Perspectives on Mitigating Exposures to Engineered Nanomaterials in the Workplace

Pat Rasmussen

Exposure & Biomonitoring Division, Healthy Environments and Consumer Safety Branch, Health Canada

Adjunct Professor, University of Ottawa

(no conflict of interest)

Occupational & Environmental Health Seminar, Toronto Ontario. December 7, 2018

Overview of presentation

- Unique properties of engineered nanomaterials (definitions)
- Control Banding Approach: selection of control measures based on hazard and exposure (CSA/ISO)
- Harmonized Tiered Approach: to assess potential exposures in workplaces (OECD)
- How research feeds into CSA/ISO and OECD exposure measurement and mitigation efforts
- Accessing nano workplace safety information in Ontario

Engineered nanomaterials (ENMs) are exploited for their unique properties

Nano ZnO/TiO_2 *vs* bulk ZnO/TiO_2

Photo from “www.nanoandme.org”

“Nanoscale" means 1- 100 nanometres (incl.) in one or more dimensions.

The term "nanoscale properties/phenomena" means properties which are attributable to size and their effects.

These properties are distinguishable from the chemical or physical properties of individual atoms, individual molecules and bulk material.

https://www.canada.ca/en/health-canada/services/science-research/reports-publications/nanomaterial/policy-statement-health-canada-working-definition.html

Impact on aquatic ecosystems:
Palau 1st country to ban sunscreens (Nov 2018)

Photo credit: www.badgerbalm.com

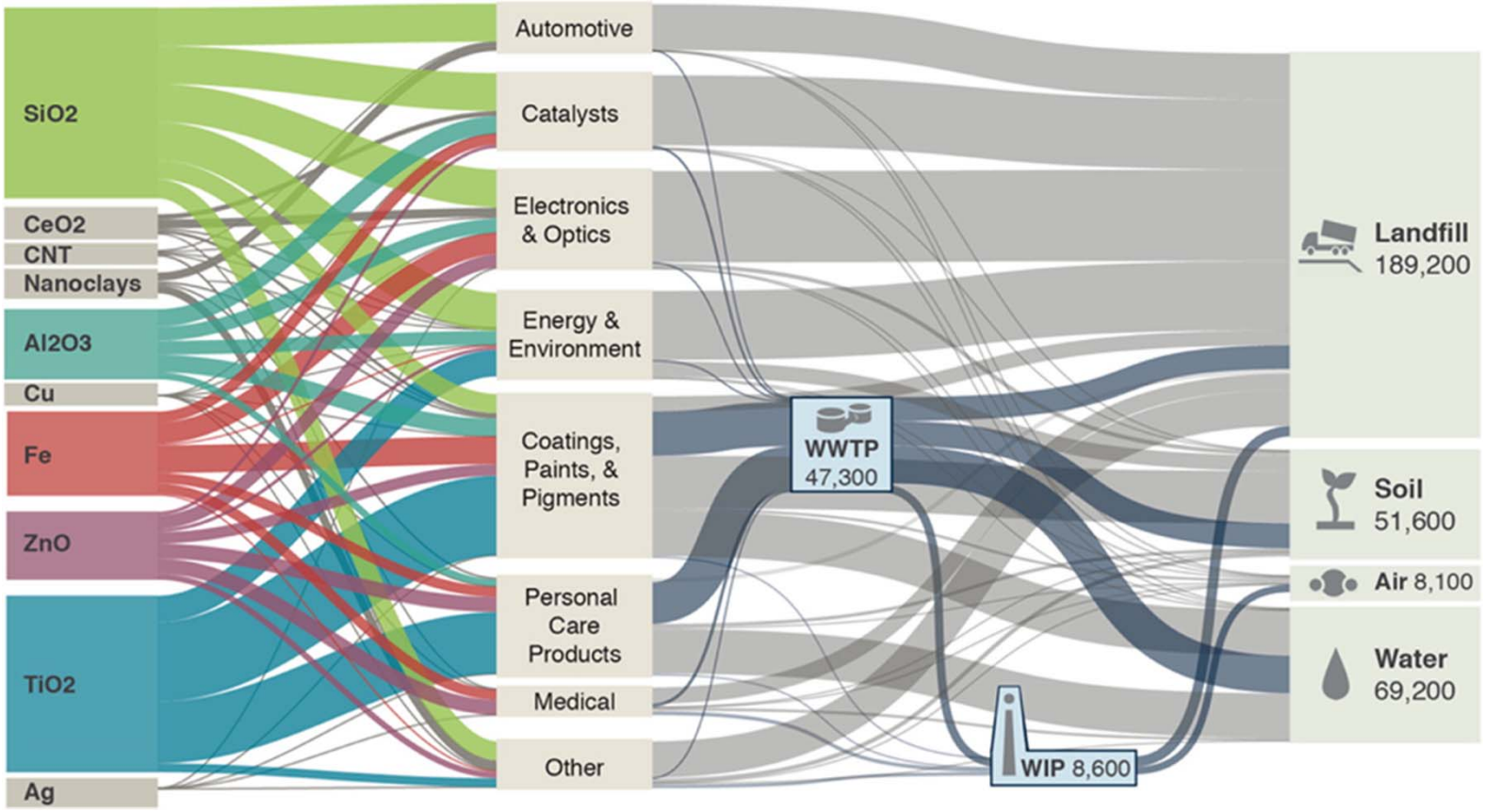
Sunscreen loading on coral reefs estimated up to 14,000 tons/year.

Reef-toxic sunscreen ingredients include:

- Oxybenzone
- Parabens
- Octinoxate
- 4-methylbenzylidene camphor (4MBC)

Research is underway to assess the impact of **engineered nanomaterials** like zinc oxide and titanium dioxide (in combination with matrix ingredients).

Modelling global releases of engineered nanomaterials (to estimate concentrations)



Keller and Lazareva (2014) *Environ. Sci. Technol. Lett.* (1) 65-70.

Predictive Toxicology of Nanomaterials: A Regulatory Challenge

Compositions

Metal Oxides

TiO_2, CeO_2, ZnO
CuO, NiO, Cr_2O_3

Metals

Au, Ag, Pt, Co

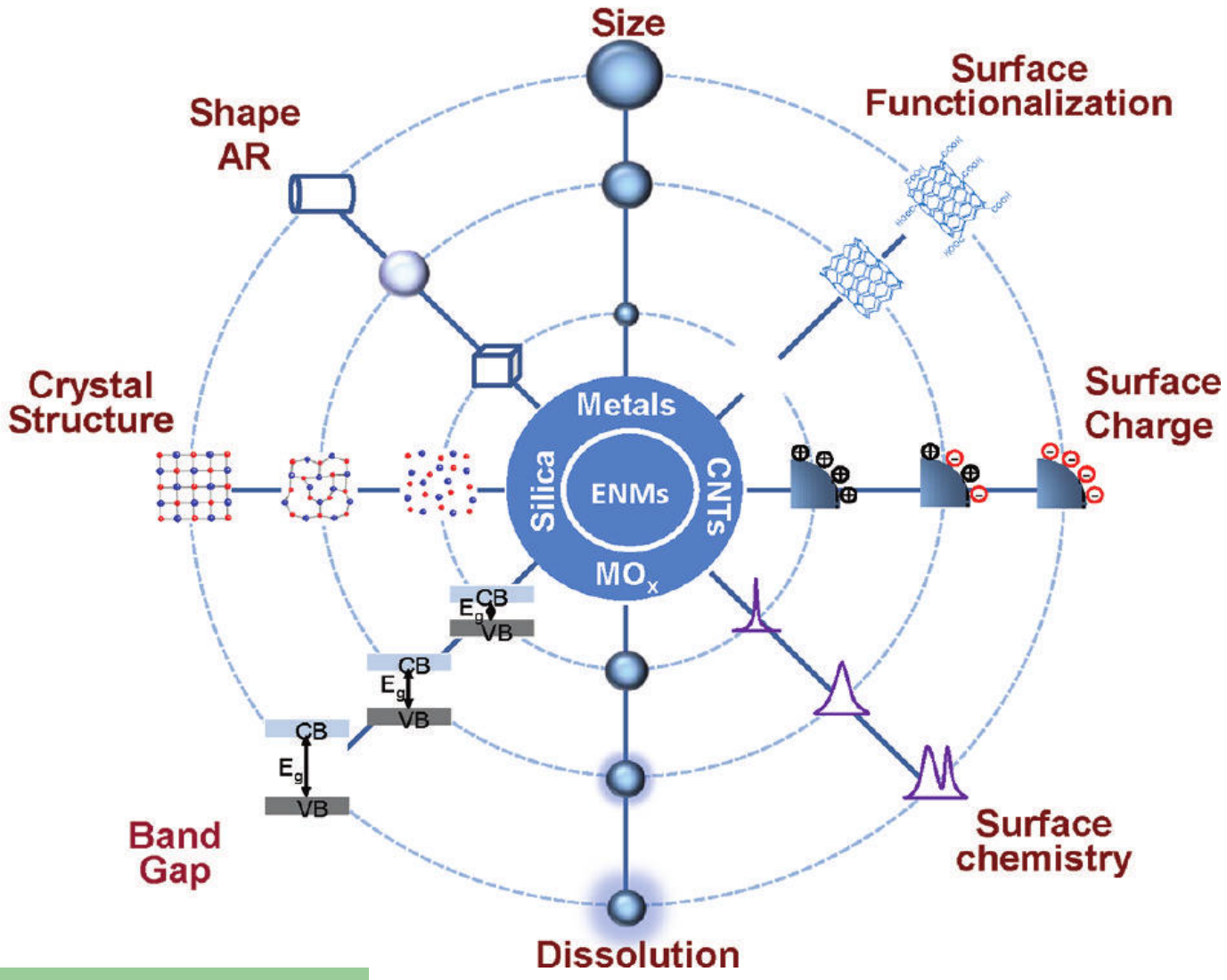
Carbon Nanotubes

SWCNT, MWCNT

Silica

Amorphous
Fumed,
Crystalline,
Mesoporous

Combinatorial variation of properties



Nel et al. (2013) *Accounts Chem. Research* (46) 607–621

“Engineered” nanoparticles (NPs) are distinguished from “incidental” or “background” NPs

photo credit www.nederman.com

Diesel exhaust and welding fumes are examples of “incidental NPs”

See ISO/TC229 definitions for engineered, manufactured and incidental nanomaterials on the ISO Online Browsing Platform at https://www.iso.org/obp/ui/
(select ‘Terms and definitions’ and enter the term)

Access OECD Working Party on Manufactured Nanomaterials publications at:
http://www.oecd.org/env/ehs/nanosafety/publications-series-safety-manufactured-nanomaterials.htm

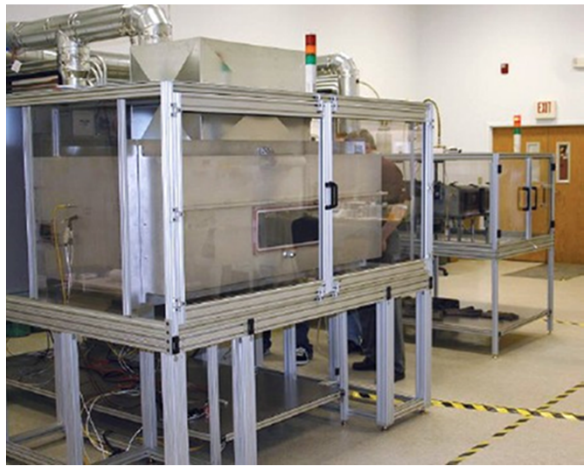
Workplace Exposures

- **Main focus: inhalation exposures**
  - Nano-Objects and their Aggregates and Agglomerates (NOAA)
  - Subset of airborne particulate matter
- **Occupational Exposure Limits (OELs) are under development**
  - Gaps in knowledge about toxicology (unique properties of ENMs)
  - High diversity of newly developed ENMs
  - Debate about metrology (which exposure metrics)
  - See Mihalache et al. (2017) *Nanotoxicology* 11: 7–19 review of OELs
- **In the meantime, implement protection against worker exposure**
  - Understand the hazard (e.g. biopersistence) and the likelihood of exposure (e.g. potential for dust generation)
  - Use effective control measures (increased ventilation in combination with hoods) and personal protective equipment (P100 filter mask, gloves, clothes)
  - See Kuhlbusch et al. (2018) *NanoImpact* 10 (2018) 11–25 exposure review

Selection of Control Measures Based on Hazard & Exposure

www.healthtipsenglish.com

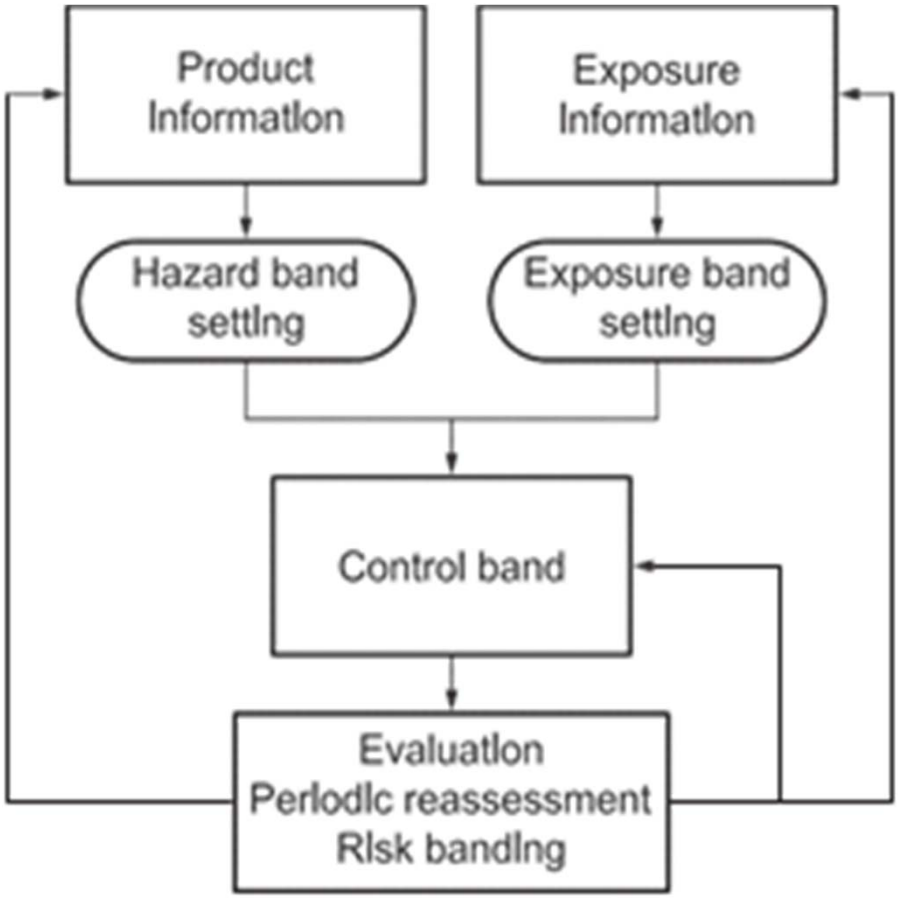
www.nanocomptech.com



Examples of control measures: chemical fume hoods, enclosure hoods or glove boxes, snorkels, respirators, protective clothing

= “Control Banding Approach”

Control Banding Process
adopted by CSA from ISO/TS 12901-2:2014



Assessing potential hazard: solubility is key for setting hazard band

low solubility = high biopersistence in the lung environment

- **nano-specific solubility test methods are needed**
- **OECD guidance being developed**

Environ Sci Pollut Res (2017) 24:1553–1564
DOI 10.1007/s11356-016-7932-2

RESEARCH ARTICLE

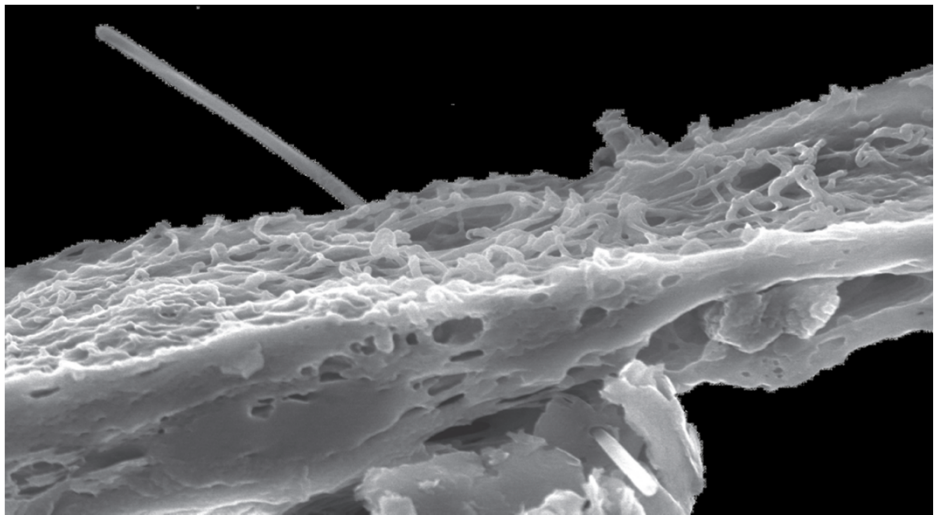
Influence of pH, particle size and crystal form on dissolution behaviour of engineered nanomaterials

M.-L. Avramescu[1] · P. E. Rasmussen[1,2] · M. Chénier[1] · H. D. Gardner[1,2]

Assessing potential hazard: aspect ratio is another key parameter

Carbon nanotubes are biopersistent fibres

- fibres have high aspect ratio (ratio of length to diameter)
- biopersistence of fibres is defined as the ability of a fibre to remain in the lung in spite of the lung's physiological clearance mechanisms.
- part of the toxicity of CNTs is due to redox activity of metal impurities (transition metals used as catalysts)



Carbon nanotube (CNT) penetrating out of lung surface into the pleural space (NIOSH CIB 65).

Mercer et al. *Particle and Fibre Toxicology* 2010, 7:28 (Fig 7D)

NOAA = nano-objects, their agglomerates and aggregrates

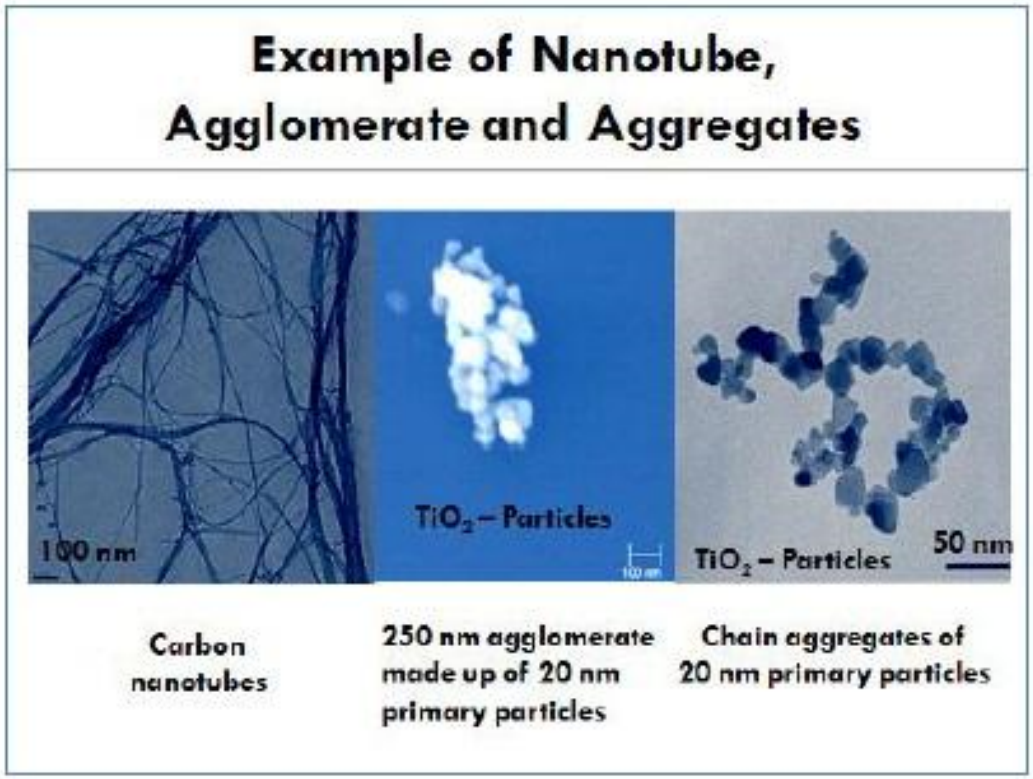
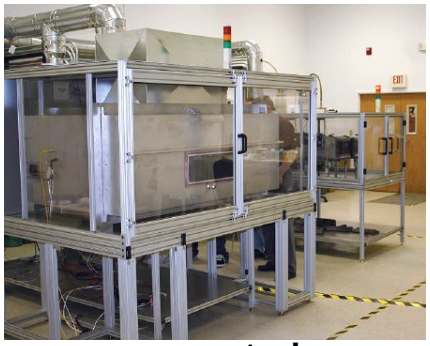


Figure from ehs.research.uiowa.edu/nanomaterials-handling-safety-guide-laboratories#6

Tasks That Are Likely To Release Airborne Carbon Nanotubes (CNTs)

- **In a CNT Manufacturing Facility:**
  - **emissions during production**
  - **scraping out furnace**
  - **bagging/packaging of dry CNT powder**
  - **maintenance (replacing filters on dust collection systems and vacuum cleaners)**



www.nanocomptech.com

- **In a CNT User Environment:**
  - **any handling of CNTs in dry powder form**
  - **opening bags of dry CNTs and adding them to a hopper**
  - **weighing out powder**
  - **sample transfer, measurement, vortexing, grinding**

Assessing potential exposure: dustiness is key for setting exposure band

- **Dustiness is the tendency for particles to become airborne**

- **Dustiness of nanomaterials**
  - **is greatest in dry powder form: nanopowders tend to pose the greatest risk for inhalation exposure.**
  - **influences the selection of the appropriate engineering control.**
  - **is difficult to predict from intrinsic properties: electrostatic forces, ambient humidity, water content all influence dustiness**

- **Dustiness tests are designed to mimic dust generation encountered in workplaces**
  - **next year (2019) European Union will publish five different standard methods for quantifying dustiness (EN 17199-1 to EN 17199-5)**

Life Cycle Example: Nanomaterials in Reinforced Concrete and Cement

Nanomaterials added to improve properties of concrete and cement

- **nano-calcium oxide**
- **nano-silica**
- **nano-polymers**
- **nano-titanium dioxide**

Above photos from: DA Koleva, Department Materials and Environment, 2628CN Delft, The Netherlands

http://www.ekalandscapesupplies.co.uk/products/cement/

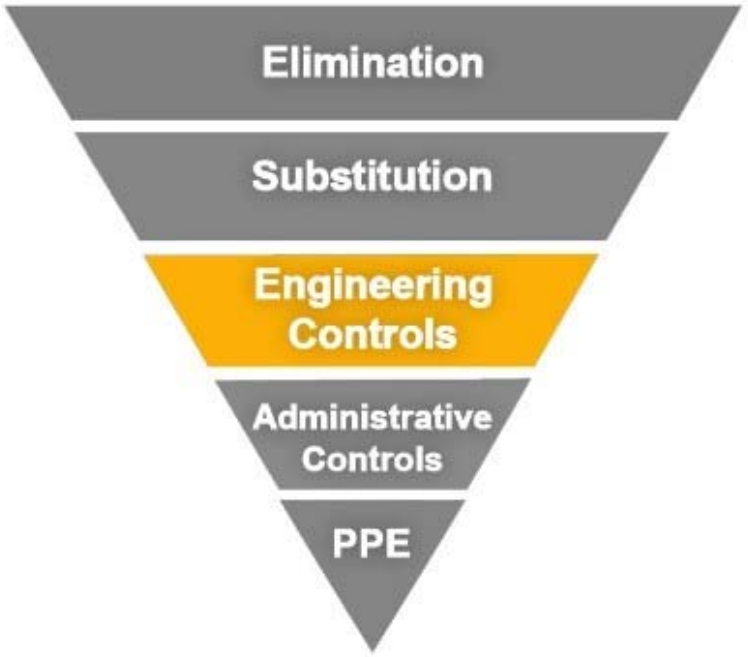
Selection of Control Measures Based on Hazard & Exposure

www.healthtipsenglish.com

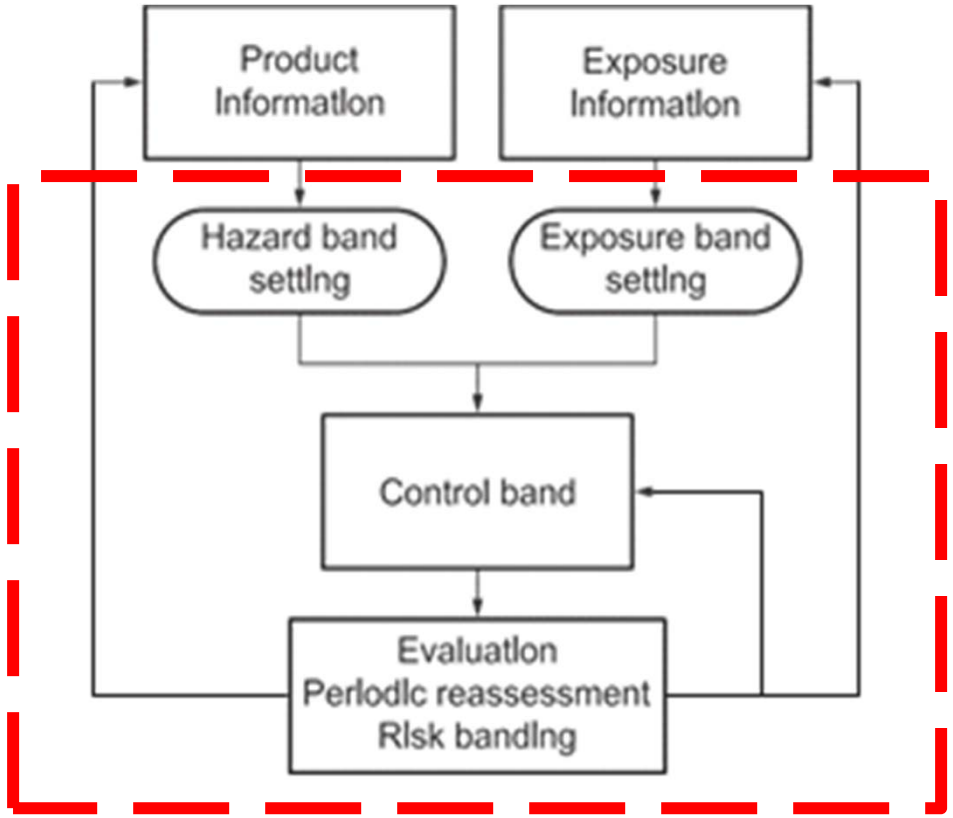
www.nanocomptech.com

STOP principle (CAN/CSA Z12901-2:15)
Substitution, Technical measures, Organizational measures, Personal protective equipment (PPE)

CDC-NIOSH Hierarchy of control



Control Banding Process
adopted by CSA from ISO/TS 12901-2:2014



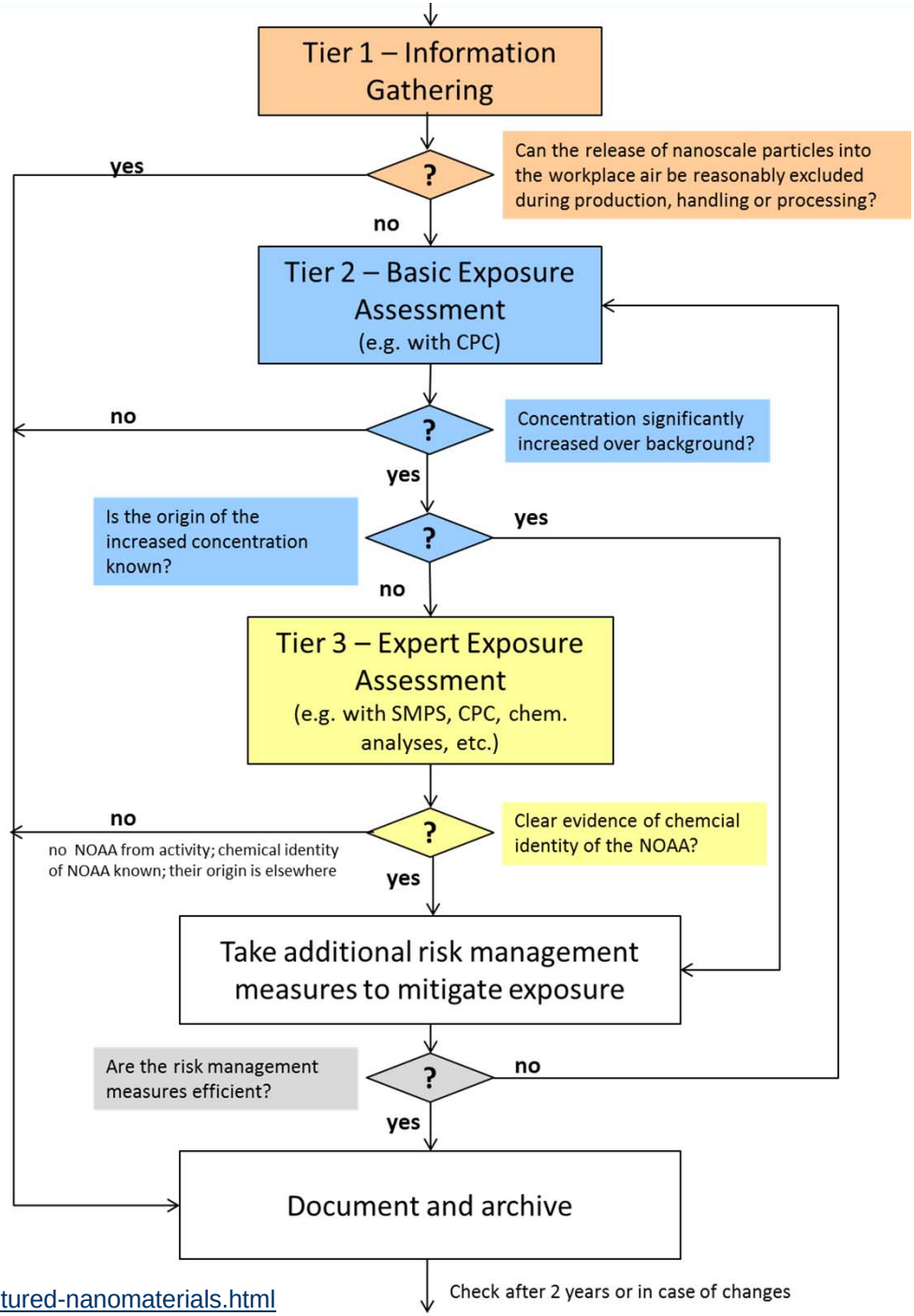
"In the absence of hazard information, the precautionary principle shall apply."

i.e. err on the side of caution

Harmonized Tiered Approach

OECD #55 (2015)

Harmonized Tiered Approach to Measure and Assess the Potential Exposure to Airborne Emissions of Engineered Nano-Objects and their Agglomerates and Aggregates at Workplaces



http://www.oecd.org/science/nanosafety/publications-series-safety-manufactured-nanomaterials.html
Also cited in CSA Z12885-12

OECD #55, 2015 and
OECD #82, 2017

Harmonized Tiered Approach for Exposure Assessment in Workplaces

Tier 1 Information-gathering

- Determine whether exposure assessment needed (releases are suspected)

Tier 2 Basic Exposure Assessment:

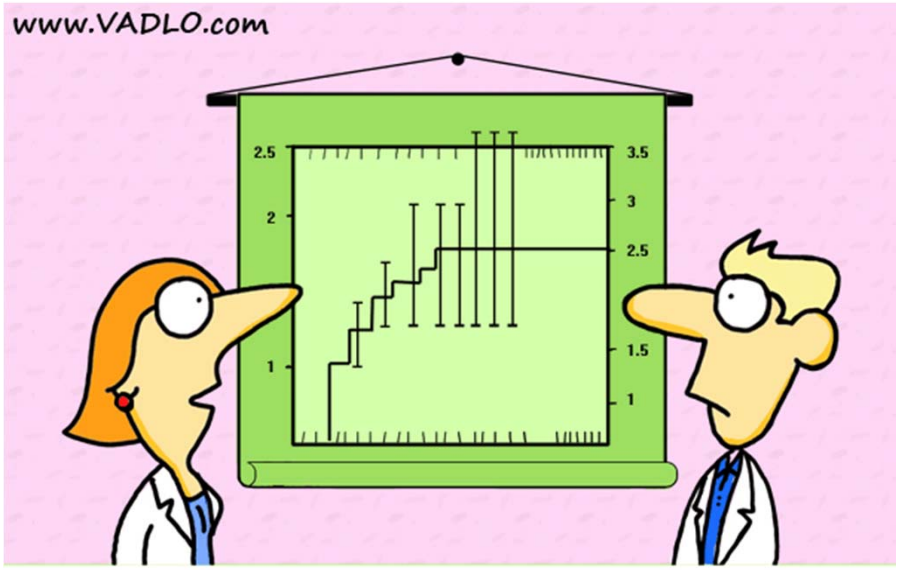
- Check for presence of NPs above background
- Direct-reading instruments

Tier 3 Expert Exposure Assessment:

- Collect NPs for further characterization by TEM, ICP-MS etc.
- Filter-based methods in addition to direct-reading instruments

OECD #55, 2015 and
OECD #82, 2017

How to define “background”?



“Did you really have to show the error bars?”

- **one recommended definition is 3 x sd of background number concentration**
- **“exceeding background” may be defined as 10% above background**

Environmental Science
Processes & Impacts

PAPER

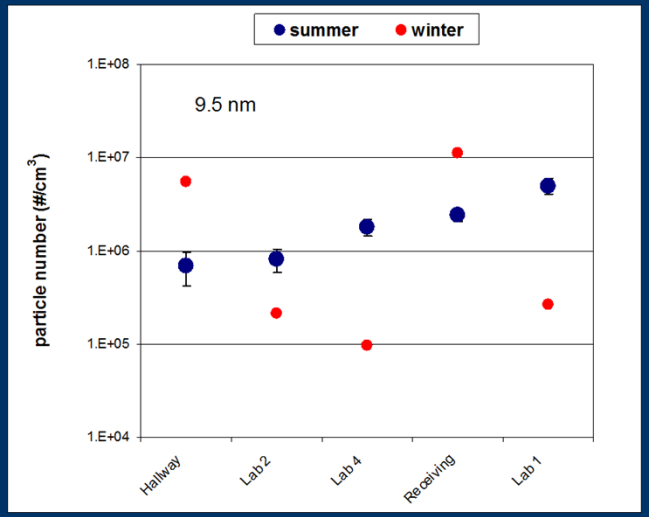
CrossMark click for updates

Cite this: *Environ. Sci.: Processes Impacts*, 2015, 17, 98

Spatial and temporal variability of incidental nanoparticles in indoor workplaces: impact on the characterization of point source exposures

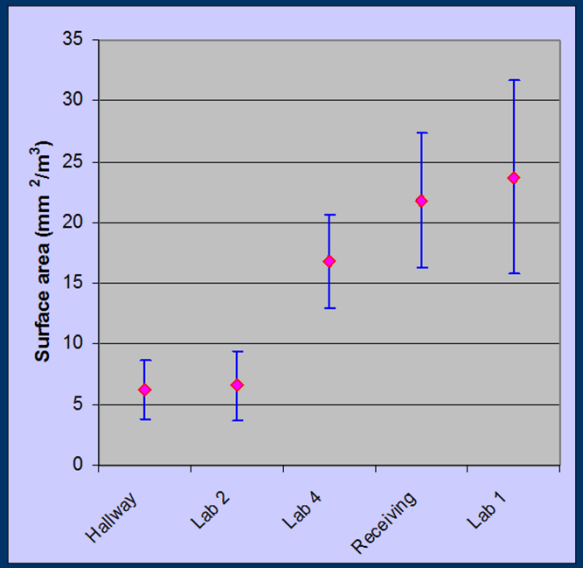
Jianjun Niu,[a] Pat E. Rasmussen,*[ab] Robert Magee[c] and Gregory Nilsson[c]

Background "incidental" nanoparticles are highly variable!



Particle Size Distribution using TSI SMPS

Surface area using EcoChem DC2000CE



OECD #55, 2015 and
OECD #82, 2017

Multiple instruments needed to quantify NP exposures in the workplace

(particle count, size distribution, surface area, mass)

CHALLENGES

- **Temporal variability**
- **Spatial variability**
- **Multiple sources of NPs**
  - **Process-related releases of engineered nanomaterials**
  - **Infiltration of outdoor air, vehicular emissions**
  - **Indoor sources of incidental nanoparticles**

Environmental Science & Technology

Article

pubs.acs.org/est

Detection of Carbon Nanotubes in Indoor Workplaces Using Elemental Impurities

Pat E. Rasmussen,*[,†,‡] Mary-Luyza Avramescu,[†] Innocent Jayawardene,[†] and H. David Gardner[†,‡]

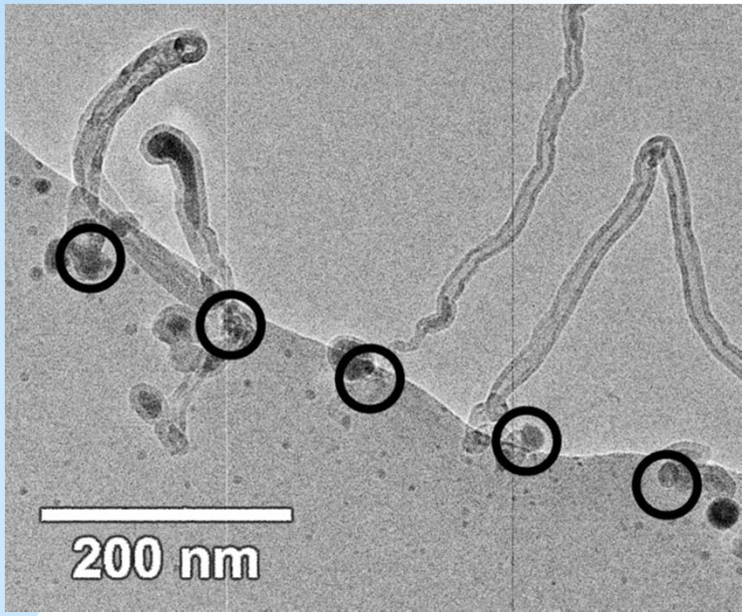
Health Canada tracks workplace carbon nanotube exposure

Monitoring control measures

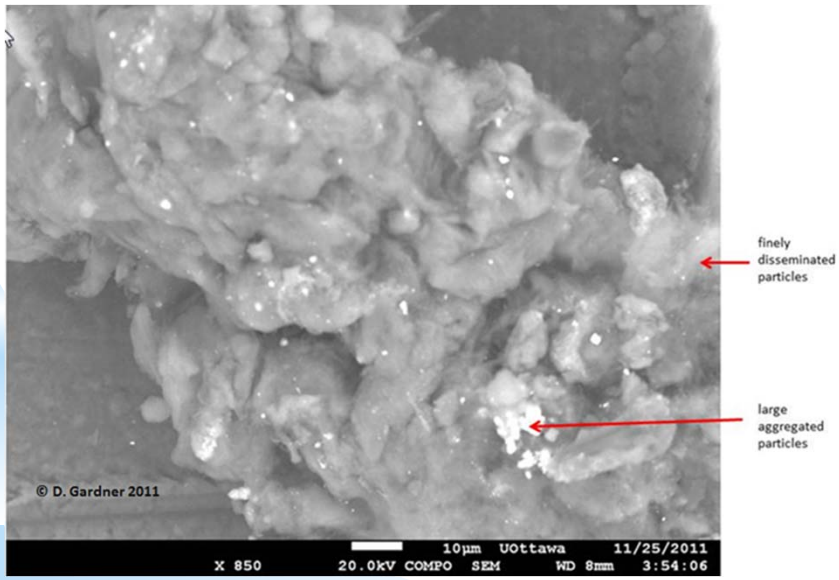
15 October 2015 / Canada, Risk assessment

A team from Health Canada is developing ways to check for releases of carbon nanotubes (CNTs) in the workplace, using residual trace metals left from manufacturing processes.

Metals are used as catalysts in the manufacture of carbon nanotubes



Chee and Sharma, *Micron* **43, 1181-1187 (2012)**



Rasmussen et al, *Environ Sci & Technol* **49, 12888-12896 (2015)**

- **Metals appear as dark spots in TEM (top Left)**
- **Metals appear as bright spots in SEM backscatter mode (bottom left)**
- **Metal catalysts identified in bulk CNT powder using ICP-MS scan* (below)**

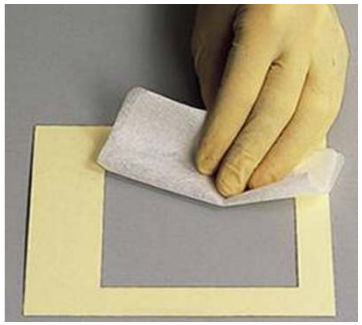
	mean (n=3) µg/g
Sc	6.6
Ti	14.1
V	1.2
Cr	35.3
Mn	37.8
Fe	1189
Co	158
Ni	131425
Cu	1.7
Zn	70.2
Ga	nd
Ge	nd
As	2.4
Se	7.1
Br	28.5

	mean (n=3) µg/g
Rb	nd
Sr	3.2
Y	25836
Zr	3.9
Nb	nd
Mo	73.6
Ru	nd
Rh	nd
Pd	0.1
Ag	nd
Cd	nd
Sn	13.1
Sb	0.2
Te	0.1

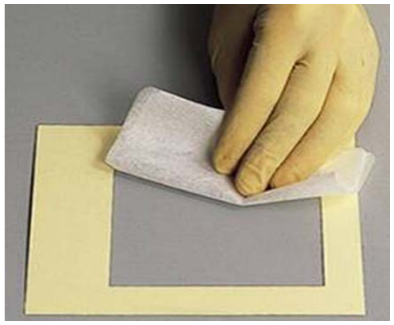
***Metals (ppm) in SWCNT from Aldrich**

OECD 2016; # 79

Strategy for Using Metal Impurities as Tracers of Released Carbon Nanotubes



Thermal optical carbon analysis



Metals by ICP-MS

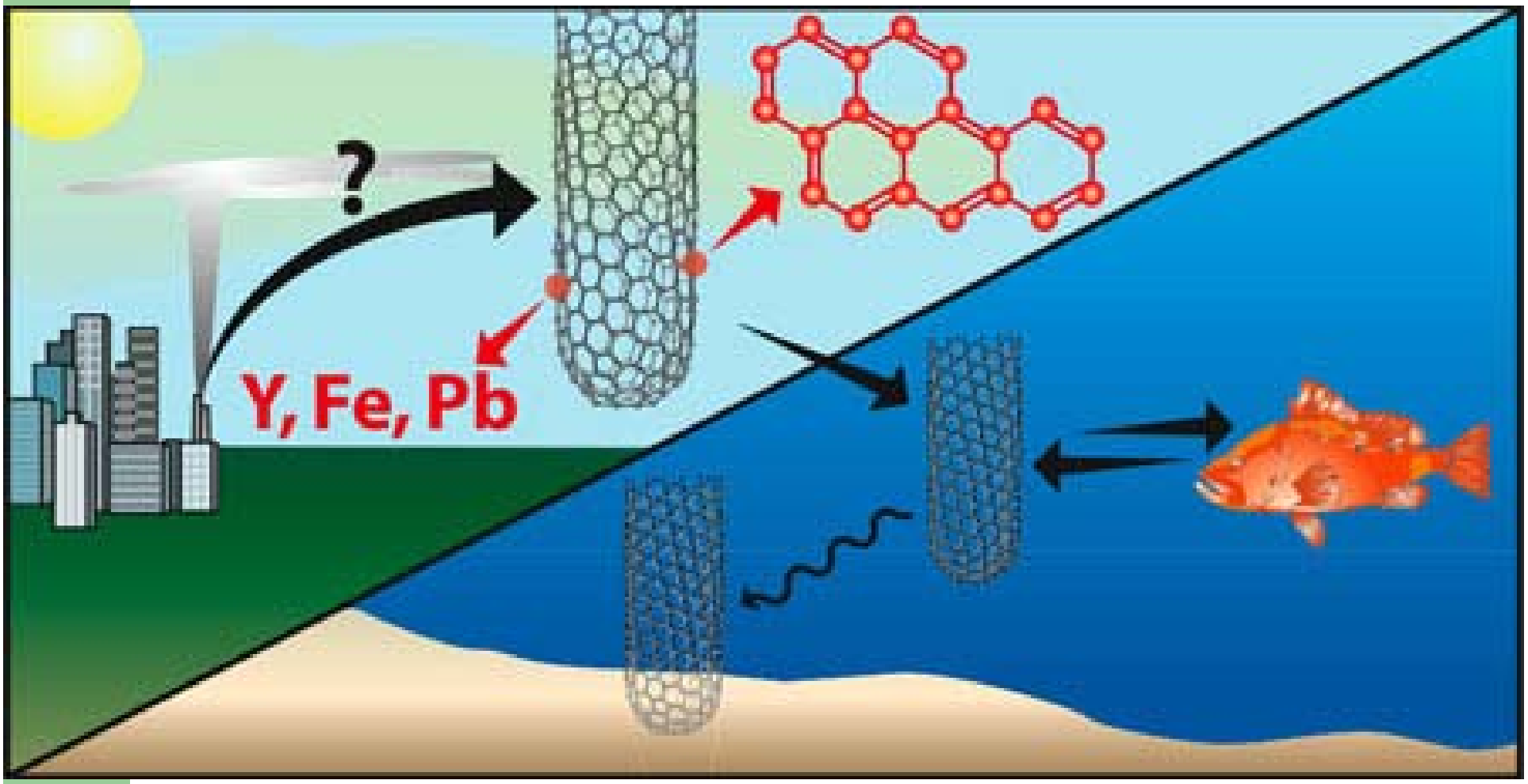
CNT tracer approach was evaluated in large CNT manufacturing facility using co-located floor wipe samples and air samples.

- Wipe sampling emerged as a practical, cost-effective (Tier 2) method for monitoring the effectiveness of control measures.

-"Active" floor dust samples showed strong, significant correlation (p <0.001) between cobalt catalyst and CNT carbon

Rasmussen et al, *Environ Sci & Technol* 49, 12888-12896 (2015)

Metal impurities have potential for detecting CNT releases to the environment



http://nanotechweb.org/cws/article/lab/33934

Summary of Approaches for Assessing & Mitigating Occupational Exposures

- **Control banding**
  - Understanding the likelihood of exposure (e.g. potential for dust generation) and hazard of nanomaterial (e.g. biopersistence)
  - Use of effective control measures
- **Tiered approach**
  - Real-time particle counters (Tier 2) to determine if there is a significant increase above background (e.g. 10%)
  - Wipe sampling to monitor effectiveness of control measures (Tier 2)
  - Expert assessment involving off-line analysis of filter samples (Tier 3)

Accessing nano workplace safety information in Ontario

Occupational Health Clinics for Ontario Workers (OHCOW) and Canadian Centre for Occupational Health and Safety (CCOHS) collaborated on a free e-course:

"Nanotechnology and Health"

https://www.ccohs.ca/products/courses/nanotechnology/

This is an awareness course that discusses nanomaterials that may be found in Canadian workplaces, the potential health hazards they present, and how workers can be protected. (released October 29, 2018).

It was the first product of the **"Nanotechnology and Health Network"**

- includes representatives from labour, government (research and regulatory, federal and provincial) and workplace health and safety organizations
- current focus is identifying workplaces where nanomaterials are used; best methods to assess and control exposures
- open invitation to all who are interested in joining (write to Todd Irick **tirick@ohcow.on.ca**)

International/National Nanotechnology Working Groups: International Standards Organisation (ISO) and Canadian Standards Association (CSA)

ISO/Technical Committee 229: Nanotechnology Working Group 3-*Health, Safety and Environmental Aspects*

CSA Nanotechnology - Occupational Health and Safety (OHS) Technical Committee

- **CSA Z12885-12, Nanotechnologies — Exposure control program for engineered nanomaterials in occupational settings**
- **CAN/CSA Z12901-2:15, Nanotechnologies – Occupational risk management applied to engineered nanomaterials – Part 2: Use of the control banding approach**

Access ISO/TC229 standards and technical reports at:
https://www.iso.org/committee/381983/x/catalogue/p/1/u/1/w/0/d/0

Access CSA standards and technical reports at:
https://shop.csa.ca/

International Guideline Development: Organization for Economic Cooperation and Development (OECD) Working Party on Manufactured Nanomaterials (WPMN)

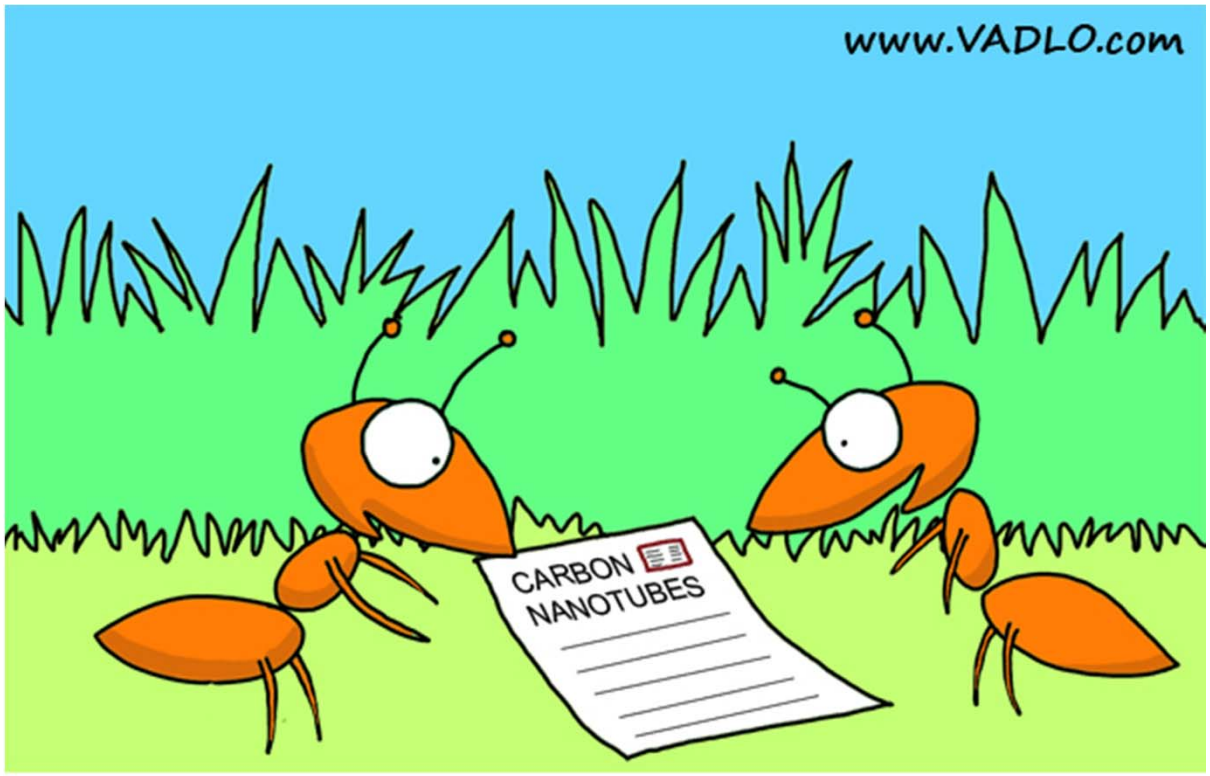
The purpose of the OECD Series on the Safety of Manufactured Nanomaterials is to provide up-to-date information on OECD activities related to human health and environmental safety (88 publications to date).

- **No. 55 - Harmonized Tiered Approach to Measure and Assess the Potential Exposure to Airborne Emissions of Engineered Nano-Objects and their Agglomerates and Aggregates at Workplaces (2015)**
- **No. 79 - Strategy for Using Metal Impurities as Carbon Nanotube Tracers (2016)**
- **No. 82 - Strategies, Techniques and Sampling Protocols for Determining the Concentrations of Manufactured Nanomaterials in Air at the Workplace (2017)**

Access OECD WPMN publications at:

http://www.oecd.org/env/ehs/nanosafety/publications-series-safety-manufactured-nanomaterials.htm

Questions?



"Finally, we can drink Coke with a straw."

Acknowledgments

RESEARCH TEAM:

**Jianjun Niu, Luyza Avramescu,
Marc Chénier, Christine Levesque,
Dave Gardner (Innocent Jayawardene)**

FUNDING:

Health Canada Chemicals Management Plan