NanoMONITOR guidance on the sampling methods and analytical techniques for the measurement and monitoring of ENMs in the environment and their use in proving compliance with EU chemical regulations

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Introduction

- Why should nanomaterials be monitored.
- NanoMONITOR Guidance document.
    - How to sample and analyse for nanomaterials.
- Regulatory obligations to users of chemicals
- Challenges for users of nanomaterials to prove compliance.
- Tips for users nanomaterials to prove compliance.

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Why monitor nanomaterials?

- Health risks from particulates becoming apparent
  - Mainly regarding PM10 and PM2.5, less is known about the smaller fractions
  - Carey *et al.* (2018). Are noise and air pollution related to the incidence of dementia? A cohort study in London, England. BMJ Open, **8**, 1-11.
  - BBC (2018). Illegal levels of air pollution linked to child's death [Available at https://www.bbc.co.uk/news/science-environment-44612642]
- Very high surface area to mass ratio of nanomaterials <u>may</u> lead to increased/new health risks.
- Governments and regulators need to identifying emerging risks
- Industry needs to prove compliance with regulations and to develop safer products

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NanoMONITOR Guidance

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Nanomonitor Guidance document - Aims and scope

- Covers workplace and environment (different compartments and localities)
- Overview of current knowledge
- Development of sampling and analysis strategy
  - Why, where, how
- Summary of available technology
- What to do with results
- Summary of regulatory obligations that might require sampling/analysis

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Nanomonitor Guidance document: Current Knowledge – Sources of ENM

- Manufacture
  - CVD; milling; flame-spraying, liquid reaction
- Handling/transfer
  - Powder vs suspension; blending; weighing; manual vs automatic
- Use of nanomaterial
  - Formulation into suspensions; entraining into solid matrix
- Use of nano-enabled products
  - Application of suspensions; use of articles with embedded nanomaterials
- Degradation and waste
  - Road and rail traffic; degradation during usual use; recycling vs incineration vs landfill.

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Nanomonitor Guidance document: Current knowledge – Characteristics of released ENMs

- Chemical composition
- Particle size and shape
- Degree of aggregation
- Coating (intentional and natural)
- Weathering
- May change during the lifecycle of the ENM

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Nanomonitor Guidance document: Current knowledge – measured values

- Workplace: 20 – 10,000 particles/cm^3
  - Varies with activity
  - Difference in sizes analysed; chemical composition; analytical technique
- Airborne in Urban areas: 3000 – 125,000 per cm^3
  - Difficult to distinguish between natural, anthropogenic and ENM; chemical composition; particle characteristics beyond size.
  - Different analytical techniques used.
- Other environmental compartments. Water: 0.5 – 200 µg/L; Soil 0.01 – 3000 µg/kg (estimated).
  - No information on particle characteristics other than chemical composition.

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Sampling and measurement strategy

- Where should measurement be made; what amounts are expected; what parameters are important
- Use as simple methods as possible to give a justified result
- Consider sampling, sampling preparation, temporal and spatial aspects also
- How effective are risk management measures

Information gathering

Basic exposure assessment (in situ PNC)

Expert assessment (sampling)

Risk management

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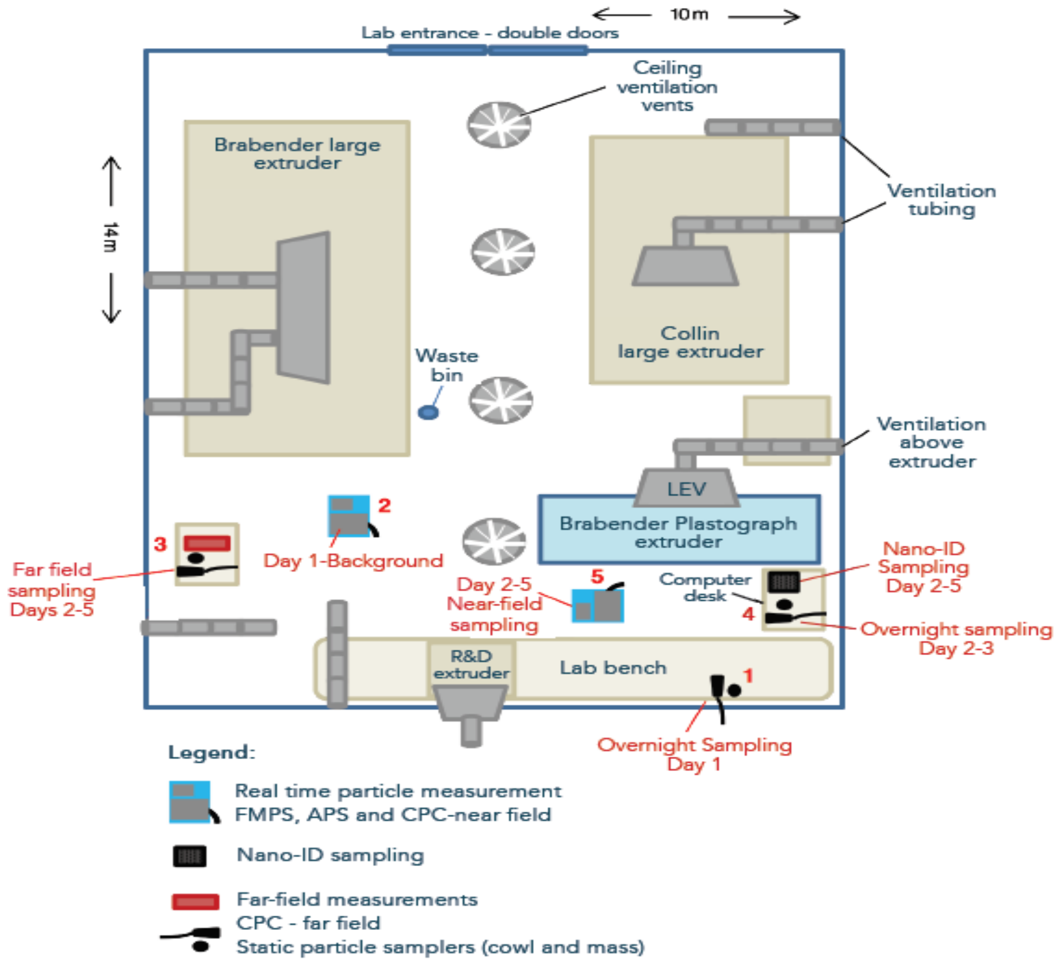
Strategy – Information gathering

- What concentrations are expected?
- Why are you gathering information?
- Is it important to measure background measurements?
- Should temporal aspects be considered?



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Strategy – Basic assessment

- In-situ analysis
- Results should be immediately available
- Instrument selection important.
- Be aware of exactly what it is and is not measuring.
- Can the results answer the problem or is sampling required?

Instrument	Remarks
Particle counters	10 -100 nm 0 – 100,000 particles
Optical particle sizer	300 – 10,000 nm 10 – $1x10^6$ particles
Surface Area monitor	300 – 10,000 nm Size distribution
Scanning mobility particle sizer	10 – 1,000 nm Measures surface area
Fast mobility particle sizer	5 – 550 nm Size distribution
Electrical low pressure impactor	6 – 10,000 nm Size distribution
Inertial spectrometer	Chemical composition

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Strategy – Sampling and off-site analysis

- Background readings important
- Concentrate on high exposure regions (from tier 2)
- Choose appropriate filter
  - Can collect correct size range; no contamination; does not change particle characteristics
- Choose appropriate analytical technique
  - Microscopy – particle shape and agglomeration behaviour
  - Particle tracking analysis – size distribution based on number
  - Single particle ICP-MS – chemical composition

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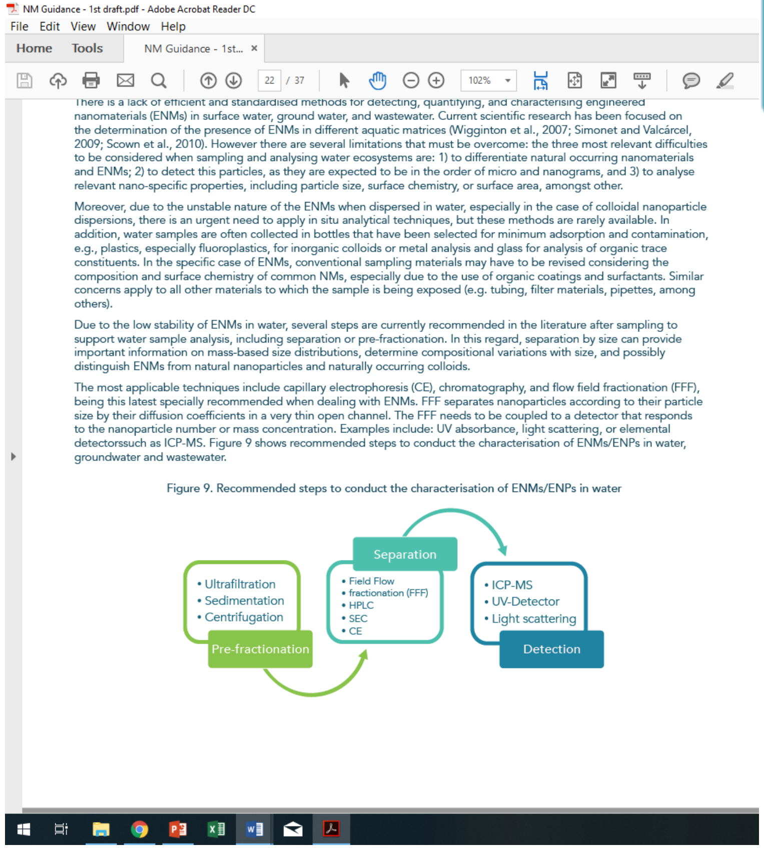
Strategy - Sampling of environmental samples (water)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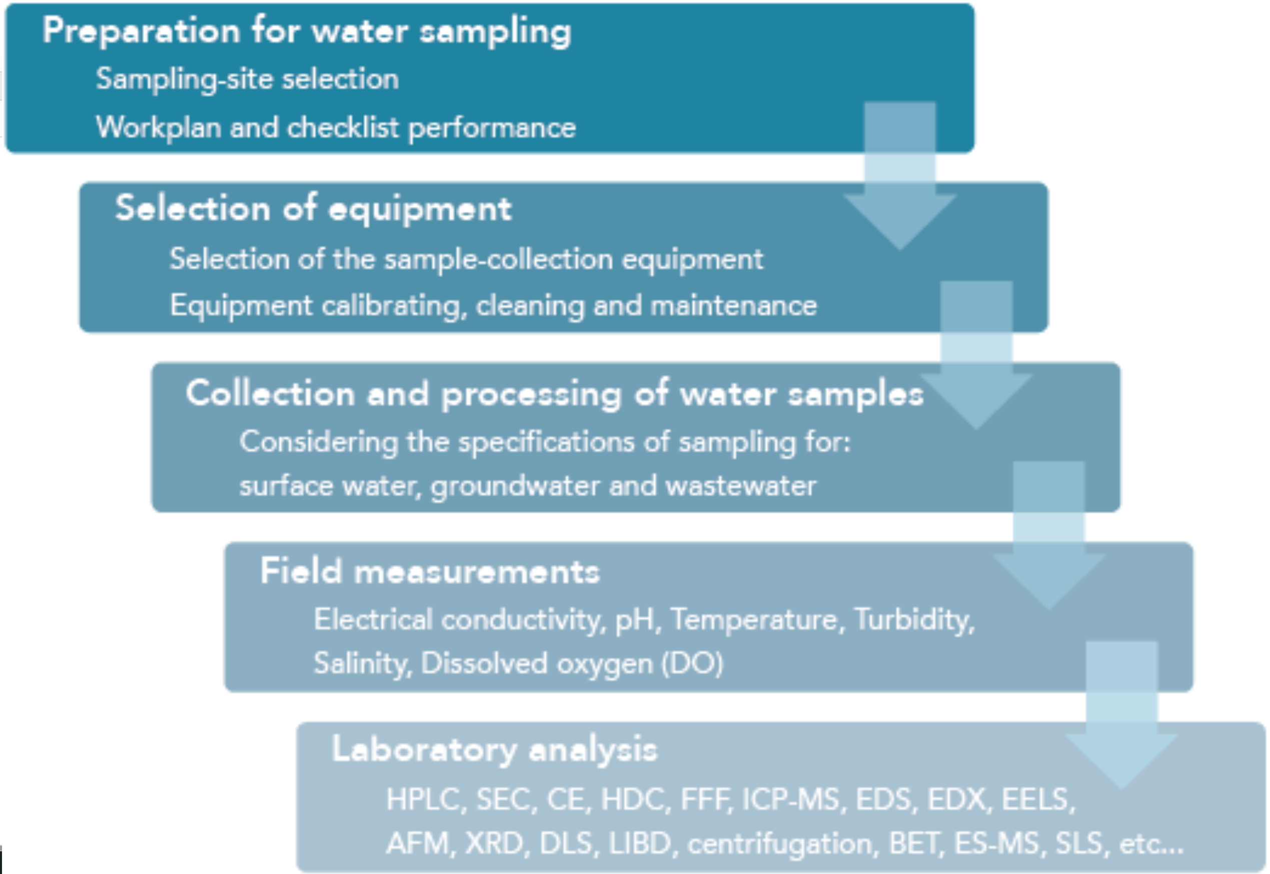
There is a lack of efficient and standardised methods for detecting, quantifying, and characterising engineered nanomaterials (ENMs) in surface water, ground water, and wastewater. Current scientific research has been focused on the determination of the presence of ENMs in different aquatic matrices (Wigginton et al., 2007; Simonet and Valcárcel, 2009; Scown et al., 2010). However there are several limitations that must be overcome: the three most relevant difficulties to be considered when sampling and analysing water ecosystems are: 1) to differentiate natural occurring nanomaterials and ENMs; 2) to detect this particles, as they are expected to be in the order of micro and nanograms, and 3) to analyse relevant nano-specific properties, including particle size, surface chemistry, or surface area, amongst other.

Moreover, due to the unstable nature of the ENMs when dispersed in water, especially in the case of colloidal nanoparticle dispersions, there is an urgent need to apply in situ analytical techniques, but these methods are rarely available. In addition, water samples are often collected in bottles that have been selected for minimum adsorption and contamination, e.g., plastics, especially fluoroplastics, for inorganic colloids or metal analysis and glass for analysis of organic trace constituents. In the specific case of ENMs, conventional sampling materials may have to be revised considering the composition and surface chemistry of common NMs, especially due to the use of organic coatings and surfactants. Similar concerns apply to all other materials to which the sample is being exposed (e.g. tubing, filter materials, pipettes, among others).

Due to the low stability of ENMs in water, several steps are currently recommended in the literature after sampling to support water sample analysis, including separation or pre-fractionation. In this regard, separation by size can provide important information on mass-based size distributions, determine compositional variations with size, and possibly distinguish ENMs from natural nanoparticles and naturally occurring colloids.

The most applicable techniques include capillary electrophoresis (CE), chromatography, and flow field fractionation (FFF), being this latest specially recommended when dealing with ENMs. FFF separates nanoparticles according to their particle size by their diffusion coefficients in a very thin open channel. The FFF needs to be coupled to a detector that responds to the nanoparticle number or mass concentration. Examples include: UV absorbance, light scattering, or elemental detectorssuch as ICP-MS. Figure 9 shows recommended steps to conduct the characterisation of ENMs/ENPs in water, groundwater and wastewater.

Figure 9. Recommended steps to conduct the characterisation of ENMs/ENPs in water



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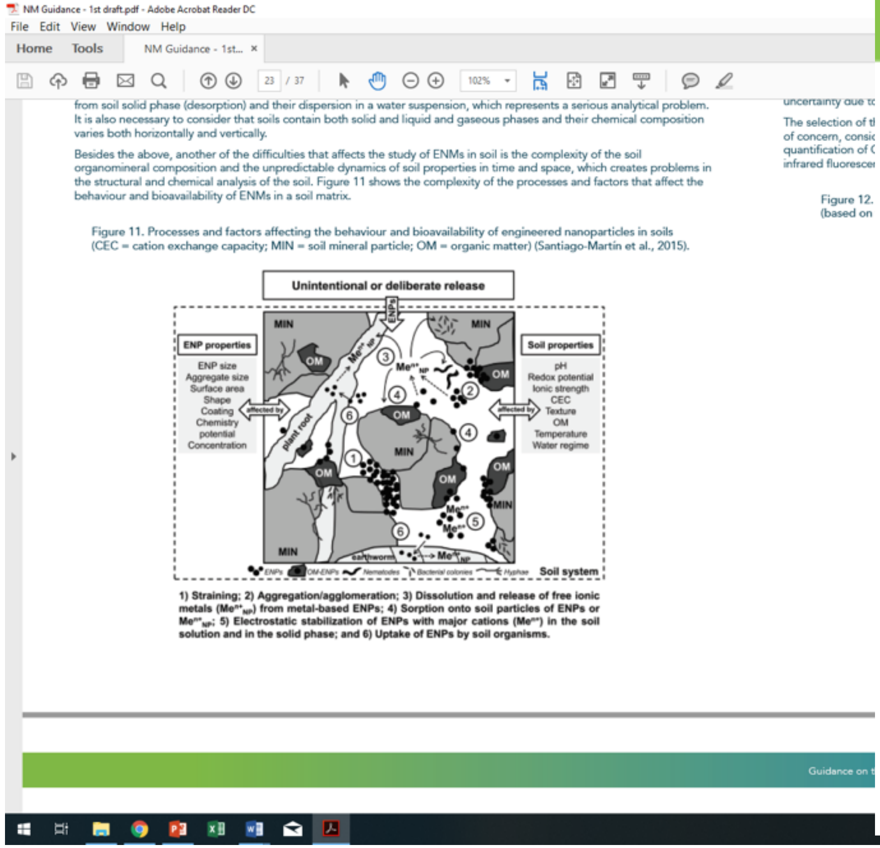
Strategy – Sampling of soil/sediment



from soil solid phase (desorption) and their dispersion in a water suspension, which represents a serious analytical problem. It is also necessary to consider that soils contain both solid and liquid and gaseous phases and their chemical composition varies both horizontally and vertically.

Besides the above, another of the difficulties that affects the study of ENMs in soil is the complexity of the soil organomineral composition and the unpredictable dynamics of soil properties in time and space, which creates problems in the structural and chemical analysis of the soil. Figure 11 shows the complexity of the processes and factors that affect the behaviour and bioavailability of ENMs in a soil matrix.

Figure 11. Processes and factors affecting the behaviour and bioavailability of engineered nanoparticles in soils (CEC = cation exchange capacity; MIN = soil mineral particle; OM = organic matter) (Santiago-Martín et al., 2015).

1) Straining; 2) Aggregation/agglomeration; 3) Dissolution and release of free ionic metals (Me^{n+}_{NP}) from metal-based ENPs; 4) Sorption onto soil particles of ENPs or Me^{n+}_{NP}; 5) Electrostatic stabilization of ENPs with major cations (Me^{n+}) in the soil solution and in the solid phase; and 6) Uptake of ENPs by soil organisms.

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Figure 12. (based on

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Preparation for soil and sediment sampling
- Sampling-site selection
- Workplan and checklist performance

Selection of equipment
- Selection of the sample-collection equipment
- Equipment calibrating, cleaning and maintenance

Collection and processing of soil and sediment samples
- Considering the specifications of sampling for: sediments, metal and metalloids, hydrocarbons, volatile organic compounds or volatile hydrocarbons in soil gases or vapours and pesticides

Field measurements
- Electrical conductivity, pH, Temperature, Texture, Salinity

Laboratory analysis
- HPLC, SEC, CE, HDC, FFF, ICP-MS, EDS, EDX, EELS, AFM, XRD, DLS, LIBD, centrifugation, BET, ES-MS, SLS, etc…

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Strategy – Airborne environmental (urban)

- Choose sample site carefully
  - Macroscale setting: Avoid atypical sites; high concentration sites; consider atmospheric impacts such as prevailing wind; consider temporal aspects
  - Microscale setting: Free airflow around device; inlet in breathing zone but not pointing at point source; access; security; safety; availability of utilities
- Site properties must be fully characterised.
- Similar equipment available to workplace monitoring

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Regulatory requirements for users of chemicals

- Registration
  - Hazard endpoints satisfied (> 1 tonne per year)
  - Safe exposure to humans and environment calculated (> 10 tonne per year)
  - Uses of substance identified and exposure to substance estimated. Adequate risk management measures identified (> 10 tonne per year)
- Communication
  - All registrants of a hazardous chemical on > 10 t.p.a. must include Exposure Scenarios (ES) as an Annex to the Safety Data Sheet (SDS) for the substance.
- Downstream Users
  - Must comply with ES requirements OR prove their measures are equivalent or superior OR do their own risk assessment.
  - Communicate relevant information along supply chain.

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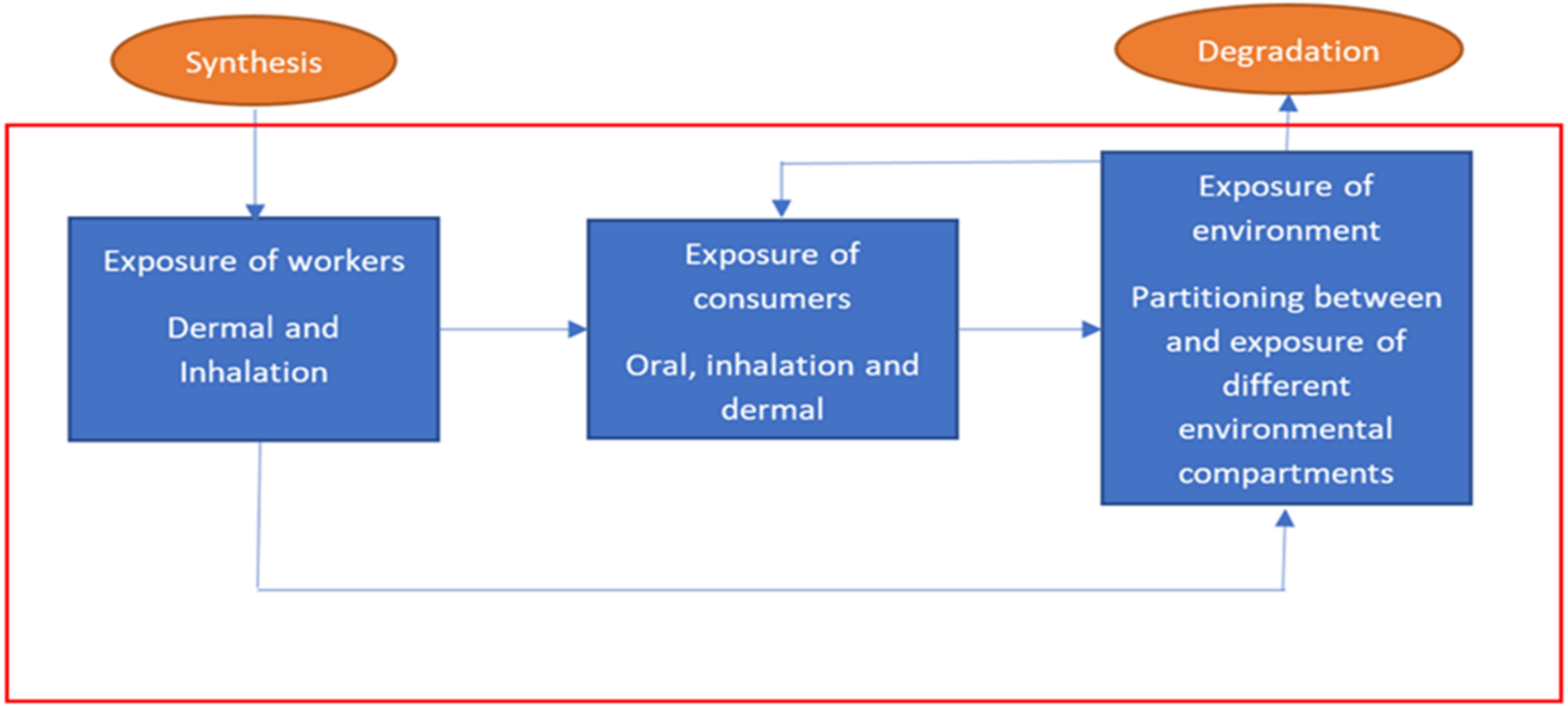
Issues that make nanomaterials difficult to assess



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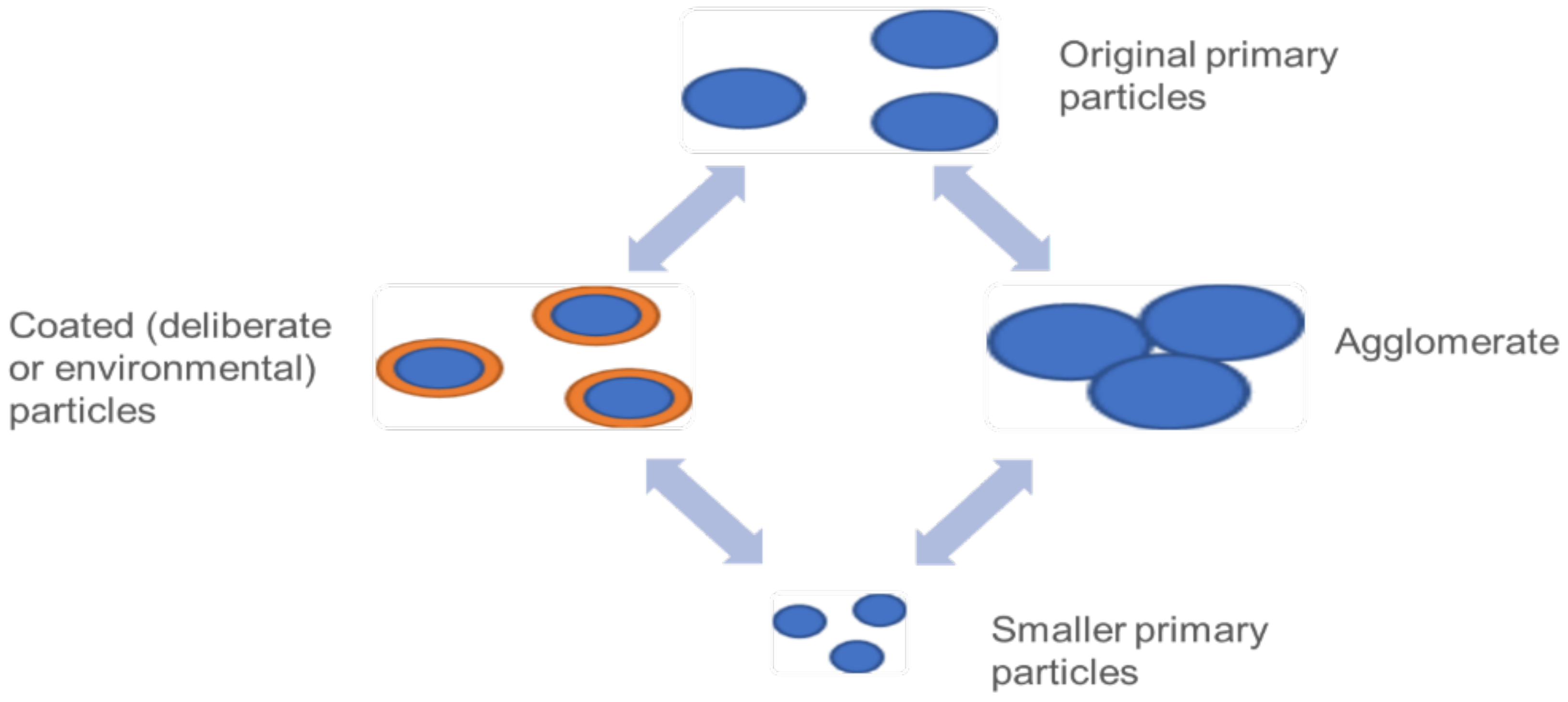

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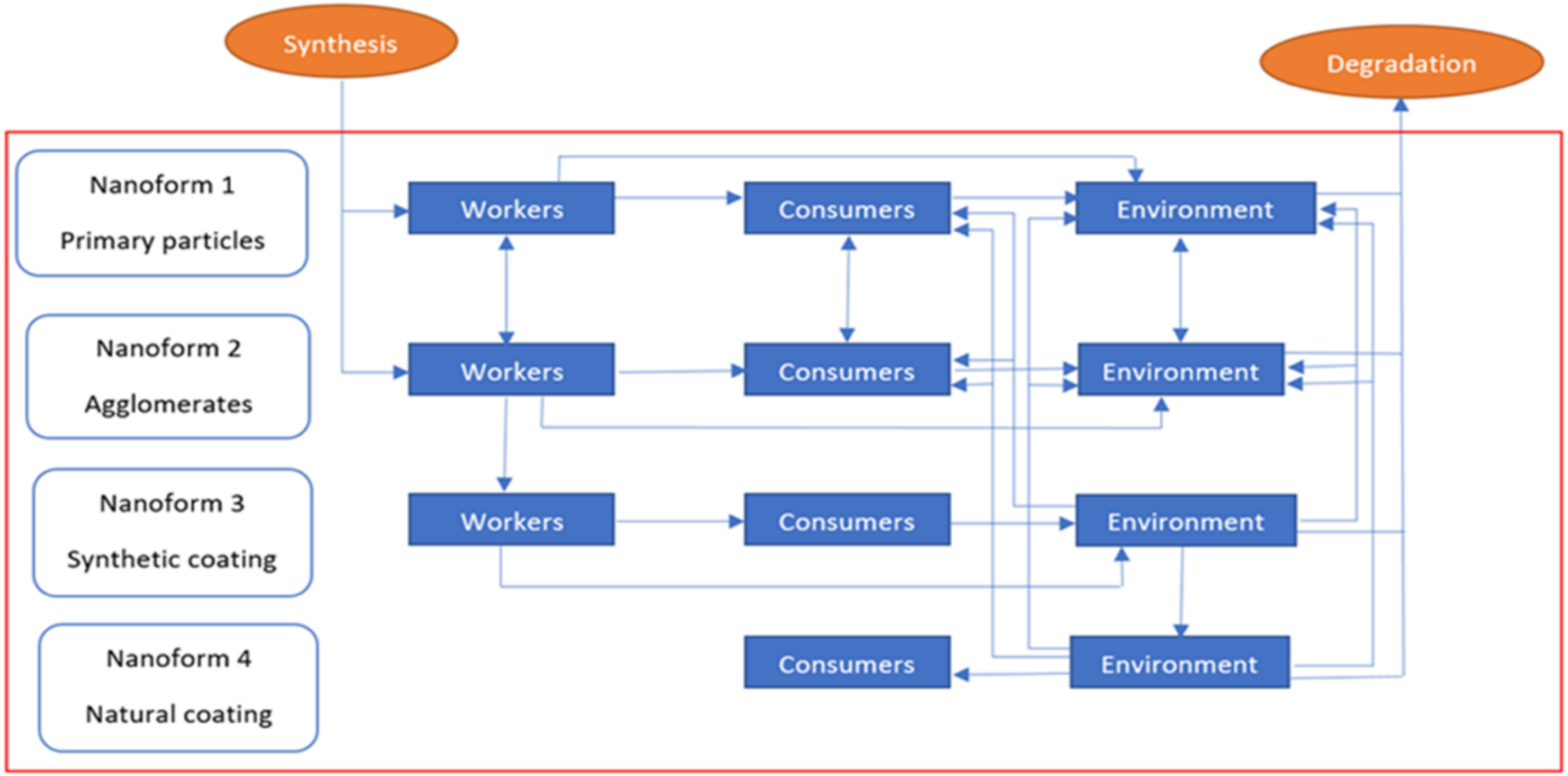

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Nanomaterials and REACH: Current and future

- Nanomaterials are not different substances to the same chemical in bulk form.
- REACH requires that different hazard data is relevant to the substance placed on the market.
- Currently no obligation to include particle characterisation in registration BUT
- Proposed revision of REACH will clarify obligations for nanomaterials.
  - Introduces nanoforms
  - May require particle characterisation of all particulate substances
  - Adapted endpoint testing requirements for nanomaterials

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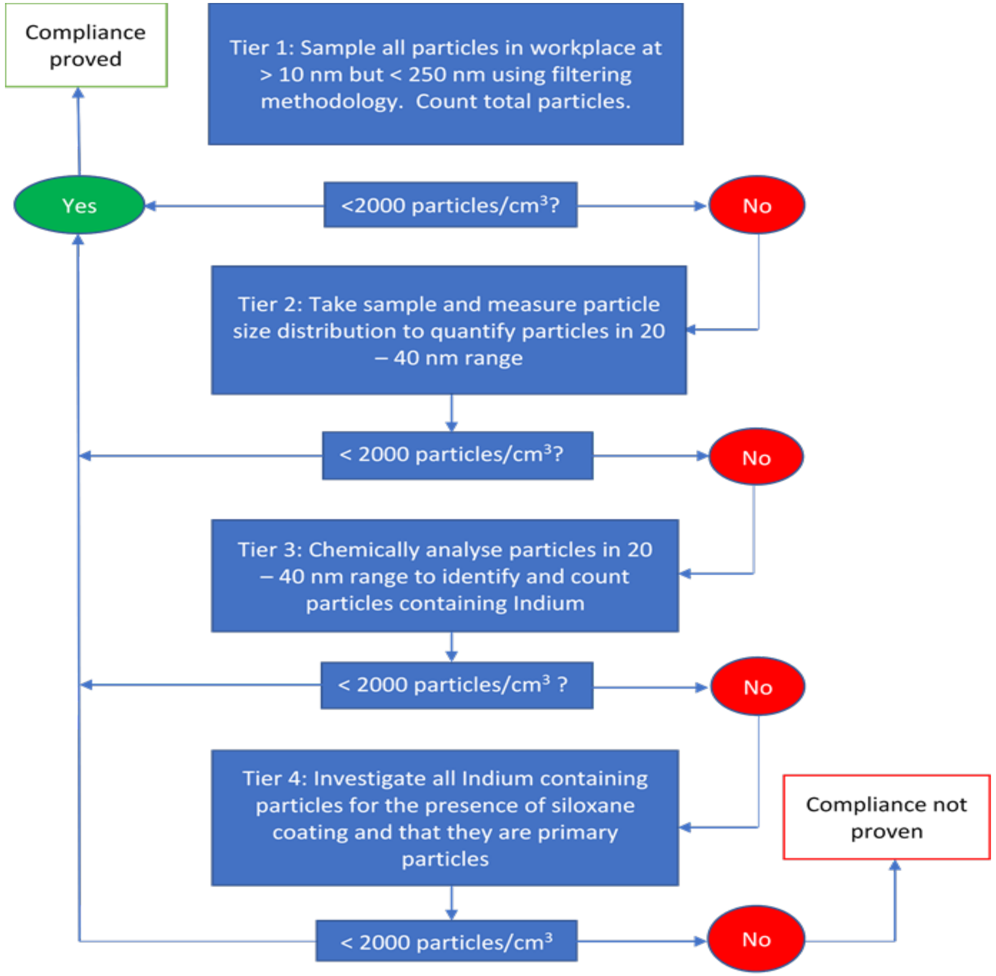
Proving compliance with REACH for users

- Example. Hazard information shows the most toxic nanoform of an indium salt is spherical primary particles coated in a siloxane in the 20 – 40 nm. Safe exposure in calculated as 2000 particles per cm^3.
- Use an iterative process using "worst-case assumptions"
- Only proceed as far as required.



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Thank you

Any Questions?

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