A Briefing on Carbon Nanotubes

Mike Ellenbecker (TURI)

Molly Jacobs (U Mass Lowell – Lowell Center for Sustainable Production)

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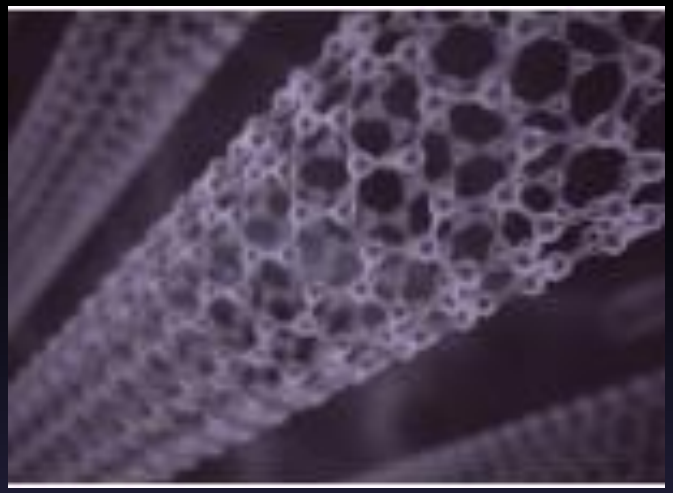
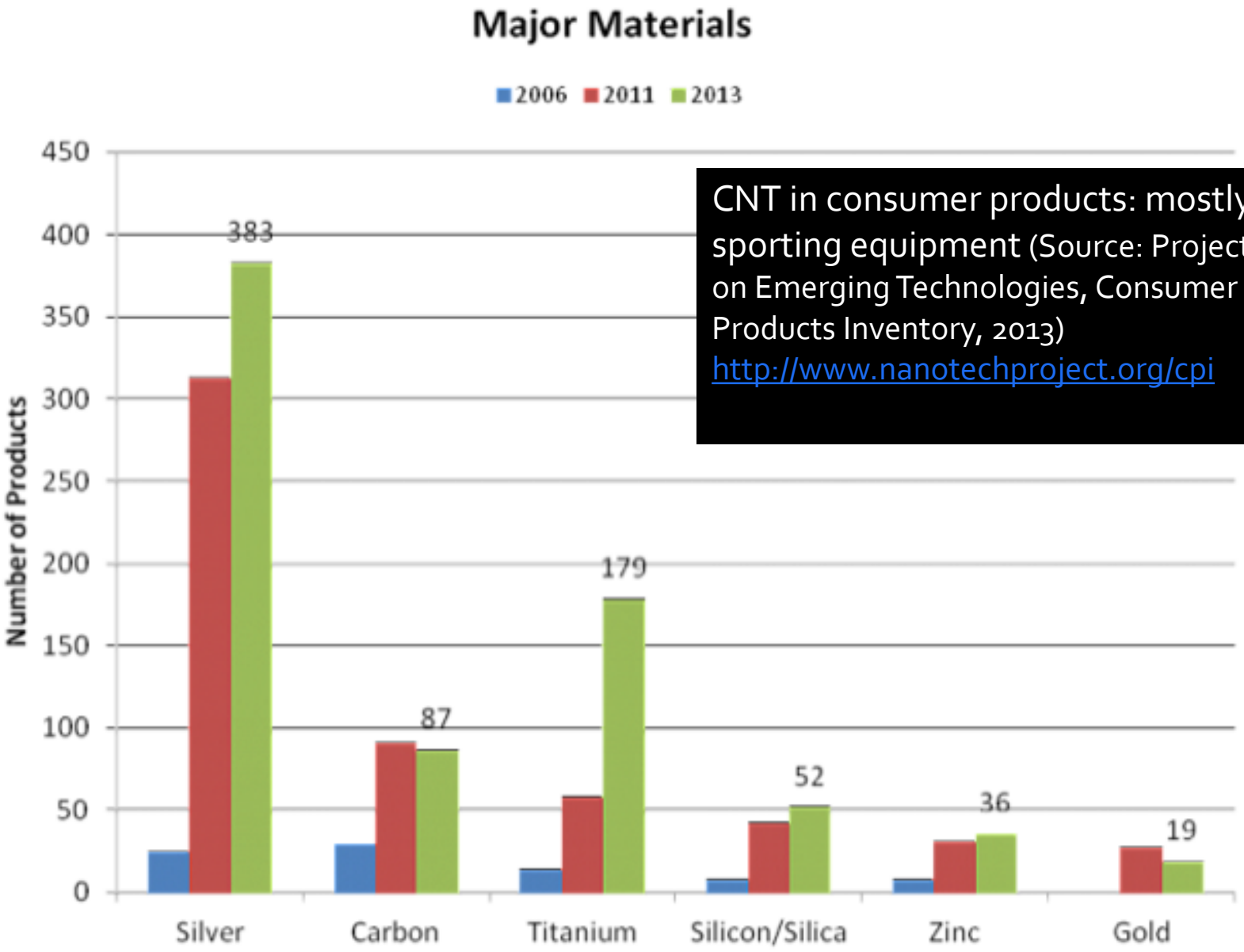
Overview

1. Essential background "what are CNTs?"
2. Massachusetts Context
3. Overview on the state of the science – ES&H
4. Regulatory landscape

Engineered Carbon Nanotubes – what are they?



- Discovered in 1991
- Divided into 2 broad categories:
  - Single-walled CNTs (SWCNTs)
  - Multi-walled CNTs (MWCNTs)
- Important: CNTs are not a single material. ~50,000 SWCNTs and likely even more potential combinations of MWCNTs
  - Vary based on size, shape, chemical composition, reactivity, etc.



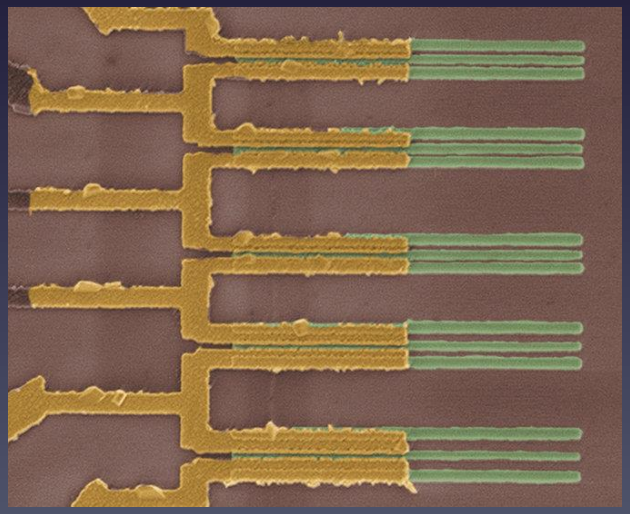
CNT in consumer products: mostly sporting equipment (Source: Project on Emerging Technologies, Consumer Products Inventory, 2013) http://www.nanotechproject.org/cpi

Figure 5. Numbers of products associated with specific materials.

New York Times, 1 Oct 2015

"IBM Scientists Find New Way to Shrink Transistors"

- CNT field effect transistors
- Increase speed and/or reduce power use by a factor of 7

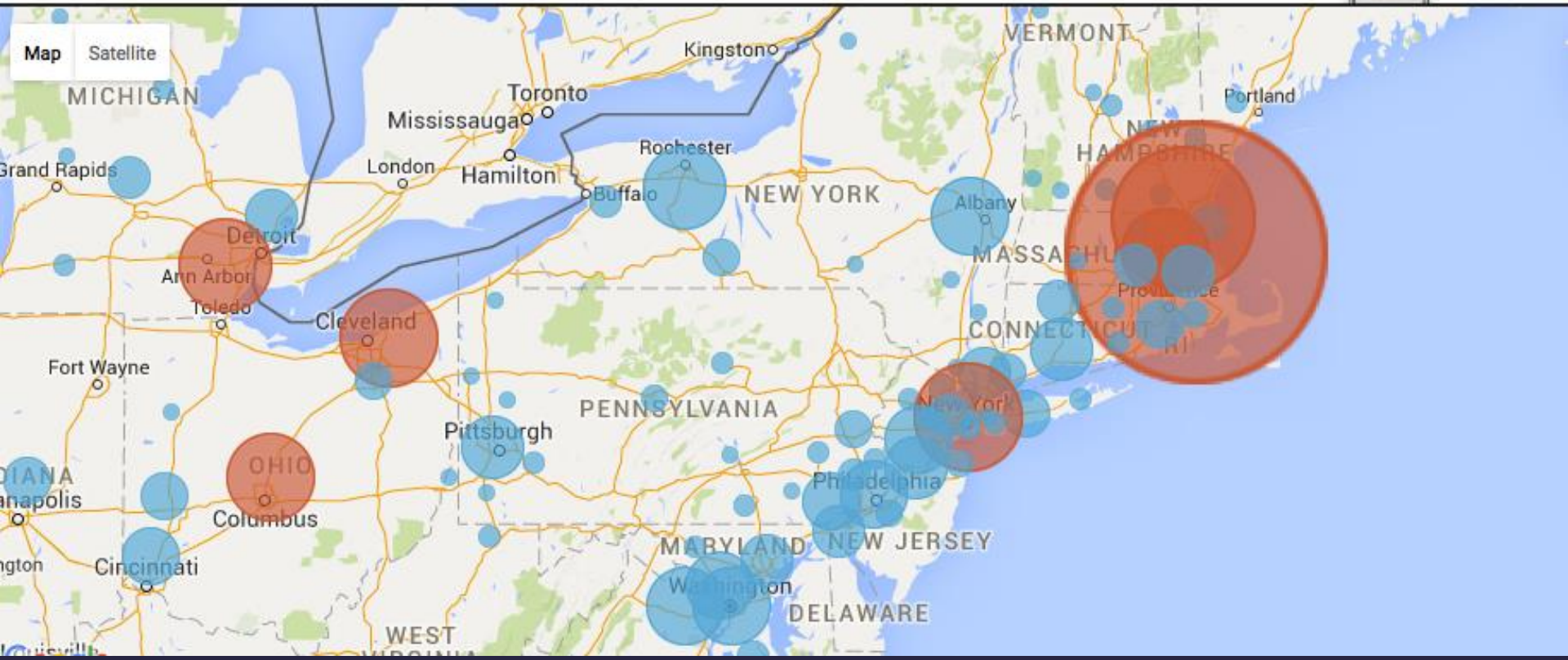


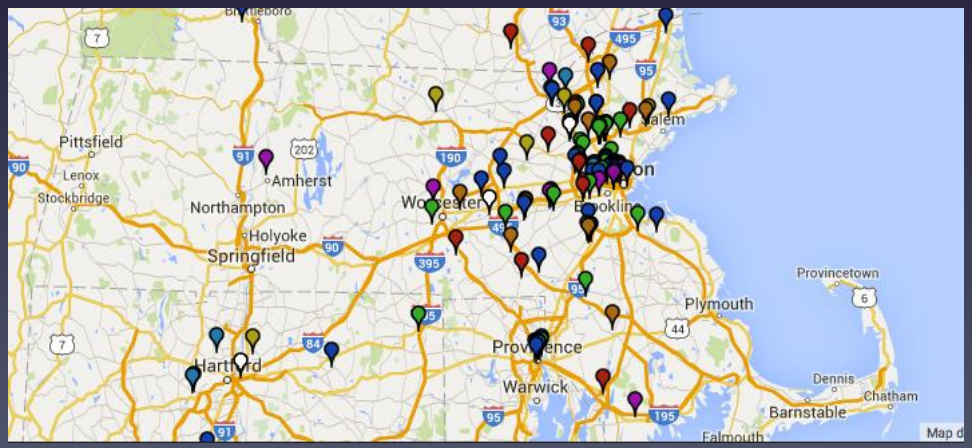
CNTS: One of the superstars of the nanotechnology revolution

Emerging as substitutes for chemical toxicants

Anti-fouling marine paints
[substitutes for tributyltin, copper boat paints, etc]

Flame retardants for electronics, wire/cable, textiles, foams [substitutes for halogenated flame retardants]





MA is among the top 5 in the country for commercial and R&D activity on nanomaterials/nanotechnology

Commercial Use Activity of Carbon Nanotubes in MA

Manufacturing/Production

- Hyperion Catalysis – Cambridge [among the top international suppliers]
- Nano C - Westwood
- Nano Lab - Waltham

Use in product manufacturing

- Nantero (memory devices) – Woburn
- Alpha Szenzor (biosensors) – Carlisle
- Ambit Corp (electronic and optical devices) – Ashland
- Eikos (coatings) – Franklin

R&D

- Busek (CNT manufacturing for aerospace applications) – Natick

Source: Nanowerk & website research Apr 2016

Use Volume?

	Manufacturers	Annual production capacity (Metric tonnes)	Processing routes	Country
SWCNTs	Unidym, Inc. (acquired by Wisepower Co.), http://www.unidym.com	1.5	High-pressure carbon monoxide (HiPco)	USA
	Toray Industries, Inc. http://www.toray.com	1.5	CCVD	Japan
	Mitsubishi Rayon Co. Ltd. http://www.mrc.co.jp/english/index.html	1.2	CVD	Japan
	SouthWest NanoTechnologies Inc. http://www.swentnano.com	1.0	Cobaltmolybdenum catalyst (CoMoCAT)®	USA
	Kleancarbon Inc. http://www.kleancarbon.com	1.0	CVD	Canada
MWCNTs	Showa Denko K.K http://www.sdk.co.jp/english	500	CCVD	Japan
	CNano Technology Limited http://www.cnanotechnology.com	500	CCVD	USA
	Nanocyl S.A., http://www.nanocyl.com*	400	CCVD	Belgium
	Bayer MaterialScience AG http://www.bayermaterialscience.com	260	CCVD	Germany
	Arkema Inc. http://www.arkema-inc.com	50	CCVD	France
	Hyperion Catalysis International, Inc. http://www.hyperioncatalysis.com	50	CVD	USA

*Table 2: Major Carbon Nanotubes Producers and their Annual Production Capacity for 2010. **

Source: Nanowerk, Oct 2011: http://www.nanowerk.com/spotlight/spotid=23118.php

Research & Development Activity of Carbon Nanotubes in MA

Dozens of R&D programs

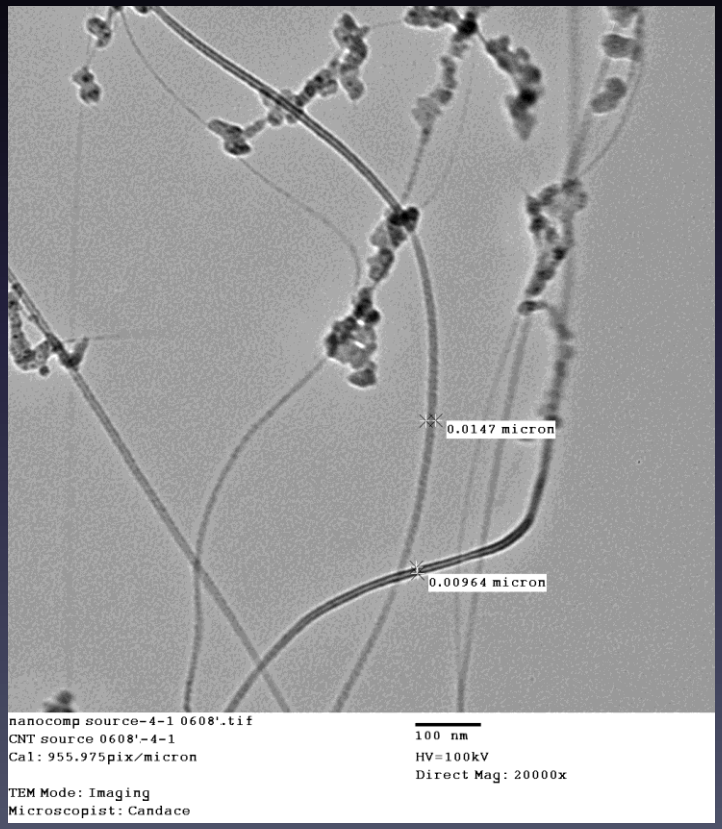
within MA universities

CNT Toxicity

- Many studies published in the last 10 years
- End point studied:
  - Fibrosis
  - Inflammation
    - Lung tissue
    - Cardiac tissue
- Mesothelioma

Asbestos

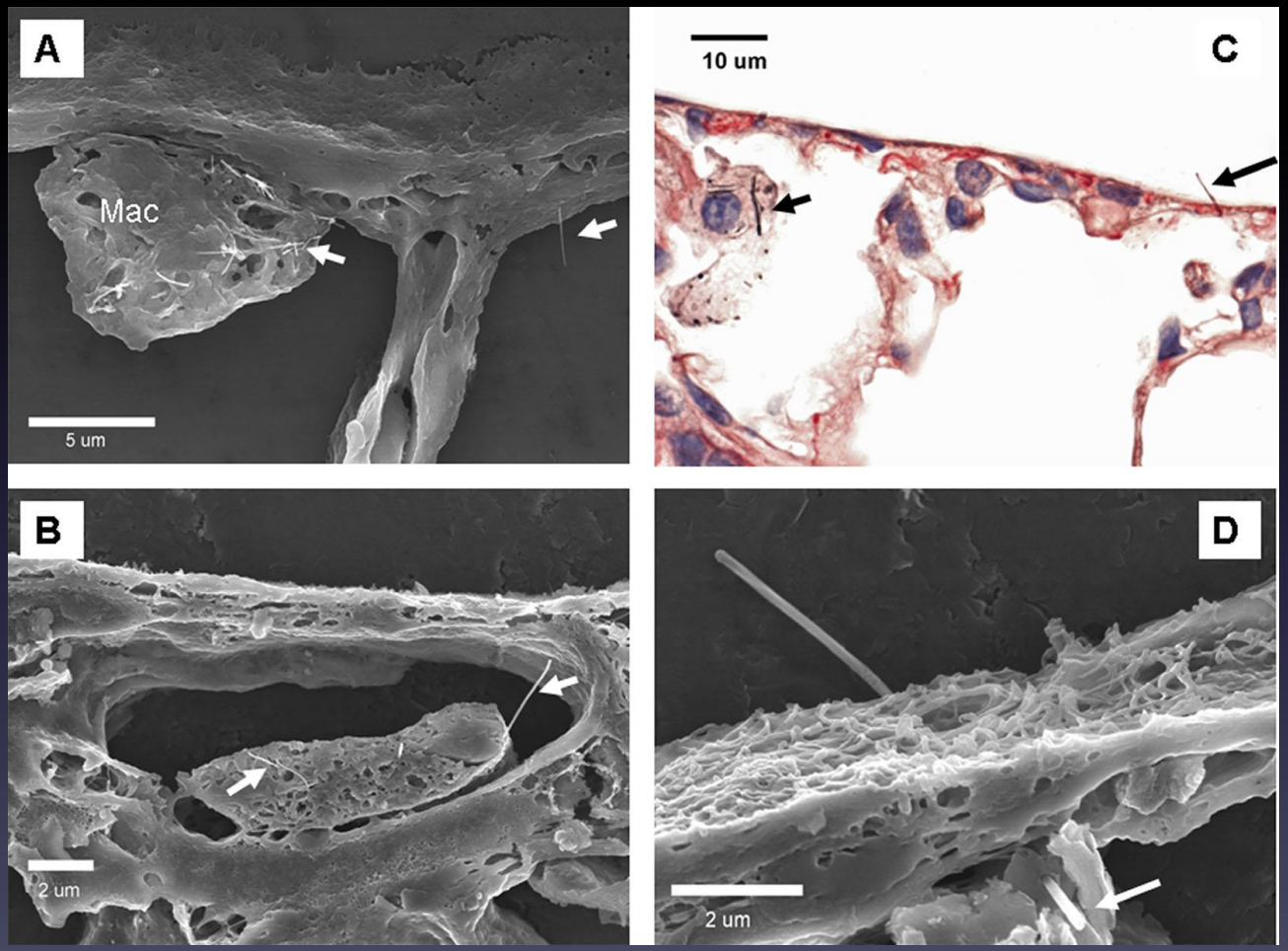
CNTs



CNTs cause Mesothelioma?

- Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study, Poland, et al., Nature Nano., 2008.
- Induction of mesothelioma in p53+/- mouse by intraperitoneal application of multi-wall carbon nanotube, Takagi, et al., J. Toxicol. Sci, 2008.

Mercer, et al., Distribution and persistence of pleural penetrations by multi-walled carbon nanotubes, *Part. Fibre Tox.*, 2010.



CNTs cause Mesothelioma? *Cont.*

Poland: "Here we show that exposing the mesothelial lining of the body cavity of mice, as a surrogate for the mesothelial lining of the chest cavity, to long multiwalled carbon nanotubes results in asbestos-like, length-dependent, pathogenic behaviour… Our results suggest the need for further research and great caution before introducing such products into the market if long-term harm is to be avoided."

Dec 2014 – IARC designates "certain MWCNTs" as 2B, Suspect Human Carcinogen

Fiber Morphology May be Important

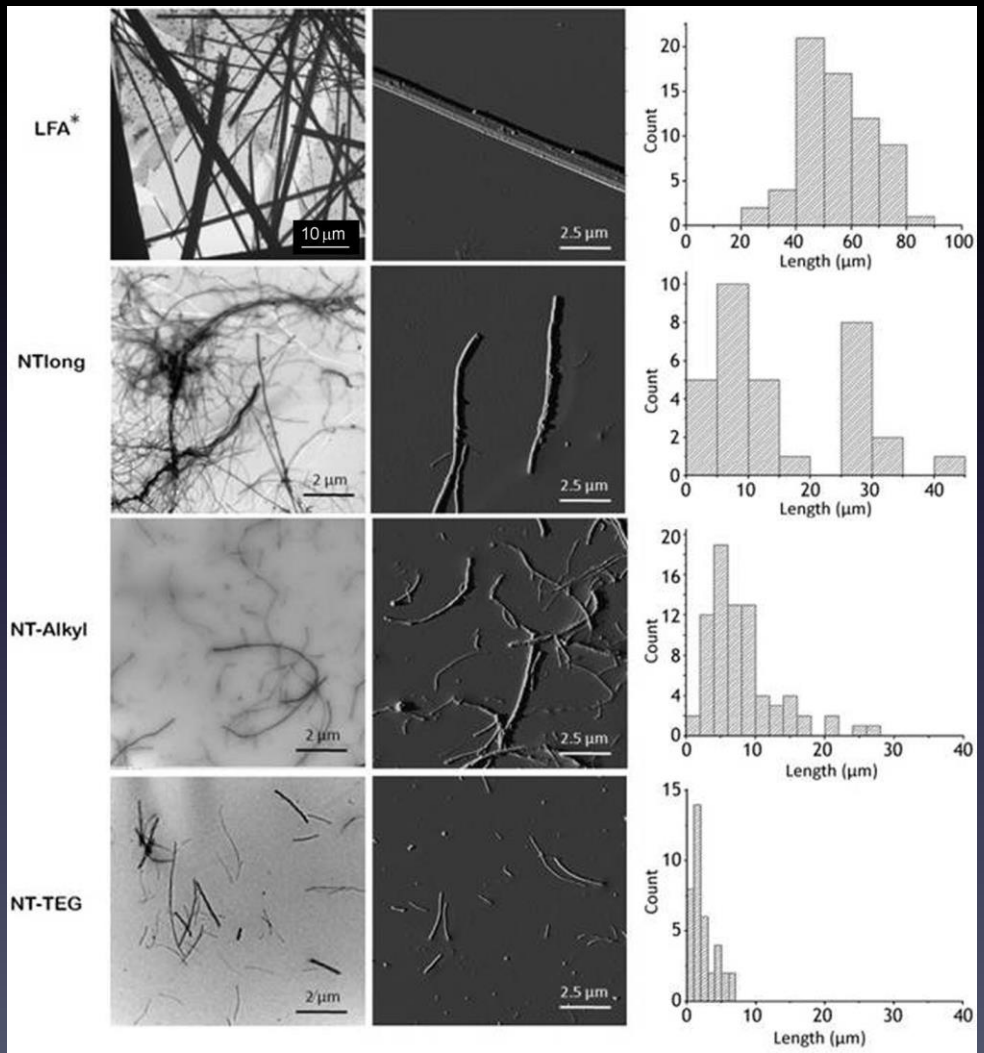
In animal studies thus far:

- SWCNTs do not cause mesothelioma
- Thin (d < 15 nm) MWCNTs – ditto
- Thick (d > 150 nm) MWCNTs – ditto
  - But – all commercially available MWCNTs :

    15 nm < d < 150 nm
- Short (L < 1-5 μm) MWCNTs – ditto

Can we make them all short?

Functionalization can Affect Length



Ali-Boucetta, *et al.*, Angew. Chem. Int. Ed. 2013, 52, 2274 –2278, DOI: 10.1002/anie.201207664

Emerging Ecotoxicity Concerns

- Daphnids *(Daphnia magna)*
  - Interferes with food uptake & movement at low concentrations [MWCNTs & SWCNTs]; More toxic with longer exposures; Impaired growth and reproduction at very low levels
- Juvenile rainbow trout *(Oncorhynchus mykiss)*
  - Systemic toxicity at very low levels (consistent with GHS classification of "extremely toxic to aquatic life)
- Powerful anti-microbial agent
  - Implications for sewage treatment plants

Source: Petersen, et al. *Env Sci Technol* 2011; 45(23):9837-9856.

Regulatory landscape: EPA

- 2008, CNTs considered a "new chemical" under TSCA – Requires Pre-Manufacturing Notice (PMNs)
  - Consent orders: mandate tox testing (90-day inhalation studies) and specific industrial hygiene practices
  - Dozens of CNTs have been added to the TSCA inventory
- Subject of dozens of Significant New Use Rules (SNURs)
- 2015, Issued a proposed record-keeping and reporting rule (final rule expected in fall 2016)
  - Exempted: manufacturing/use for R&D purposes; small businesses/manufacturers (defined as less that 4 million in annual sales)

Regulatory landscape: Occupational

- OSHA
  - No Permissible Exposure Limit for CNTs (no occupational standard for nanomaterials)
- NIOSH
  - 2013 "Current Intelligence Bulletin"
    - CNTs may pose a respiratory hazard for workers (pulmonary fibrosis & inflammation)
    - Recommended exposure limit = 1 ug/m^3
      - based on technical feasibility, not safety
      - Doesn't reflect carcinogenicity data/evidence

Regulatory landscape: Europe

- REACH
  - CNTs are considered different than graphite (bulk counter part)
  - A few CNT registrations
  - Major barrier: 1 metric ton (2,000 lb) threshold
- EU Member States - Registries
  - France: 2012 decree, manf, import, or use 100 g of any nanomaterials
    - 65% of the nanomaterial declarations in the French registry (1st reporting year) below the REACH reporting threshold
  - Similar registries now in place in Belgium, Denmark Norway and under consideration in Sweden and Italy
- EU exposure limit – 0.01 CNTs/cm^3