Assessing and managing risks of CNTs under TSCA - Representative Case Studies

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Office of Pollution Prevention and Toxics

Background

- The purpose of this “case study” is to illustrate how EPA is assessing and managing the risks of carbon nanotubes under the Toxic Substances Control Act
- The data for these two case studies is a generic amalgamation of all carbon nanotubes reviewed by EPA

Toxic Substances Control Act (TSCA)

- TSCA provides broad authority to:
  - Gather information on new and existing chemical substances and mixtures
  - Require testing of chemicals
  - Screen and control unreasonable risks of new and existing chemicals
  - Coordinate with other Federal agencies

New Chemicals Program

Chemicals not on the TSCA Inventory

- Manufacturers or importers of new chemicals submit premanufacture notices (PMN) [TSCA §5 (a)]
- Regulation Pending Development of Information [TSCA §5(e)]
- Significant New Use Rules (SNUR) [TSCA §5 (a) (2)]

Carbon Nanotubes (CNTs)

- EPA has received new chemical notices under the Toxic Substances Control Act (TSCA) on over **100 nanoscale materials** and over **30 carbon nanotubes and fibers**
- Each CNT is considered a distinct chemical substance. Some key parameters:
  - # walls
  - inner diameter, outer diameter and length
  - functionalization
  - capped or open ended
  - straight, branched, or tree structure
- Production volumes have ranged from kg scale to greater than 10,000 kg

Production Volume/Use

Property	MWCNT #1	SWCNT #2
Production volume	20,000 kg imported	5 kg
Use	Used in thermosets and thermoplastics for mechanical strength and electrical conductivity. Also in metals for mechanical reinforcement	Used as a conductive ink in microelectronic applications

Identity

Property	MWCNT #1 PMN	SWCNT #2 LoREx
Purity	Two levels of purity: 85% and >95% pure	Unspecified
Catalyst	Cobalt and nickel catalyst	Iron
Forms for sale	Sold as solid powder, liquid or liquid resin, solid resin	Sold as liquid ink dispersion

Identity

Property	MWCNT #1	SWCNT #2
Length	1.5 µm average	3 µm average
Width	ID: 3 nm OD: 15 nm	OD: 2 nm
Walls	3 – 14 walls	1
Agglomeration state	Forms agglomerates 300-400 µm in diameter	No information provided.

Identity

Property	CNT #1	CNT #2
Functionalization	Not functionalized	Functionalized w/ COOH
Branching	Not branched	Not branched
Capped or open-ended	Open-ended	Open-ended

Physical-chemical properties

Property	MWCNT #1	SWCNT #2
Solubility	< 1 ppb estimated	< 1 ppb estimated
Vapor pressure	Est. <0.000001 Torr @ 25 C	Est. <0.000001 Torr @ 25 C
Molecular weight	MW: 100000.00 g/mol	MW: 100000.00 g/mol
Bulk density	0.1 – 0.2 g/cm^3	0.1 – 0.2 g/cm^3 (from parent compound)
True density	2. g/cm^3	~2. g/cm^3 (from parent compound)

Challenges

- No nomenclature system has been developed
- Generally, insufficient data to identify relevant properties
- Unclear test methods/relevance of results
- How do chemical-structural and material characterization properties correlate with physical-chemical properties

Environmental Fate and Exposure

- The Agency does not have models or methods designed to predict the fate of, or exposure to, CNTs in the environment.
- Combined with the lack of test results for nanomaterials, there is uncertainty in estimating removal efficiencies, degradation half-lives, partitioning, and transport of nanomaterials.
- To address this uncertainty, EPA uses a bounding, “what-if” scenario that assumes CNTs are released into the environment, are persistent, bioaccumulate, and are highly mobile until a submitter demonstrates otherwise.

Guideline posted on EPA public website

http://www.epa.gov/oppt/exposure/pubs/guidance.htm

Environmental Exposure

Screening level estimates used to determine if manufacture, processing, or use of nanomaterials result in releases sufficient to warrant control

Two exposure scenarios for nanomaterials:

One simulates **releases to water** (0% wastewater treatment removal)

Second simulates **releases from sludge** (100% adsorption to wastewater treatment sludge followed by 100% desorption from sludge to groundwater)

Purpose of these scenarios is to create bounding estimates for maximum concentrations

Environmental Releases - Manufacturing

Property	MWCNT #1	SWCNT #2
Releases to water	Imported	None expected
Releases to air	Imported	None expected
Releases to landfill	Imported	None expected
Releases to incineration	Imported	~5 g/day over 200 days – 90% of this release is from equipment cleaning losses

Environmental Releases
Processing

Property	MWCNT #1	SWCNT #2
Releases to water	1.3 kg/day over 250 days/year	None expected
Releases to air	0.2 kg/day from over 250 days/year	None expected
Releases to landfill	1.3 kg/day over 250 days/year	None expected
Releases to incineration	1.3 kg/day over 250 days/year	0.3 g/day over 200 days from dilution/bottling/ coating

Environmental Releases
Use

Property	MWCNT #1	SWCNT #2
Releases to uncertain media	0.03 kg/day over 280 days from excess liquid resin disposal if not controlled. None expected from other forms, but testing required. to ascertain long-term potential releases from solid forms	0.4 g/day over 250 days/year at 14 sites from application excess, etching, and developer residual disposal. Regulated releases to incineration or hazardous waste landfill to meet LoREx criteria.

Environmental Exposures

	MWCNT #1	SWCNT #2
manufacturing	NA (import)	< 1 ppb
processing	1.6 ppm	< 1 ppb
use	30 ppb	< 1 ppb

Average surface water concentrations, based on 7Q10 stream flow data

Ecotoxicology

No established concern concentration for CNTs:

- CNT toxicity generally reported in the 10s to 100s ppm for both water and sediment borne material
- Sublethal effects have been noted in fish as low as 100 ppb.
- The solubility of CNTs is predicted < 1 ppb, but stable dispersions may be created in the presence of natural organic matter or via functionalization (which is environmentally feasible).
- Uptake studies in whole aquatic organisms indicate that CNTs do not cross the gut lumen suggesting uptake is limited to ingested material.
- The broad range of potential CNT forms that may affect ecotoxicology: functionalization; length and end-capping; presence of catalyst metals; level of purity

Environmental Risk Assessment

- Based on the framework for other new chemicals, EPA models predict no ecological effects at saturation of CNTs in water which would generally lead EPA to conclude low environmental hazard and risk for CNTs, as manufactured.

- However, due to the transformation potential of CNTs and uncertainty of the relevance of existing data, EPA considers the ecological hazard and risk of CNTs to be inconclusive.

- Generation of additional data would be required if a company wanted to release CNTs to the environment.

Human Health – Occupational Exposure

Property	MWCNT #1	SWCNT #2
Relevant occupational exposures during manufacture	Not applicable	Inhalation: negligible (VP < 0.001 torr). Dermal: 36 mg/day (Liquid 2.0%) to liquids

Human Health – Occupational Exposure

Property	MWCNT #1	SWCNT #2
Relevant occupational exposures during processing (formulation)	Inhalation: 3 mg/day to particulates Dermal: 2600 mg/day to particulates 480 mg/day to liquids	Inhalation: negligible (VP < 0.001 torr). Dermal: 36 mg/day (Liquid 2.0%) to liquids

Human Health – Occupational Exposure

Property	MWCNT #1	SWCNT #2
Relevant occupational exposures during use	Inhalation: 0.2 mg/day to particulates Dermal: 470 mg/day to particulates 180 mg/day to liquids	Inhalation: Negligible. Coating is done in an enclosure. Dermal: Worst case – 0.09 mg/day; Typical – 0.02 mg/day to mist (0.01%)

Occupational Exposures - Challenges

- Do large agglomerates break down into respirable and inhalable particles that can reach the deep lung?
  - No metric to describe the propensity to break down

- How do CNTs disperse in lung/other biological fluids?

- Occupational inhalation exposures to respirable particles are a key concern
  - No consensus approach
  - Highly dependent on model and assumptions
  - Unclear how to interpret/utilize experimental data

Occupational Exposures - Challenges

- Validated exposure monitoring data
- Early studies focused on identifying and reducing emission hotspots in facilities,
  - did not quantify worker exposures
  - may represent worst case exposure scenarios,
  - but did not identify which particle forms
- What percentage of particle detections are of actual CNTs rather than soot or organic carbon?
- What are the characteristics of the actual CNTs from such exposures compared to the CNTs as manufactured or generated for a toxicity study

Human Health – Environmental Exposure

Property	MWCNT #1	SWCNT #2
Relevant general population exposures during manufacture	NA	No exposure criteria met - releases not high enough to run the models
Relevant general population exposures during formulation	78 µg/kg/day acute drinking water exposures 0.6 µg/kg/day lifetime drinking water exposures	No exposure criteria met - releases not high enough to run the models

Human Health – Environmental Exposure

Property	MWCNT #1	SWCNT #2
Relevant general population exposures during use	0.06 µg/kg/day from landfill releases 0.5 µg/kg/day acute from stack air 0.03 µg/kg/day over a lifetime from stack air 5 µg/kg/day acute from fugitive air 0.1 µg/kg/day lifetime from fugitive air	No exposure criteria met - releases not high enough to run the models

Human Health - Consumer Exposure

- The following forms of CNTs may be distributed to consumers:
  - completely reacted (cured);
  - incorporated or embedded into a polymer matrix that itself has been completely reacted (cured);
  - embedded in a permanent solid polymer form that is not intended to undergo further processing except for mechanical processing;

Consumer/General Exposure - Challenges

- Are CNTs chemically bound in composites or just embedded? How stable are the CNTs in the composites? What is the material lifecycle?
  - Some consent orders may require testing to help address this issue.
- Thermogravimetric analysis suggests raw CNTs will be easily incinerated.
- What about under actual incineration and composite conditions?

Human Health – Hazards Assessment

	Respiratory	Oral	Dermal
Absorption	Poor	Poor	Poor
Concerns	Lung overload Mutagenicity Immunotoxicity Lung cancer Effects from catalysts Systemic effects from translocation	Effects from catalysts Systemic effects from translocation	Systemic effects from translocation Irritation - mild Sensitization – negative

Human Health – Respiratory Hazard

- At the current time EPA is considering data from Ma-Hock, et al 2009 when assessing CNTs
  - LOAEC at 0.1 mg/m^3 for granulomtous inflammations, alveolar histiocytosis, lipoproteinosis, and neutrophil infiltration
  - Uncertainty Factors
    - extrapolation from subchronic to chronic
    - LOAEC to NOAEC
    - interspecies variation
    - intraspecies variation
    - database incompleteness

Human Health Risk Assessment

- A typical assessment for other new chemicals would establish an exposure limit based on the best available analogue to estimate potential risk.
- Due to the uncertainty of the relevance of both hazard and exposure data. EPA considers the human health hazard and risk of CNTs to be inconclusive.
- Generation of additional data would be required if a company wanted to manufacture CNTs without the current restrictions found in consent orders.

CNT Case #1 risk – Risk management

- Further material characterization data
  - Key to chemical identity and risk assessments
- Use restrictions
  - PPE for industrial settings
  - Must be embedded in a polymer/metal matrix for commercial or consumer settings
  - Only specific uses allowed
- 90-day inhalation tox studies (to date)
- Limit releases to environment

CNT Case #2 risk – Risk Management

- Notice is binding- meets LoREx criteria
  - No releases to water or landfill
  - Incineration releases are below 1µg/m^3
  - No occupational exposures unless EPA is satisfied that appropriate controls are in place
    - No occupational inhalation exposures found
    - Appropriate dermal protective equipment use
  - No consume exposure
- EPA typically requires volume caps for nano-LoREx in this case 5 kg.