors."

³ For detection of chemical or biological agents, or material effects.

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Producer	Use (Client, Applications)	Reference
Carbolex	Researchers in academia and industry	Rawstern 2004b
Carbon	650 customer entities	Roper 2005, Karohl 2005.
Nanotechnologies,	10% universities,	_
Inc.	90% commercial companies, research organizations	
	(40% to Asia,	
	40% to North America,	
	20% to Europe); Flat screen displays, plastics,	
	batteries, water purification systems, aerospace,	
	defense, space exploration, fuel cell MEAs	
CNRI	Plastics and electronics manufacturers	Rawstern 2004b
Catalytic	Materials and Battery companies, Catalyst and	Rawstern 2004b
Materials	Automobile manufacturers	
ec systems	Industrial research labs- catalysis, sensors, field	Rawstern 2004b
	emissions	
Hyperion	Automotive and Electronics Industry	Rawstern 2004b
Catalysis		
Nanocarblab	Major academic institutions and universities in the	Rawstern 2004b
	Russian Federation. For laboratory research and	
	industrial applications.	
NanoCyl	University labs and research institutes, and	Rawstern 2004b, Decroly
	corporate R&D departments. Mainly for research	2005
	and evaluation purpose, and some developmental	
	stage; 100% composite materials (not yet	
	commercially available –expected 06)	-
Nanoamor	Academic research & industrial applications; Flat	Rawstern 2004b
	Panel Display, conductive polymers, reinforcement,	
	dispersion, composites	<u> </u>
NanoLab, Inc.	primarily universities	Carnahan 2005
NanoLedge	Aerospace, Materials and Chemical Companies	Rawstern 2004b
Rosseter	Chemical, electronics, aircraft, and automotive	Rawstern 2004b
	industries, and defense	P
Shenzhen	Companies that use CNTs for Multi-functional	Rawstern 2004b
Nanotech	composites; Electrode material of supercapacitors;	
	Electro-conductive agent material in lithium ion	
	batteries; Field emission material; Composites,	
	supercapacitors, lithium ion batteries, field	
	emission material	D (20041
SWeNT	variety of industries; main focus: Flat Panel Display	Rawstern 2004b
1	materials and structural and conducting composites.	

 Table 5: Nanotube Use Information by Company

As shown in the figure below, the distribution of nanotubes from one company, Shenzhen Nanotech Port Co (NTP) in China, to research institutes and universities has shifted somewhat. In 2004, enterprises purchased the largest share of nanotubes. Other companies may be experiencing a similar trend.



Figure 5: Carbon Nanotube Distribution for NTP

Because few products are commercially available and many carbon nanotubes applications are still in the early research and development stages, characterizing nanotubes in the economy for the SFA proves challenging. In addition, applications of nanotubes are expected to change radically in the next few years. Karohl indicates that he expects no correlation between sales today and in ten years (2005a). He indicates that if prices come down, nanotubes will be used in any products that contain plastics because nanotubes behave like specialty polymers.⁴ The *Boston Business Journal* (2004) estimated that the market for carbon nanotubes will grow from \$12 million in 2002 to \$500-700 million in 2005. Business Communications Co., Inc. forecasts a more modest growth to \$232 million in 2006 (BCC 2003). The Mitsubishi Research Institute projects that the Japanese market for carbon nanotubes will total \$1.4 billion by 2010 (Zhang 2005a). These and other market estimates are displayed in the next table.

Reference	2000	2001	2002	2004	2005	2006	2007	By 2009
Frost & Sullivan 2004		\$10					\$540	
(cited in Kelly 2004)		million					million	
Research and Markets			\$12		\$700			
2002			million		million			
Nanocyl 2005	\$1.4			>\$430				Several
	million			million				\$billion
Boston Business Journal			\$12		\$500-			
2004 (cited in Zhang			million		700			
2005a)					million			
BCC 2003			\$11.9			\$232		
			million			million		

 Table 6: Global Estimates of the Market for Carbon Nanotubes by Source

Although it is difficult to characterize the dissipation of nanotubes into end use applications based on general or limited company data, patents provide some useful information. Figure 6 presents a breakdown of nanotube applications based on international patent filings and issuance.

Source: Zhang 2005a. Note: "Individuals" refers to independent researchers purchasing carbon nanotubes.

⁴ Cientifica (2005) estimates that prices for carbon nanotubes will drop by a factor of 10-100 over the next five years.



Figure 6: Carbon Nanotube Applications: International Patent Filings & Issuance (2002)

Source: Based on Zhang 2005a.

Based on the percentages above, I made rough approximations of the dissipation of the produced carbon nanotubes into use for the SFA. Using an assumption that 1 percent of international patent filings and issuance for each application equates to 1 percent of nanotube material use, I estimated the following regarding the 108 metric tons of carbon nanotubes produced in 2004:

- 44.3 metric tons goes into synthesis and processing,
- 27.0 metric tons into electron emission product research and development,
- 9.7 metric tons into battery and supercapacitor product research and development,
- 6.5 metric tons into electronic product research and development,
- 6.5 metric tons into hydrogen storage research and development,
- 3.2 metric tons into sensor and probe product research and development, and
- 3.2 metric tons into other developments.

These estimates may not necessarily correspond correctly with actual tonnage in use for each application. As Professor Nathan Swami of the University of Virginia pointed out, the pharmaceutical industry has the largest number of patents, but uses the least amount of material compared to structural applications. In this case, the percentage of carbon nanotube patents are highest for synthesis and processing possibly because "companies want to patent material forms and synthesis routes, and thereby affect other markets such as displays, electronics, etc.," (Swami 2005). However, the synthesis and processing sector may not actually consume as much as 44 metric tons of carbon nanotubes estimated with patent information. Because of the limited information publicly available on end uses and the limited penetration of carbon nanotubes into commercial products, improved tonnage estimates are difficult to quantify at this time.

Sales information and projections for specific products can help us better understand the potential diffusion of nanotubes within applications. Nanotubes are gradually making their way into product development, and a few products containing nanotubes are commercially available.

One product that is available is the Babolat tennis racquet, using Nanoledge⁵ nanotubes; however this product contains very few nanotubes. Dr. Loutfy of Materials and Electrochemical Research Corporation explains that nanotubes produced in Japan are already in use in cell phone lithium batteries (2005). According to Dr. David Tomanek, Professor of Physics at Michigan State University, the proportion of lithium-ion batteries currently containing carbon nanotubes is over 60 percent (Rawstern 2004a). In 2005, sales of single-walled nanotubes were expected to comprise 22 percent of conductive plastic sales (\$3.6 billion) and 9 percent of advanced composite sales (\$12.5 billion) (based on Colbert 2003). Over the next 5 years, nanotubes are expected to penetrate 70 percent of all fuel cells (Cientifica 2005).⁶

Development of displays containing carbon nanotube emitters is also growing. Companies purchasing carbon nanotubes for field emission application development include: Samsung, DuPont, Saito, Noritake, Mitsubishi, Motorola, French Atomic Energy Commissariats Laboratory of Electronics and Information Technology in Grenoble, and cDream (Mann 2004). A 40 inch computer display uses one-sixth of a gram of carbon nanotube powder (roughly 10,000 nanotubes) (Mann 2004). If all 25 metric tons of carbon nanotubes going to electron emission applications (estimated above) are used for computer displays, they would enter into 150 million displays. These nanotube field emission displays reduce monitor weight and power use and improve video quality (NanoMarket 2005).

Carbon nanotube researchers were surveyed by *NanoNews-Now* to give their opinions on the most promising (or likely) applications of nanotubes and buckyballs in next five to ten years (Rawstern 2004a). Researchers projected the following:

- "In order of my choice of importance and market magnitude...large area CNT TVs, nanobiosensors, catalysts for methanol fuel cells, catalysts for NO_x reduction," (Dr. Zvi Yaniv, President, Director, and CEO Applied Nanotech).
- "In my biased opinion, most promising is as a component or coating in orthopedic implantsagain a lot more work is needed especially in animal studies for this context," (Dr. Thomas J. Webster, Assistant Professor of Biomedical Engineering and of Materials Engineering, Purdue University).
- "Conductive coatings, adhesives, and composites; passive electronic devices, flat panel displays; fuel cell & battery electrodes," (Mike Moradi, Founder and Former Vice President of SouthWest NanoTechnologies, Inc.).

If carbon nanotube sales projections were available for multiple products or industry lines, the estimates of material used could potentially be estimated using dollars, rather than patent information.

Qualitative Risk Information

Some companies are taking the lead in addressing toxicity issues before introducing products into industrial applications. One such company, ApNano Materials, Inc. based in Israel, performed initial toxicity testing of its nano-sphere and tube based NanoLub lubricant in accordance with the European Commission's Good Laboratory Practices (Nano Techwire.com

⁵ Company based in France.

⁶ Multi-walled nanotubes can improve performance of fuel cells tenfold and reduce the cost of catalyst material by 50% (Cientifica 2005).

2005). CNRI has adopted a policy "not to supply product in the powder form" in order to avoid any dispersion risks (Rawstern 2004a).

Others suggest that limited risks arise from carbon nanotubes in our environment. For instance, Dr. Mark Weisner of Rice University explains that nanotubes clump together and thereby present a low risk as compared to single fibers, such as asbestos (ETC Group 2002). Yet, some researchers are exploring ways to reverse this clumping effect in order to use single fibers for other purposes. Research by Silvana Fiorito revealed that the immune system responds when a micrometer-sized carbon particle enters a cell, but not when a nano-sized carbon particle enters. This is helpful when nanotubes need to deliver medicine in the body, but not when the body should be fighting off these unwanted substances (ETC Group 2002).

4.3 End-of-Life

Because limited amounts of nanotubes are actually in use on the market, predicting or quantifying end-of-life outcomes of products is difficult. Incineration is already occurring. For nanotubes out of company specification, NanoLab incinerates them. Carnahan (2005) explains that nanotubes burn at about 400 degrees Celsius, like other carbon structures. Thus, NanoLab recommends that other researchers or users of nanotubes dispose of them through incineration or oxidation as well. However, he also points out: "I don't know if other researchers follow our disposal recommendations, so they could end up in landfills," (Carnahan 2005). David Karohl of CNI indicates that nanotubes can be recycled because reprocessing will not break apart the nanotubes (2005b). He seemed to suggest that this quality is a benefit compared to typical polymers; however, if these materials are disposed improperly they could present serious problems in the environment.

At this point, trying to quantify end-of-life outcomes would be purely speculation. However, to provide a crude estimate of end-of-life outcomes, one option involves using estimated breakdowns of waste management scenarios. These vary by source, location, and materials included. An EPA report characterizing U.S. municipal solid waste, estimates that 30.6 percent of materials generated were recovered, 14.1 percent were combusted, and 55.4 percent were landfilled (EPA 2005). Applying these estimates to the 108 metric tons of carbon nanotubes produced, would indicate that 33.0 tons will be recovered for recycling, 15.1 tons combusted, and 59.8 tons discarded to a landfill. Please note that variations in waste management practices in other countries (especially Japan) where nanotubes are produced have not been evaluated.

4.4 Combined SFA Findings

The flow diagram below presents a general overview of the SFA findings discussed in this paper.



Certainly the estimates presented here are quite generalized based on limited information, the small quantity of nanotubes in commercial applications, and a rapidly changing market. They are meant to provide an initial framework for understanding the flows of carbon nanotubes throughout the economy.

5. Conclusions

The results of this paper demonstrate the difficulty in characterizing the flow of nanomaterials within the economy. This is due to the newness of the development of these technologies, the broad range of potential applications of nanotubes, and limited publicly available data. The small number of products currently on the market containing carbon nanotubes also makes it difficult to track the actual fate of these materials. Yet, the widespread projected application of these nanomaterials into so many everyday products makes the characterization of the flow of nanotubes even more important.

Narrowing the scope of an SFA to evaluate a substance (nanotube) within one particular endproduct, such as a lithium battery or field emission display, may provide clearer insight into the penetration and potential impacts of these substances from cradle to grave. Increased collaboration with both material producers and product developers would also aid in this effort.

REFERENCES

BCC. 2003. "Nanotubes: Directions and Technologies." Business Communications Co.

Bringezu, S., H. Schutz, and S. Moll. 2003. "Rationale for and Interpretation of Economy-Wide Materials Flow Analysis and Derived Indicators." *Journal of Industrial Ecology*. 7(2):43-64.

Carnahan, David. 2005. E-mail communication with David Carnahan, NanoLab, <u>dcarnahan@nano-lab.com</u>. April 7, 8, and 14.

Cientifica. 2004. "Nanotubes." Cientifica. March. http://www.cientifica.com/html/docs/Nanotubes%202004 ExSum.pdf

Cientifica. 2005. "Nanotubes for the Energy Market." Executive Summary. Cientifica. April.

Clark, Karin. Director of Marketing & communications. 4-22-05, Luna nanoWorks. kclark@lunainnovations.com

CNRI. 2005. Carbon Nanotech Research Institute Website. http://www.xnri.com/English/rd/cnri/index.html

Colbert, Daniel. 2003. "Single-wall nanotubes: a new option for conductive plastics and engineering polymers." Plastics Additive & Compounding. Carbon Nanotechnologies, Inc. January/February.

Daenen, M., R.D., de Fouw, B. Hamers, P.G.A. Janssen, K. Schouteden, and M.A.J. Veld. 2003. "The Wondrous World of Carbon Nanotubes." Eindhoven University of Technology. February 27.

Decroly, Olivier. 2005. E-mail communication with Olivier Decroly, Global Business Development Manager, Nanocyl S.A., <u>odecroly@nanocyl.com</u>, April 21.

EPA. 2005. "Municipal Solid Waste Generation, Recycling, and Disposal in the United States: Facts and Figures for 2003." U.S. Environmental Protection Agency. EPA530-F-05-003. April.

ETC Group. 2002. "No Small Matter! Nanotech Particles Penetrate Living Cells and Accumulate in Animal Organs." ETC Communiqué, The Action Group on Erosion, Technology and Concentration. May/June. 76:1-8.

Graedel, T. E., D. van Beers, M. Bertram, K. Fuse, R. B. Gordon, A. Gritsinin, A. Kapur, R. J. Klee, R. J. Lifset, L. Memon, H. Rechberger, S. Spatari, and D. Vexler. 2004. "Multilevel Cycle of Anthropogenic Copper." *Environmental Science & Technology*, 38 (4):1242-1252.

Hood, Ernie. 2004. "Nanotechnology: Looking As We Leap." Environews, *Environmental Health Perspectives*. 112(13). September. <u>http://ehp.niehs.nih.gov/members/2004/112-13/EHP112pa740PDF.PDF</u>

Iijima, Sumio. 1991. "Helical microtubules of graphitic carbon." Nature. 354(6348):56-58.

Karohl, David. 2005a. E-mail communication with David Karohl, Director of Business Development, Carbon Nanotechnologies, Inc., karohl@cnanotech.com, April 5.

Karohl, David. 2005b. Personal communication with David Karohl, Carbon Nanotechnologies, Inc., (281) 492-5730, April 14.

Kelly, Matt. 2004. "Atomate on Path of Building Better Nanoscale Tools." *Small Times*. November 12.

Lam, Chiu-Wing, J.T. James, R. McCluskey, and R.L. Hunter. 2004. "Pulmonary Toxicity of Single-Wall Carbon Nanotubes in Mice 7 and 90 Days After Intratracheal Instillation." *Toxicological Sciences*. 77:126-134. January.

Loutfy, Raouf. 2005. Personal communication with Raouf Loufty, MER, 520-574-1980, April 7.

Lovy, Howard. 2004. "Can Nano Create New Markets?" White Paper: Quantifying the disruptive power of nanotechnology. NanoMarkets, LC. April.

Mann, Charles. 2004. "Nanotech on Display." Technology Review. November.

Nanocyl. 2005. "What is the Market for Carbon Nanotubes?" Frequently Asked Questions on Nanocyl Website. <u>http://www.nanocyl.com/faq/answer.php?id=8</u>

NanoMarket. 2005. "Plastics, Nanotubes and the Mobile Displays of the Future." Excerpt from the report <u>The Market for Flexible Displays and Field Emission Displays</u>. April 12.

NanoSpace. 2002. "Carbon Nanotubes - Worldwide Status and Outlook: Applications, Applied Industries, Production, R&D and Commercial Implications." NanoSpace Technologies, Inc. January. <u>http://www.nanospace.org/new_page_64.htm</u>

Nano Techwire.com. 2005. "World's First Commercial Nanotechnology-Based Solid Lubricant Declared Non-Toxic." Nano Techwire.com. April 7.

NIOSH. 1995. "Documentation for Immediately Dangerous to Life or Health Concentrations (IDLH): NIOSH Chemical Listing and Documentation of Revised IDLH Values." National Institute for Occupational Health and Safety, Center for Disease Control. NTIS Publication No. PB-94-195047. March 1. <u>http://www.cdc.gov/niosh/idlh/intridl4.html</u>

NIOSH. 2005. "International Chemical Safety Cards." National Institute for Occupational Safety and Health, Center for Disease Control. Last Updated April 1.

NTP. 2005. Shenzhen Nanotech Port Co (NTP) Website. http://www.seasunnano.com/ntp/products.htm Rawstern, Rocky. 2004a. "<u>Nanotubes and Buckyballs</u>." *NanoNews-Now*. Issue 11. May <u>http://www.nanotech-now.com/products/nanonewsnow/issues/011/011.htm</u>

Rawstern, Rocky. 2004b. "Nanotube Surveys." Disruptive Technology Series, Nanotechnology Now. November 3, 2004 Version. <u>http://www.nanotech-now.com/nanotube-survey-april2003.htm</u>

Roper, John. 2005. "Tiny tubes loom large. Company is poised to be a force as nanotechnology gains momentum." Houston Chronicle, March 5.

The Royal Society. 2004. "Nanoscience and nanotechnologies: opportunities and uncertainties." The Royal Society of Engineering. July 29. <u>http://www.nanotec.org.uk/finalReport.htm</u>

Shelley, Suzanne. 2003. "Carbon Nanotubes: A Small-Scale Wonder." *Chemical Engineering*. February.

Small Times Survey. 2004. "2004 National Small Tech Commercialization Survey." Presented at NanoCommerce 2004. September.

Steinfeldt, Michael, Ulrich Petschow, and Rüdiger Haum. 2004. "Nanotechnology and Sustainability." *Partnerships for Sustainability Development*, 12th International Conference of Greening of Industry Network, Hong Kong. November 7-10, 2004.

Swami, Nathan. 2005. Comments received from Professor Nathan Swami, University of Virginia on the draft of this report, June 8, 2005.

Udo de Haes, H., R. Heijungs, G. Huppes, E. van der Voet, and J. Hettelingh. 2000. "Full Mode and Attribution Mode in Environmental Analysis." *Journal of Industrial Ecology*. 4(1):45-56.

Walsh, Scott. 2005. Personal communication with Scott Walsh, Project Manager, Environmental Defense, (202) 387-3500, March 8, 2005.

Warheit, D.B., B.R. Laurence, K.L. Reed, D.H. Roach, G.A.M. Reyolds, and T.R. Webb. 2004. "Comparative Pulmonary Toxicity Assessment of Single-wall Carbon Nanotubes in Rats." *Toxicological Sciences*. 77:117-125. January.

Zhang, Christine. 2005a. "Applications and Market of Carbon Nanotubes (CNTs)." Shenzhen Nanotech Port Co., Ltd. Presentation given February 2005 at the International Nanotech 2005 Exhibition in Japan. Accessed from website May 2005. http://www.seasunnano.com/ntp/index.htm

Zhang, Christine (Chuanyi). 2005b. E-mail communication from Christine (Chuanyi) Zhang, Shenzhen Nanotech Port Co., Ltd., <u>chuanyi.zhang@gmail.com</u>, on May 13, 2005.

APPENDIX A: CARBON NANOTUBE PRODUCERS

Degion/Company and Location	Wabaita	Making Commercial Quantities ^a (V or N)		
Region/Company and Location	website	(Y OF N)		
Abwahnaa Taahnalagu San Jasa CA	http://www.ahwahneetech.com/			
RuckyUSA Houston TY	http://www.anwaniceteen.com/			
Carbolay Lovington KV	http://carboley.com/	V		
Carbon Nenotochnologios (CNI)	http://www.cnanotech.com			
Houston TX	http://www.enanoteen.com	I		
Carbon Solutions. Inc. Riverside CA	http://www.carbonsolution.com/			
Catalytic Materials LLC Holliston	http://www.catalyticmaterials.com/	Y		
MA		1		
ec systems		Y		
Fullerene International Corp.	http://www.fullereneinternational.com/			
Tucson AZ	-			
Concerci Flootuio	http://geglobalresearch.com/			
General Electric	01_coretech/nanotechnology.shtml			
Hyperion Catalysis International,	http://www.fibrils.com	Y		
Matorials and Floatrochomical	http://www.mercorp.com	V		
Research Corp. (MER). Tueson, A.7		I		
NenoCraft Ing Penton WA	http://www.nanocraftinc.com/			
Nanoci att Inc., Kenton, WA	http://www.nanocs.com/			
Nanol ab Inc. Brighton MA	http://nano-lab.com	V		
NanoLab Inc., Brighton, MA	http://www.papo-	1		
Nano-Proprietary, Austin, TX	proprietary.com/index.htm			
NanoSonic Inc., Blacksburg, VA	http://www.nanosonic.com/			
Nanostructured & Amorphous	http://www.nanoamor.com	Y		
Materials, Houston, TX				
SES Research, Houston, TX	http://www.sesres.com/index.asp			
SouthWest NanoTechnologies Inc.	http://www.swnano.com/	Y		
(SWeNT TM), Norman, Oklahoma				
Xintek, Research Triangle Park, NC	http://www.xintek.com/			
Zyvex, Richardson, TX	http://www.zyvex.com/			
ASIA				
Carbon Nanotech Research Institute	http://www.xnri.com/English/	Y		
(CNRI), Tokyo, Japan		-		
Showa Denko, Tokyo, Japan	http://www.sdk.co.jp/index_e.htm	unknown		
ILJIN Nanotech, Seoul, Korea	http://www.iljinnanotech.co.kr/	Y		
Shenzhen Nanotech Port Co (NTP),	http://www.seasunnano.com/	Y		
Shenzhen, China				
Yorkpoint New Energy Science and		unknown		
Technology Development Co.,				
Guangzhou, Guangdong Province				
EUROPE	http://www.papogyl.com/	X7		
Nanocyl, Namur, Belgium.	http://www.nanocyl.com/	Y		
NanoLedge, Clapters, France	http://www.nanoicuge.com/	Y		
Rosseter Holdings Limited, Limassol, Cyprus	http://www.e-nanoscience.com/	Y		
Nanocarblab (NCL) Moscow Russian	http://nanocarblab.com	V		
Federation	· ·	1		

^aAccording to Rawstern 2004b. Source: Rawstern 2004b, Small Times 2004, Company websites.

APPENDIX B: EXPOSURE LIMITS AND HEALTH RISKS FROM SOME NANOTUBE PRODUCTION INPUTS AS REPORTED BY THE NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY & HEALTH (NIOSH)

Inputs ^a		Occupa	tional Exposure	Limits ^b		Other Risks ^b			
	Revised Immediately Dangerous to Life (IDLH) Value ^c	Threshold Limit Value (TLV)	Maximum Workplace Concentration (MAK)	OSHA Permissible Exposure Limit (PEL)	NIOSH Recommende d Exposure Limit (REL)	Exposure Routes	Inhalation Risk	Effects of Short-term exposure	Effects of Long- term or Repeated Exposure
Process gases:		i						i	
Acetylene	8 ppm (acetylene tetrabromide)	Simple asphyxiant	not established.	none	C 2500 ppm (2662 mg/m ³)	can be absorbed into the body by inhalation.	On loss of containment this gas can cause suffocation.	Suffocation.	Not given
Ammonia	300 ppm	25 ppm; 17 mg/m ³ (as TWA); 35 ppm; 24 mg/m ³ (as STEL)	20 ppm; 14 mg/m ³	TWA 50 ppm (35 mg/m ³)	TWA 25 ppm (18 mg/m ³) ST 35 ppm (27 mg/m ³)	can be absorbed into the body by inhalation.	A harmful concentration of this gas in the air will be reached very quickly on loss of containment.	Corrosive to the eyes, the skin, and the respiratory tract. Inhalation of high conc. may cause lung oedema Rapid evaporation of the liquid may cause frosthite	Not given
Methane		Simple asphyxiant	not established.			can be absorbed into the body by inhalation.	On loss of containment can cause suffocation.	Rapid evaporation of the liquid may cause frostbite.	Not given
Hydrogen	30-100 ppm (depending on type)	Simple asphyxiant				can be absorbed into the body by inhalation.	On loss of containment, a harmful concentration of this gas in the air will be reached very quickly.	Simple asphyxiant.	Not given.

Inputs ^a		Occupa	tional Exposure	Limits ^b			Other Risks ^b			
	Revised Immediately Dangerous to Life (IDLH) Value ^c	Threshold Limit Value (TLV)	Maximum Workplace Concentration (MAK)	OSHA Permissible Exposure Limit (PEL)	NIOSH Recommende d Exposure Limit (REL)	Exposure Routes	Inhalation Risk	Effects of Short-term exposure	Effects of Long- term or Repeated Exposure	
Metal compounds								1	1	
Iron compounds	Iron oxide dust and fume: 2,500 mg Fe/m ³									
Cobalt compounds	Cobalt metal, dust and fume: 20 mg Co/m ³	0.02 mg/m ³ as TWA	(inhalable fraction) Sah; Carcinogen category: 2; Germ cell mutagen group: 3A	TWA 0.1 mg/m ³	TWA 0.05 mg/m ³	can be absorbed into the body by inhalation.	A harmful concentration of airborne particles can be reached quickly when dispersed.	Substance (as fume or dust) is mildly irritating to the respiratory tract.	Contact may cause skin sensitization. Inhalation exposure may cause asthma. Lungs may be affected by repeated or prolonged exposure. Possibly carcinogenic.	
Nickel compounds	Nickel metal and other compounds: 10 mg Ni/m3	1.5 mg/m ³ (I) as TWA A5				can be absorbed into the body by inhalation of the dust.	Evaporation at 20°C is negligible; a harmful concentration of airborne particles can, however, be reached quickly when dispersed.	May cause mechanical irritation. Inhalation of fumes may cause pneumonitis.	Contact may cause skin sensitization. Inhalation exposure may cause asthma. Lungs may be affected by repeated or prolonged exposure. Possibly carcinogenic.	
Acid bath										
Nitric acid	25 ppm	2 ppm; 5.2 mg/m ³ (as STEL: 4 ppm; 10 mg/m ³)		TWA 2 ppm (5 mg/m ³)	TWA 2 ppm (5 mg/m ³) ST 4 ppm (10 mg/m ³)	can be absorbed into the body by inhalation of its vapour and by ingestion.	A harmful contamination of the air can be reached very quickly on evaporation of this substance at 20°C.	Very corrosive to the eyes, the skin and the respiratory tract. Corrosive on ingestion as well. Inhalation of vapour may cause lung oedema.	Not given.	

Inputs ^a	Occupational Exposure Limits ^b Othe						other Risks ^b		
	Revised	Threshold	Maximum	OSHA	NIOSH	Exposure	Inhalation	Effects of	Effects of Long-
	Immediately Dangerous to	Limit Value (TLV)	Concentration	Permissible Exposure	Recommende d Exposure	Routes	Risk	Short-term	term or Repeated
	Life (IDLH)	(11)	(MAK)	Limit (PEL)	Limit (REL)			exposure	Exposure
	Value ^c								1
Hydrochloric acid, anhydrous	50 ppm	5 ppm		C 5 ppm (7 mg/m ³)	C 5 ppm (7 mg/m ³)	can be absorbed into the body by inhalation.	A harmful concentration of this gas in the air will be reached very quickly on loss of containment.	Rapid evaporation of the liquid may cause frostbite. Corrosive to the eyes, the skin and the respiratory tract. Inhalation of high concentrations of the gas may cause pneumonitis and lung oedema, resulting in reactive airways dysfunction syndrome. Effects may be delayed	Substance may have effects on the lungs, resulting in chronic bronchitis. May have effects on the teeth, resulting in erosion.
Hydrofluoric acid, anhydrous		3 ppm	3 ppm; 2.5 mg/m ³ ; MAK as STEL: 6 ppm; 5 mg/m ³	TWA 3 ppm	TWA 3 ppm (2.5 mg/m ³) C 6 ppm (5 mg/m ³) 15- minute	can be absorbed into the body by inhalation, through the skin and by ingestion.	A harmful concentration of this gas in the air will be reached very quickly on loss of containment.	nay be delayed. corrosive to the eyes, the skin and the respiratory tract. Inhalation of this gas or vapour may cause lung oedema. May cause hypocalcemia. Exposure above the OEL may result in death. Effects may be delayed.	May cause fluorosis.

Note: STEL: short-term exposure limit; TWA: time-weighted average ^a Inputs to CVD process, as shown in Table 4. ^b NIOSH 2005. ^c NIOSH 1995.