

Detailed guidance on tiered assessment using the NanoFASE Exposure Assessment Framework: a worked example

Part of the [NanoFASE “Clickable Framework”](#)

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What is NanoFASE?

The NanoFASE project (<http://nanofase.eu/>) received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 646002. The aim of the project is to predict environmental distribution, concentration and form (speciation) of nanomaterials. Such outcomes aim to allow early assessment of potential environmental and human exposure and risks, and to facilitate safe product design and could inform nano regulation.

The overarching objective of NanoFASE is to deliver an integrated Exposure Assessment Framework (protocols, models, parameter values, guidance ...) that:

- Allows all stakeholders to assess the environmental fate of nano releases from industrial nano-enabled products,
- Is acceptable in regulatory registrations and can be integrated into the EUSES model for REACH assessment,
- Allows industry a cost-effective product-to-market process, and
- Delivers the understanding at all levels to support dialogue with public and consumers.

The ambition is to reach a level of engineered nanomaterial fate and exposure assessment at least comparable with that for conventional chemicals.

The project delivered a NanoFASE Exposure Assessment Framework (EAF), which includes models of varying degrees of complexity with guidance on their use. Resources to learn about the EAF may be accessed through the “Clickable Framework” presented on the project website: http://nanofase.eu/exposure_assessment_framework.

*The present document provides **detailed guidance** on conducting a tiered environmental exposure assessment for engineered nanomaterials (ENMs). It is downloadable from the Modelling area of the Clickable Framework, where further information about the NanoFASE models and assessment approach may be found.*

*In particular, read the summary explanation of the [Workflow for a tiered exposure assessment](#), including three PPTs that summarize the example (**Photocatalytic coating for roads**) that is worked in detail in the present guidance document.*



The NanoFASE Exposure Assessment Framework: a worked example

1 What is an environmental exposure assessment?

An environmental exposure assessment for a chemical is an exercise to predict the concentrations of that chemical in the environment, and sometimes within organisms, as a result of its use by humans.

Environmental exposure assessments are typically conducted as a component of an environmental risk assessment. The projected exposure concentrations (**PECs**, Predicted Environmental Concentrations) are combined with hazard assessment outcomes (e.g. **PNECs**, Predicted No–Effect Concentrations) to provide assessments of the chemical risk.

The specific purpose of an environmental exposure assessment varies widely, but broadly will be either a:

- Screening level assessment, to rapidly determine whether or not the chemical may pose a risk to the environment and thus require more in–depth assessment; *or a*
- High level assessment, to predict exposure using a level of model realism concomitant with the scientific state of the art.

Regardless of the purpose and complexity of an exposure assessment, the data typically required to conduct the assessment fall into one of three categories:

- Environmental scenario data, which define the properties of the environmental compartments (atmosphere, soil, freshwater, marine water, etc.) for which assessment is being conducted, including parameters which define how the chemical may move from one compartment to another;
- Environmental emission rates for the chemical, which define the amount of chemical entering the environment;
- Chemical fate descriptors - parameters which collectively determine the way in which the chemical behaves within the environment. For example, the rate at which nanomaterials in surface waters attach to suspended sediment is important in determining how rapidly they might settle out onto a river or lake bed.

Environmental scenario data are independent of the specific chemical being studied, although for complex assessments there may be scenario data requirements that are specific to a chemical or to a group of similar chemicals.

Environmental emission rates can be defined at differing levels of complexity. At the simplest level, a rate of emission can be defined assuming that all the chemical produced enters the environment (this is an example of a 'worst case' scenario). At more complex, realistic levels of assessment, emission rates can be based on generic patterns of release related to broad categories of chemical use, or specific patterns of release related to narrow categories of chemical use (e.g. uses specific to that chemical). At the highest levels, the specific locations where releases occur, and the patterns of release through time, may also need to be specified.

Chemical fate descriptors are by their nature specific to the chemical under consideration. Groups of chemicals of broadly similar behaviour typically share the same collection of types of fate descriptor. Nanoforms are particularly notable because they share a common set of fate descriptors, related to their behaviour as particles (for example, the rate at which they become attached to particles of soil or sediment) - but there are subgroups with their own sets of behaviour, for example nanoforms which can dissolve, as opposed to those which cannot.

2 Tiered exposure assessment

For the purposes of chemical safety assessment, it is typical to perform an exposure (and hazard) assessment in a tiered fashion.

The essence of a tiered approach is to assess exposure (and hazard) using progressively more complex approaches. If a simple(r) approach suggests that the chemical poses no significant risk, then there is no need to move to the next tier - the assessment ends. This is efficient because performing a full exposure assessment, in the greatest detail possible, can be time consuming and require large amounts of data. If a simpler assessment, designed to be more conservative than more complex assessments, can demonstrate no risk then there is no need to perform more complex assessments.

The diagram (**Figure 1**) sets out the generic structure of a tiered approach. It comprises a repeating cycle of data collection and collation and model choice prior to assessment, followed by the assessment itself and an appraisal of whether risk is indicated. At any stage, if no significant risk is indicated, the assessment process ends with this conclusion. If significant risk remains at the final tier, a number of options (such as the implementation of additional risk management measures for the chemical) may be specified. The specific measures will depend upon the overall purpose of the assessment process.

The number of tiers in an assessment framework is flexible and can be specific to the purpose of the assessment as well as the nature of the chemical under assessment. For demonstration purposes, a three-tier framework is used here:

1. Low tier: simple worst case assessments using hand calculations;
2. Intermediate tier: assessment using [SimpleBox4Nano](#);
3. Higher tier: assessment using the [NanoFASE WSO model](#).

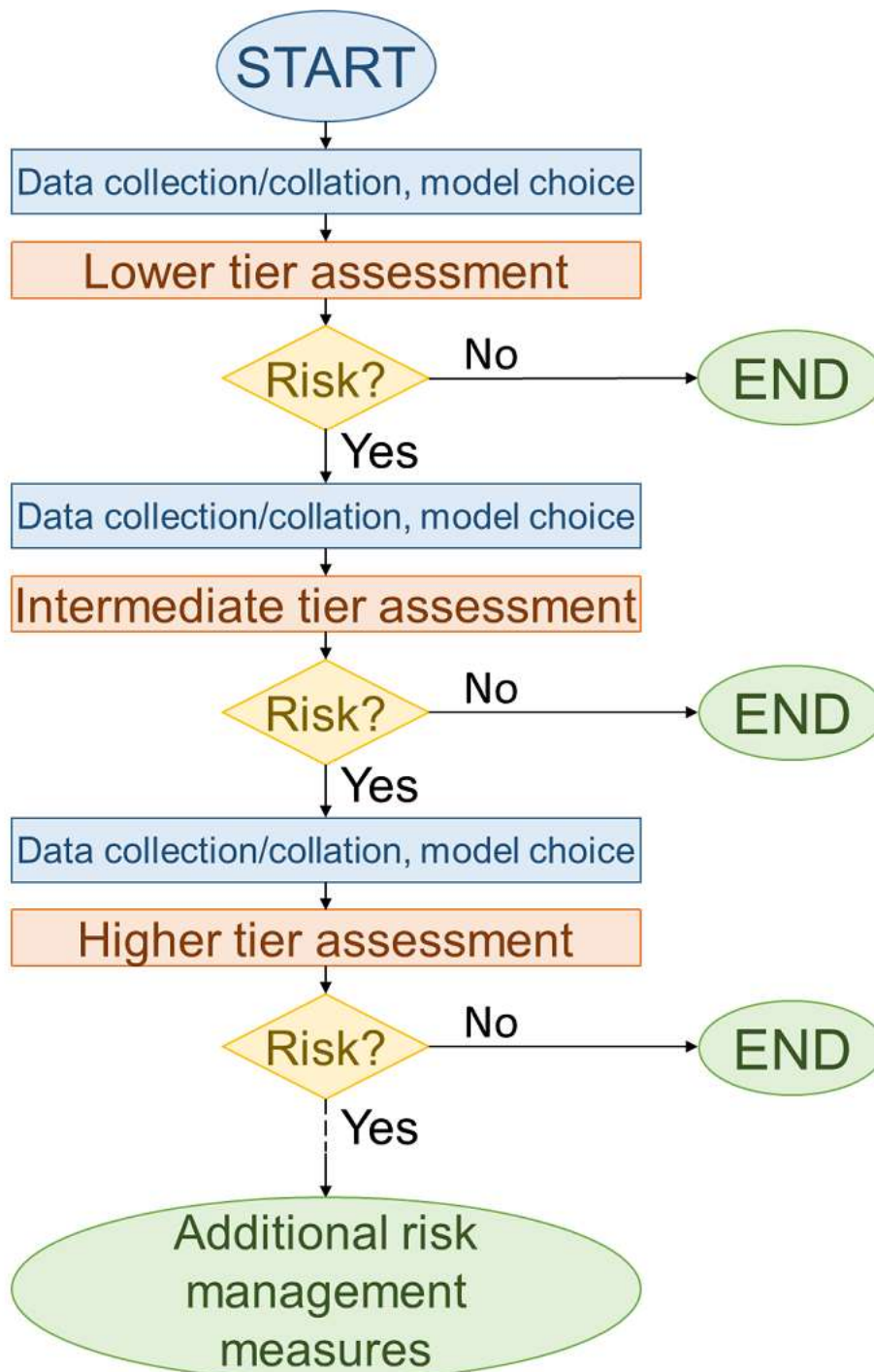


Figure 1: Generic structure of a tiered exposure assessment approach.

2.1 Lower tier exposure assessment

For lower tier assessment, the aim is to produce a simple assessment which can be done without use of purpose-built modelling tools, but instead by constructing a 'worst case' exposure scenario that can be reduced to a set of equations simple enough to do the computations by hand or in a spreadsheet.

The main purpose of a lower tier-type assessment is to check whether exposure under worst case conditions attains potentially hazardous levels. If no such indication of hazard is found in results, this can be an argument for not requiring more refined assessment. It is important to appreciate that prediction of risk at lower tiers is not definitive, but instead indicates that more refined assessment is required.

Nanomaterial emissions and fate

A [pathway analysis](#) is required of where in the product lifecycle emissions to the environment are likely to occur, and to which environmental compartments. This includes analysis of whether nanomaterials will pass into the managed waste systems (e.g. landfill, wastewater treatment, incineration).

The pathway analysis provides a set of environmental compartments into which the nanomaterial can be assumed to be emitted. The basis of the assessment is then to perform computations of the PEC within each compartment, based on some straightforward assumptions:

- That the nanomaterial emission occurs entirely into that compartment;
- The nanomaterial is persistent, i.e. that it does not degrade or change over time into a form that is not of interest for the exposure assessment.

Using a knowledge of potential fate pathways following discharge, a set of environmental compartments in which exposure must then be considered can be inferred, taking into account possible transfers of nanomaterial from one compartment to another (**Table 1**):

Table 1. Emission-assessment compartment matrix for lower tier fate assessment.

Emitted into:	Assess fate in:			
	Soil	Surface water	Groundwater ^a	Sediments
WWTP	✓1,2	✓7,8	✓13	✓17,18
Air	✓3	✓9	✓14	✓19
Soil	✓4	✓10	✓15	✓20
Surface water	✓5	✓11		✓21
Groundwater	✓6	✓12	✓16	✓22

Transfer processes inferring need for exposure assessment in each compartment:

- ¹ incorporation into biosolids → spreading of biosolids on land
- ² incorporation into biosolids → incineration of biosolids → deposition to land
- ³ deposition to land
- ⁴ retention in soil
- ⁵ irrigation of land with surface water
- ⁶ irrigation of land with surface water → percolation to groundwater
- ⁷ discharge into surface water → retention in water column
- ⁸ incorporation into biosolids → incineration of biosolids → deposition to water
- ⁹ deposition to water → retention in water column
- ¹⁰ runoff to surface water → retention in water column
- ¹¹ retention in water column
- ¹² seepage into surface water → retention in water column
- ¹³ incorporation into biosolids → spreading of biosolids on land → percolation to groundwater
- ¹⁴ deposition to land → percolation to groundwater
- ¹⁵ percolation to groundwater
- ¹⁶ retention in groundwater
- ¹⁷ discharge into surface water → deposition to sediment
- ¹⁸ incorporation into biosolids → incineration of biosolids → deposition to water → deposition to sediment
- ¹⁹ deposition to water → deposition to sediment
- ²⁰ runoff to surface water → deposition to sediment
- ²¹ deposition to sediment
- ²² seepage into surface water → deposition to sediment

Notes

^a Exposure in groundwater need be assessed only if the presence of the material constitutes a direct ecological hazard in groundwater.

For a low tier, worst case assessment, we do not consider how much nanomaterial may be transferred from one compartment to another. Instead, we assume that all emitted nanomaterial will enter each compartment. **This is clearly physically unrealistic, but it simplifies calculations and provides worst case exposure estimates for each environmental compartment, which serves the purpose of a low tier screening assessment.**

Nanomaterial transformations

For a low tier assessment the need to consider nanomaterial transformations should be minimised. If a nanomaterial is known to be potentially water-soluble, then this can be assumed to have no effect on its fate, since worst case exposure conditions are being assumed. If a risk assessment is being carried out, this may influence the choice of hazard data to be used (e.g. hazard of the nanomaterial vs. hazard of the dissolved chemical(s)).

Environmental scenario

For a low tier exposure assessment, the definition of an environmental scenario is limited to defining the capacity of each environmental compartment that represents a potential sink for the nanomaterial (**Table 2**). The capacity of the compartment is limited by the geographical scope set for the scenario as a whole.

Table 2. Definitions of the capacities of environmental compartments and the information required to define them.

Compartment	Capacity definition	Other information required to define capacity.
Surface water	Daily mean volume of water present (m ³)	
Soil	Mass of soil receiving ENP (kg)	Active soil depth (m) Soil area (m ²) Soil bulk density (kg/m ³)
Sediment	Mass of sediment receiving ENP (kg)	Active sediment depth (m) Sediment area (m ²) Sediment bulk density (kg/m ³)
Groundwater	Volume of groundwater (m ³)	

Then the computation of PECs entails applying the general calculation:

PEC (chemical mass per unit capacity) = chemical mass present in compartment ÷ compartment capacity

or

PEC (chemical mass per unit capacity at time t) = chemical mass present in compartment to time t ÷ compartment capacity

Depending on the receiving compartment, there may be a time element to calculations. For the surface water compartment, because the receiving water transports material out of the catchment, calculation of the PEC can be done on the assumption of a 'steady state' where the rate at which material enters and leaves the compartment is constant. In this situation there is no time element. For soils and sediments, the conservative assumption made is that the chemical will gradually accumulate over time and so a basic calculation is made (e.g. the PEC resulting from emission and accumulation in one year) from which PECs for longer time periods can be calculated. For groundwater, a conservative assumption of no water loss from the aquifer allows the same approach to be taken.

The worked example (section 3 below) shows how such exposure calculations can be done.

2.2 Intermediate tier exposure assessment

Exposure assessment above the lower tier typically involves the application of a model that is specifically designed to predict the fate of nanomaterials. For intermediate tier application a number of models as available, including SimpleBox4Nano ([SB4N](#)).

The model simultaneously considers the fate of a nanomaterial emitted into one or more environmental compartments (air; freshwaters, estuarine waters, marine waters and their sediments; soil). Each environmental compartment is assumed to be 'fully-mixed'. This means that, like the lower tier assessment, a single PEC is produced for each compartment. The key difference between an intermediate-type model and the lower tier assessment is that the nanomaterial can move from one compartment to another, based on the properties of the environment and the nanomaterial. The nanomaterial can also be permanently removed from the environment, by the burial of sediments (or by transformation to a non-nano chemical).

This type of exposure model typically provides PECs calculated under conditions of 'steady state'. Steady state is the situation where the inputs (emissions) rate of the chemical into the environment is balanced by the rate of its removal. The annual emission rate of the chemical has to be assumed constant to allow the calculation to be done.

Nanomaterial transformations

An intermediate tier exposure model will require parameters defining nanomaterial transformations that influence its fate. These might include the rate at which it attaches to suspended sediments in waters, or the rate at which it dissolves.

Environmental scenario

The definition of an environmental scenario at intermediate level typically includes (a) the capacity of all the environmental compartments and (b) the rates of processes that influence the transfer of nanomaterial from one compartment to another. The latter may include, for example, the rate of soil erosion into surface waters and the rate at which sediment in waters settles to the bottom.

2.3 Higher tier exposure assessment

The scope of higher tier exposure assessment varies greatly, but generally involves applying a complex model to predict how the nanomaterial PECs vary spatially and over time across one or more environmental compartments.

The [NanoFASE Water-Soil-Organism \(WSO\) model](#) is an example of higher tier exposure assessment model.

Higher tier exposure assessment is sometimes used in regulation, but not as frequently as intermediate tier assessment. A non nano-specific example of the use of higher tier assessment is the EU review process for plant protection products, [FOCUS](#). In this case a set of models are combined into a single package along with a set of predefined environmental and release scenarios, to reduce the amount of information that users have to provide to make an assessment (and to make assessments more consistent across different chemicals).

Nanomaterial transformations

A higher tier exposure model, like an intermediate one, will require parameters defining nanomaterial transformations that influence its fate. At higher level, the values of these parameters might be set to vary over space and time, for example as functions of the soil or water chemical properties at a particular location.

Environmental scenario

The definition of an environmental scenario at higher tier is complex. Each environmental compartment is subdivided (e.g. areas of soils, reaches (lengths) of rivers) in order to allow predictions to be made at a fine level of detail. The environmental scenario will typically require large amounts of data to run. For example, modelling of water and chemical movement through soils and river systems will require inputs of rainfall and other variables such as evapotranspiration, over time and space.

3 Worked example: photocatalytic coating for roads

The example is provided by a [case study](#) performed in cooperation with one of the industrial partners in the NanoFASE project, FCC Construcción (FCCCO) <https://www.fccco.com/es/>. It has been selected as an example since they have provided detailed information on the material, amounts and processes involved in their nano-enabled photocatalytic coating for roads. The road coating is applied to capture and remove environmental pollutants from transport vehicle exhaust.

The material is a commercially sourced titanium dioxide (TiO₂) with a particle diameter range of 10-20 nm. It is dispersed into a polymer resin and sprayed onto the road surface at an application rate of 2.45 g/m².

A [life cycle analysis test](#) performed in NanoFASE, which simulated wear and abrasion of a section of road surface coated with the material, estimated that 38% of the material would be abraded and released over 12 months following application. The material was released as aggregates with the resin, with a size range of 0.5–5.0µm.

3.1 Lower tier exposure assessment

A [pathway analysis](#) suggests that the major emission of nanomaterials will be during the use phase, when material may be abraded from the road surface and washed into the wastewater treatment system.

A number of conceptual fate scenarios can be constructed for this emission pathway (referring to the [emission-assessment matrix](#)):

- S1. WWTP → Soil;
- S2. WWTP → Surface waters;
- S3. WWTP → Surface waters → Sediments;
- S4. WWTP → Soil → Surface waters;
- S5. WWTP → Soil → Surface waters → Sediments;
- S6. WWTP → Soil → Groundwater;

such that for assessment purposes exposure in **soil, surface water, sediments and groundwater** can be considered.

The pathway analysis also shows that emissions may occur during incorporation of the nanomaterial into the dispersion prior to road application, and during road application. Assuming such emissions to be into air or the wastewater treatment system, they are already covered by the fate scenarios listed.

Therefore, four types of exposure scenario may be considered at Tier 1:

- E1. Soil exposure. All the material entering the wastewater treatment system during one year is incorporated into biosolids and applied to land. Biosolids application is assumed to occur entirely within the catchment;
- E2. Surface water exposure. All the material entering the wastewater treatment system during one year is retained in the liquid phase and discharged into surface water. The material is all retained within the water column;
- E3. Sediment exposure. All the material entering the wastewater treatment system during one year is retained in the liquid phase and discharged into surface water. The material all transfers to the sediment;
- E4. Groundwater exposure. All the material entering the wastewater treatment system during one year is incorporated into biosolids and applied to land, from where it

percolates through the soil into the groundwater. Biosolids application is assumed to occur entirely within the catchment.

For the purposes of this example we will do computations for scenarios E1, E2 and E3 (meaning that we will not assess the groundwater exposure scenario).

Environmental scenario parameters

At this tier, the environmental parameters needed are relatively simple.

For all the retained exposure scenarios, we need to compute the amount of material entering the environmental compartment that we are interested in.

For each exposure scenario, we need to compute the concentration of material in that compartment. To do this, we need to know the volume (for surface waters) or the mass (for soils and sediments) of material in the compartment.

For this exercise, we will use the Thames catchment (UK) as the environmental scenario. We will assume that emissions pathways of the material are influenced by UK policy – so, for example, we assume no emissions to air by the incineration of biosolids, because UK policy is not to incinerate biosolids but to spread them to land. The air pathway may be relevant in countries where biosolids are incinerated.

Amount of material released into the environment

For the purposes of this example, we make conservative assumptions of the amount of material likely to be used:

1. We assume that **major urban roads in the catchment are treated**;
2. We assume, based on release experiments, that 38% of the material is abraded and **released into the environment in the year after application**;
3. We assume that the released material is reapplied each year and that 38% is abraded each year, providing a constant rate of input into the environmental compartments.

The area of the Thames catchment is 15875 km². Of this, 0.9% is road surface. Urban roads comprise 13% of the total roads and 25% of urban roads are major roads. So we estimate the area to which material is applied:

$$\text{Application area} = 15875 \text{ km}^2 \times 0.9/100 \times 13/100 \times 25/100 = 4.64 \text{ km}^2$$

The application rate of 2.49 g/m² is 2.49×10⁶ g/km².

<p>Amount entering environment (g/a) = Amount applied (g/a) = application rate (g/km²/a) × proportion released in one year × area applied (km²) = 2.49×10⁶ g/km²/a × 0.38 × 4.64 km² = 4.39×10⁶ g/a (4.39 t a⁻¹)</p>
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Exposure in soil

For the soil exposure, we assume that all the material accumulates within a certain depth (the active soil depth). For materials that are applied to agricultural land in biosolids, it is reasonable to assume that this is the depth of the plough layer, which we assume to be 20cm (0.20m).

If we can estimate the area of soil that is subject to inputs of the material, then we can compute the volume of soil receiving inputs.

Detailed guidance on tiered assessment using the [NanoFASE Exposure Assessment Framework](#)

For this material and the Thames catchment, we can assume that inputs are to agricultural soil. The catchment area is 15875 km² (15875×10⁶ m²), and the proportion of agricultural land is 0.626 (62.6%).

So the soil volume receiving inputs (m³) = 15875×10⁶ m² × 0.626 × 0.20m = 1.98×10⁹ m³.

To compute the mass of the soil in this volume, we need an estimate of the soil bulk density. Bulk densities of soils can be measured, but for this calculation we need an average estimate for all arable soils in the catchment.

Bulk density can be estimated from soil organic matter content, and is inversely dependent on it (i.e. higher soil organic matter content means lower bulk density).

We can use an expression adapted from the scientific literature:

Bulk density (kg/m³) = 1380 – 290 × ln (% organic carbon)

In the absence of data on the specific organic carbon contents of Thames arable soils, we can use a conservative estimate based on the organic content of the OECD standard soil. This has 10% organic matter by weight, which yields 5% organic carbon if we assume that organic matter is 50% carbon¹.

So: bulk density of soil receiving inputs (kg/m³) = 1380 - 290 × ln (5) = 913 kg/m³.

And: Soil mass receiving inputs (kg) = 1.98×10⁹ m³ × 913 kg/m³ = 1.81×10¹² kg.

Annual accumulation rate (AAR) in soil (g/m³/a)

= amount applied in one year (g) ÷ receiving soil mass (kg)

= 4.39×10⁶ g ÷ 1.81×10¹² kg

= **2.43×10⁻⁶ g/kg**

[= **0.00243 µg/g**]

The AAR is also the PEC for one year of emissions. We can compute the PEC after certain number of years of addition, on the assumption that material is applied annually and that the annual emission rate is constant:

After 10 years: PEC = 0.477 µg/g/year × 10 = **0.0243 µg/g**

After 50 years: PEC = 0.477 µg/g/year × 50 = **0.122 µg/g**

After 100 years: PEC = 0.477 µg/g/year × 100 = **0.243 µg/g**

Exposure in surface waters

The volume of freshwater which the material enters is assumed to be the daily drainage volume of the catchment plus the mean volume of water in the estuary.

The combined long term mean flow of the main stem of Thames at the tidal limit, and of the tributaries entering below the tidal limit, is 30.1 m³/s, giving a total daily freshwater volume of 2.60×10⁶ m³. The volume of the estuary is 4.85×10⁹ m³, giving a mean volume of water in the catchment of 4.85×10⁹ m³ (the volume of freshwater is effectively negligible).

¹ Cabaniss, S.E., Madey, G., Leff, L., Maurice, P.A., Wetzel, R., 2005. A stochastic model for the synthesis and degradation of natural organic matter. Part I. Data structures and reaction kinetics. *Biogeochemistry*, 76, 319–347.

Unlike soils and sediments, because water is in continual flux through and out of the catchment on timescales of days, we can assume that the ratio of emissions to water volume represents a true PEC, not an accumulation rate.

The PEC is then one day of emissions, divided by the mean daily volume of water in the catchment:

$$\begin{aligned} \text{PEC in surface water (g/m}^3\text{)} &= \text{amount applied (g/d)} \div \text{receiving water volume (m}^3\text{)} \\ &= 4.39 \times 10^6 \text{ g} \div 365 \div 4.85 \times 10^9 \text{ m}^3 \\ &= \mathbf{2.48 \times 10^{-6} \text{ g/m}^3} \\ &[\mathbf{= 0.00248 \text{ }\mu\text{g/dm}^3}] \end{aligned}$$

It is useful – and likely to be necessary – to make calculations only for the freshwater compartment. For simplicity, we can make the assumption that all emissions enter freshwaters – this may not be the case, but it is conservative.

We already know that the daily freshwater volume of the Thames is $2.60 \times 10^6 \text{ m}^3$, so:

$$\begin{aligned} \text{PEC in freshwater (g/m}^3\text{)} &= \text{amount applied (g/d)} \div \text{receiving water volume (m}^3\text{)} \\ &= 4.39 \times 10^6 \text{ g/a} \div 365 \text{ d} \div 2.60 \times 10^6 \text{ m}^3 \\ &= \mathbf{0.00463 \text{ g/m}^3} \\ &[\mathbf{= 4.63 \text{ }\mu\text{g/dm}^3}] \end{aligned}$$

Exposure in sediments

For sediments, like soils, we assume that material is immobilised and accumulates within a fixed ‘active’ depth of sediment. Here we assume the active depth to be 4cm (0.04m).

We need to estimate the mass of sediment receiving material. This is done in the same way as for soils.

The surface areas of the freshwater and estuarine waters are $1.60 \times 10^6 \text{ m}^2$ and $3.78 \times 10^8 \text{ m}^2$ respectively, giving a total surface area of $3.80 \times 10^8 \text{ m}^2$.

We need an estimate of sediment bulk density to get the sediment mass. To do this we can compute the particle density of the sediment and its porosity (the proportion of the sediment volume taken up by water).

We can do this by making an assumption about the organic matter content of the sediment, and using bulk densities of inorganic and organic matter of 2600 and 1500 kg/m^3 respectively.

Assuming 10% organic matter content by mass, we get particle density = $1500 \times 0.1 + 2600 \times 0.9 = 2490 \text{ kg/m}^3$.

Assuming a porosity of 0.5, bulk density = $2490 \times (1 - 0.5) = 1245 \text{ kg/m}^3$.

So the sediment mass = $3.80 \times 10^8 \text{ m}^2 \times 0.04 \text{ m} \times 1245 \text{ kg/m}^3 = 1.89 \times 10^{10} \text{ kg} = 1.89 \times 10^{13} \text{ g}$.

$$\begin{aligned} \text{AAR in sediments (g/g/a)} &= \text{amount applied in one year (g)} \div \text{receiving sediment mass (g)} \\ &= 4.39 \times 10^6 \text{ g} \div 1.90 \times 10^{13} \text{ g} \\ &= \mathbf{2.32 \times 10^{-7} \text{ g/g/a}} \\ &[\mathbf{= 0.232 \text{ }\mu\text{g/g/a}}] \end{aligned}$$

As with soils, this AAR is also the PEC for one year of emissions. For 10 years of emissions the PEC is **2.32 µg/g**, for 50 years it is **11.6 µg/g** and for 100 years it is **23.2 µg/g**.

Again, we can compute an AAR solely for freshwater sediments, based on the freshwater sediment area of $1.60 \times 10^6 \text{ m}^2$, which gives a sediment mass of $7.97 \times 10^{10} \text{ g}$:

AAR in freshwater sediments (g/g/a)

= amount applied in one year (g) ÷ receiving sediment mass (g)

= $4.39 \times 10^6 \text{ g} \div 7.97 \times 10^{10} \text{ g}$

= **$5.51 \times 10^{-5} \text{ g/g/a}$**

[= **55.1 µg/g/a**]

3.2 Intermediate tier exposure assessment: SimpleBox4nano

Application of [SimpleBox4nano](#) to the Thames catchment requires basic information on the catchment, as is needed for the lower tier calculations, but also requires parameters that allow the model to predict the transfer of nanomaterial among environmental compartments. In this example, these include the properties of natural colloids in surface waters, soil pore waters and sediment pore waters, and of suspended sediments in surface waters. For the TiO_2 nanoforms, the key parameters are the mean particle size and density, and the attachment efficiency to natural colloids and suspended particulate matter. A full list of parameters is given in **Table 3**.

The nanomaterial transformation process simulated in this example is attachment to soils and sediments. Modelling of other nanomaterials may need to include additional processes, such as dissolution. Because titanium dioxide has a very low solubility, we assume that it does not dissolve in the environment.

- Emissions were assumed to be via the wastewater system, as for the lower tier assessment. Emissions to air during application were assumed to be negligible, as were emissions following end-of-life.
- Emissions from the wastewater system were partitioned between the biosolids and the effluent:
 - Biosolids emissions were assumed to form inputs to agricultural soil as a result of biosolids application within the catchment;
 - Effluent emissions were assumed to be directly into freshwater.

This example scenario does not include emissions to the atmosphere, but SimpleBox4nano is capable of simulating the deposition rate and ultimate fate of nanomaterials emitted into the atmosphere.

SimpleBox4nano was applied in two ways:

- A 'dynamic' calculation, to give PEC after one year of use;
- A 'steady state' calculation², to give 'worst case' PECs.

² Steady state is the state of the environment under simulation, when inputs (i.e. emissions) are balanced by losses (e.g. by permanent burial of sediment). At this point the PECs in all the environmental compartments become constant under dynamic simulation. The calculated PECs are the worst case scenario – they cannot increase beyond their steady state values.

For the analysis, two simulations were run, based on two assumptions about the state of the nanoparticles on emission into the environment:

- Scenario name 'pristine': the assumption that the nanoparticles were in their 'pristine', unaltered form. This is effectively a 'worst case' assumption since the particles enter the environment in 'free' unaggregated or unattached form;
- Scenario name 'matrix': the assumption that the particles were in a 'matrix-embedded' form. This assumption is based upon the observation that particles formed during release experiments comprised aggregates with the polymer resin carrier, with a larger overall size compared to the pristine particles.

The parameters for the two scenarios are the same except for the 'Radius primary ENP' and 'Density primary ENP', which specify the size of particles when emitted and their density. In the 'matrix' scenario the particles are set to be much larger, to account for their aggregated nature, and less dense, to account for the presence of a matrix (resin) component which is less dense than the titanium dioxide.

Table 3. SimpleBox4nano input parameters for the scenarios.

Variable	Units	Value	
		'pristine'	'matrix'
Regional emission to air	t a ⁻¹	0	0
Regional emission to lake water	t a ⁻¹	0	0
Regional emission to fresh water	t a ⁻¹	0.893	0.893
Regional emission to sea water	t a ⁻¹	0	0
Regional emission to natural soil	t a ⁻¹	0	0
Regional emission to agricultural soil	t a ⁻¹	3.18	3.18
Regional emission to other soil	t a ⁻¹	0	0
Area land	km ²	15875	15875
Fraction fresh water	-	1.01×10 ⁻⁴	1.01×10 ⁻⁴
Fraction natural soil	-	0.134	0.134
Fraction agricultural soil	-	0.626	0.626
Fraction urban/industrial soil	-	0.240	0.240
Temperature	°C	10	10
Average precipitation	mm a ⁻¹	633	633
Depth fresh water	m	1.62	1.62
Soil erosion	mm a ⁻¹	0.03	0.03
Radius natural colloids (NC, < 450 nm) in water	nm	500	500
Density natural colloids (NC, < 450 nm) in water	kg m ⁻³	2200	2200
Radius natural suspended particulate matter (SPM > 450nm) in water	µm	7	7
Density natural suspended particulate matter (SPM > 450nm) in water	kg m ⁻³	2200	2200
Radius natural colloids (NC, < 450 nm) in sediment pore water	nm	500	500
Density natural colloids (NC, < 450 nm) in sediment pore water	kg m ⁻³	2200	2200
Radius natural colloids (NC, < 450 nm) in soil pore water	nm	500	500
Density natural colloids (NC, < 450 nm) in soil pore water	kg m ⁻³	2200	2200
Radius primary ENP	nm	7.5	1375
Density primary ENP	kg m ⁻³	4230	3900
Attachment Efficiency of ENPs and fresh water NCs (<450 nm)	-	0.02	0.02
Attachment Efficiency of ENPs and fresh water SPM (>450 nm)	-	0.02	0.9
Attachment Efficiency of ENPs and fresh sediment NCs (<450 nm)	-	0.336	0.336
Attachment Efficiency of ENPs and fresh sediment grains	-	0.336	0.336

3.3 Higher tier exposure assessment: the NanoFASE WSO model

The NanoFASE Water-Soil-Organism (WSO) model is an example of a model that predicts the differences in nanomaterial concentrations [across space and over time](#) within a catchment. This type of model is used to make detailed predictions of PECs in different parts of a catchment. It works by splitting the catchment up into a series of 'cells', each with its own set of environmental compartments. Some environmental compartments, e.g. reaches of a river, connect across cells to form a river network that [transports material downstream](#) into the river [estuary](#) and ultimately to the [sea](#).

Application of the model to a catchment requires a large amount of spatial and temporal data, for example:

- Data on catchment hydrology: daily rainfall and evapotranspiration rates for the catchment. These data are used to run a hydrological model, which outputs daily volumes of water entering the soil and running off to surface water at and near the soil surface;
- Parameters influencing [water percolation through soils](#) and [soil erosion](#);
- Parameters for the [bioturbation](#) (mixing) of the upper soil through the action of organisms;
- Parameters describing the surface water in each grid cell that the model simulates, e.g. the length of [river](#) within that grid cell;
- Parameters for the movement of water through rivers, the estuary and the sea;
- Parameters for the [settling](#) and [resuspension](#) of sediments in surface waters;
- Parameters for the transformations and behaviour of nanoparticles. For this example, the parameters relate to [attachment](#) of nanomaterials to soils and sediments.

Depending on the type of nanomaterial and its known behaviour, other processes may need to be incorporated into the model, particularly [dissolution](#) and chemical transformations such as [sulphidation](#). Because titanium dioxide has a very low solubility, we assume that it does not dissolve in the environment.

Data on nanomaterial emissions are also required – at this tier they should comprise not only rates of emission, but also the locations of emissions (i.e. in which model cell they occur) and if possible and relevant (i) time trends in emission rates and (ii) forms of nanomaterials on release.

This example scenario does not include emissions to the atmosphere. If it did, then the fate of these emissions (i.e. where the material is deposited and at what rate) can be simulated by an [atmospheric transport and deposition model](#), and the deposition rates added to the other emission rates.

4 Summary of results

Table 4 summarises the results of the exposure assessment, and **Figure 2** shows graphical comparisons of PECs after one year of exposure, for soils, waters and sediments. PECs have been calculated for one year of exposure at all tiers. At the lower tier PECs for soil and sediment have also been calculated for a set of example timescales of exposure, up to 100 years. At the lower tier, the freshwater and estuarine PECs can also be considered to be for the steady state condition, and can be compared with steady state PECs output by SimpleBox4nano.

Soil PECs

Generally the PECs for the two scenarios are very similar (for the lower tier they are identical because no distinction is made between the scenarios). At intermediate and higher tiers this similarity reflects the fact that the nanomaterial attaches so strongly to soil that the difference in its assumed properties between the two scenarios makes negligible difference to the predictions.

The soil PEC after one year predicted at the lower tier is higher than the PECs predicted at the intermediate and higher tiers. This reflects the relative simplicity of the lower tier approach, where we have assumed that all the emitted nanomaterial enters the soil, and is not able to transfer out of the soil into other environmental compartments. When we apply SimpleBox4nano, the predicted PEC is lower, largely because we are only allowing a portion of the emitted nanomaterial to enter the soil compartment.

The NanoFASE WSO model produces ranges of PECs that are all below the medians produced by SimpleBox4nano and the point value of the lower tier assessment.

The steady state PECs predicted by SimpleBox4nano are notably higher (by an order of magnitude) than the PEC predicted at the lower tier after 100 years of input. This indicates that it takes a long time for the soil PEC to reach the steady state condition, likely to be over 1000 years.

Freshwater PECs

The lower tier assessment produces notably higher one year PECs than SimpleBox4nano. As with soils, this reflects the worst case nature of the scenario used: all the nanomaterial is assumed to enter freshwaters, and is assumed to stay in the water column and not transfer to the sediments.

SimpleBox4nano predicts lower PECs if the nanomaterial is assumed to be in the matrix-embedded form, compared to when it is assumed to be in pristine form. This is because the matrix-embedded particles are larger than the pristine particles, and thus more susceptible to depositing to the sediments.

The NanoFASE WSO model produces similar medians and ranges of one year PEC for both scenarios, while SimpleBox4nano produces a notably lower PEC for the matrix scenario than the pristine scenario. The median PECs for the matrix scenario are similar, while for the pristine scenario SimpleBox4nano produces a median PNEC that is about an order of magnitude higher than the median of the NanoFASE WSO, but still within the spatial range of PECs produced.

The steady state PECs predicted by SimpleBox4nano are less than an order of magnitude higher than the one year PECs. This suggests that the time needed to reach steady state concentrations in freshwaters is <10 years.

Sediment PECs

The lower tier assessment produces a slightly higher one year PEC than either of the SimpleBox4nano scenarios. In the pristine scenario the median PEC from the NanoFASE WSO model is about an order of magnitude lower, but the range encompasses the PECs predicted at the lower tiers. For the matrix-embedded scenario, the NanoFASE WSO produces a median PEC about two orders of magnitude lower than the PECs produced by both the other tiers.

The 50 year PEC in the lower tier assessment is similar to the steady state PECs predicted by SimpleBox4nano. This suggests that it is taking 50-100 years for the SimpleBox4nano predictions to reach steady state.

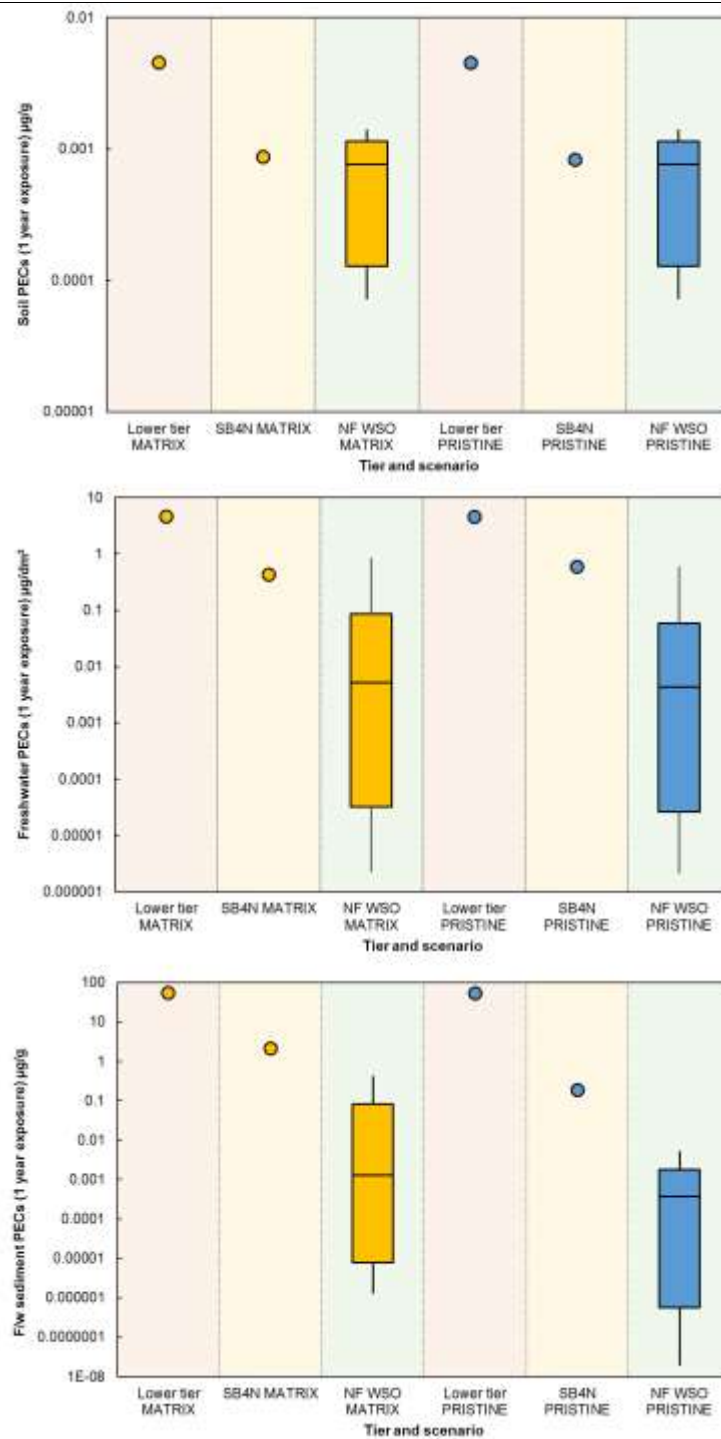


Figure 2. Comparisons of PECs for one year of emissions, computed at each tier of exposure assessment. Exposure scenarios are for matrix-embedded particles (MATRIX) and pristine particles (PRISTINE). Lower tier PECs are single calculations. Intermediate tier PECs are the median prediction considering uncertainty in emissions (not shown). Higher tier PECs are shown as spatial ranges: horizontal line is median, box limits are 5%ile and 95%ile and whiskers limits are maximum and minimum.

Table 4. A summary of the median PECs predicted by lower, intermediate and higher tier exposure assessment. Sets of PECs which can be compared directly across the assessment tiers are shown in **bold**.

Assessment tier	Model	Soil PEC ($\mu\text{g/g}$)					Freshwater PEC ($\mu\text{g/dm}^3$)		Freshwater sediment PEC ($\mu\text{g/g}$)				
		1 year	10 years	50 years	100 years	Steady state	1 year	Steady state	1 year	10 years	50 years	100 years	Steady state
Lower		0.00243	0.0243	0.122	0.243	–	4.63	4.63	55.0	550	2750	5500	–
Intermediate, assuming pristine particles	SB4N	0.000837	–	–	–	5.00	0.599	1.12	0.192	–	–	–	186
Intermediate, assuming matrix-embedded particles	SB4N	0.000870	–	–	–	5.40	0.425	0.998	2.09	–	–	–	224
Higher, assuming pristine particles	NanoFASE WSO (median)	0.00076	–	–	–	–	0.00524	–	0.000375	–	–	–	–
Higher, assuming matrix-embedded particles	NanoFASE WSO (median)	0.00076	–	–	–	–	0.00430	–	0.00131	–	–	–	–