



Environment
Agency



Characterising the hazard of highly persistent substances that exhibit low levels of bioaccumulation

Chief Scientist's Group report

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Professor Doug Wilson
Chief Scientist

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Executive summary

A recent report prepared for the European Commission investigated the possibility of a highly persistent chemical with low bioaccumulation potential being judged to meet the “B” criterion for Persistent Organic Pollutants (POPs) under the Stockholm Convention when a longer environmental residence time was considered. The report has been referenced in a recent Substance of Very High Concern (SVHC) proposal identifying perfluorobutane sulfonic acid as an ‘equivalent level of concern’ to a persistent, bioaccumulative and toxic (PBT)/very persistent and very bioaccumulative (vPvB) substance under Article 57(f) of the REACH Regulation.

The Environment Agency considers that the concept that such substances could be considered as a potential POP or SVHC is a major departure from existing thinking. This is because substances that are highly persistent, but that do not meet the criteria to be considered bioaccumulative, have been assessed using a risk assessment (exposure versus hazard) approach. One of the areas of concern that has been identified that may not be adequately considered by the current regulatory process, is that these highly persistent substances may have the potential to travel to areas far from the point of release and may eventually reach environmental concentrations that could result in adverse environmental effects. The concept is important for determining and prioritising the potential hazard and risk management of such chemicals, particularly poly/perfluorinated alkyl substances (PFAS). This short project, of which this report is the output, addressed some of the specific areas of interest to the Environment Agency in this respect.

For the specific PFAS considered in this report (GenX and PFHxA), the available modelling carried out indicates that the concentrations at a local scale are expected to be influenced mainly by local dilutions and flow rates. The predicted local concentrations in water are expected to respond rapidly to changes in release rate or cessation of emission.

At a regional scale the analysis carried out using the EUSES model suggests that both GenX and the anionic form of PFHxA will reach a 95% steady-state concentration in surface water over a period of less than one year. It is expected that changes in concentration following a change in release rate or cessation of emission will occur over a similar timescale. The reason for this is that the transport of the substance from the region into the continental/global environment is predicted to be the dominant removal process from the regional environment for highly persistent substances that occur mainly in the water phase. For such substances, this transport is predicted to occur relatively rapidly compared to other removal processes (e.g. degradation).

At the global scale, the modelling carried out indicates that steady-state will be reached only very slowly for both GenX and PFHxA, i.e., over many tens or hundreds of years. This is consistent with the persistent nature of these substances and the possibility of transport via the water phase.

The following is concluded from the work carried out for this report.

- The current quantitative approach to risk assessment at a local and regional scale is based on comparison of the predicted environmental concentration (PEC) with the predicted no effect concentration (PNEC). This quantitative approach based on the PEC/PNEC ratio appears to be equally applicable to highly persistent substances as for non-persistent substances.
- The concentrations at a global scale of highly persistent substances such as GenX and PFHxA, which are expected to occur primarily in the water phase, are predicted to build up over prolonged periods (many tens or hundreds of years).
- For the water phase in EUSES, regional concentrations will always be equal to or lower than local concentrations due to the model design. However, continental concentrations may be higher than local concentrations and this possibility should be checked during the exposure modelling.
- An approximate time to steady-state at a global scale can be estimated from the EUSES model. This is informative as it allows a distinction to be made between persistent substances for which global steady-state concentrations are predicted to be reached over relatively short periods of time (e.g. a few years), and those for which global steady-state concentrations are predicted to be reached over prolonged time periods (e.g. 100 years or more).
- The example substances considered have a relatively low bioaccumulation potential (based on the fish bioconcentration factor, the kinetics of uptake and depuration by fish is not known at the time of writing). Assuming that the accumulation occurs rapidly, the concentration in fish can be estimated directly from the concentration in water and will follow the same time-trends as the concentration in water.

A possible way forward for the regulatory hazard and risk assessment for persistent substances may be to make a distinction, based on modelling results, between those persistent substances that are predicted to reach 95% global steady-state within a few years, say up to ten years, and those that are predicted to reach 95% global steady-state over much longer periods (say 100 years or more), as follows:

- **Substances that reach 95% steady-state within a few years (e.g. <10 years).** These types of persistent substances may be better assessed using a quantitative (PEC/PNEC) approach than a qualitative hazard based approach. Only limited build up in remote regions is likely to occur, so the local and regional assessment are likely to be protective of remote

regions. In addition, the concentrations in the environment would be expected to decline reasonably rapidly following a cessation or reduction in emission.

- **Substances that reach 95% steady-state over prolonged periods (e.g. >100 years).** These types of persistent substances may build up in remote regions at a global scale and the concentrations in such regions would be expected to decline slowly following a cessation or reduction in emission. Although a quantitative (PEC/PNEC) approach may be protective, there are added uncertainties over the potential timescales involved. These uncertainties could potentially be addressed by requiring a more conservative assessment (e.g. incorporating higher uncertainty factors within a PEC/PNEC approach) or a more qualitative approach.
- **Substances that reach 95% steady-state over intermediate periods (e.g. >10 to <100 years).** These substances are intermediate between the two scenarios outlined above. It is suggested that these are considered case-by-case. Possible considerations could include the amount of information available on the substance (for example in terms of releases to the environment, the properties of the substance and the degradation rates), the uncertainty in the underlying substance data set, the level of toxicity shown by the substance and the bioaccumulation potential.

1 Background

A report prepared for the European Commission (Crookes and Fisk, 2018) investigated the possibility of a highly persistent chemical with low bioaccumulation potential being judged to meet the “B” criterion for Persistent Organic Pollutants (POPs) under the Stockholm Convention when a longer environmental residence time was considered. That report has been referenced in a recent Substances of Very High Concern (SVHC) proposal (ECHA, 2019a) identifying perfluorobutane sulfonic acid (PFBS CAS 375-73-5) as an “equivalent level of concern” to a persistent, bioaccumulative and toxic (PBT)/very persistent and very bioaccumulative (vPvB) substance under Article 57(f) of the REACH Regulation. The report was also previously circulated to the ECHA PBT Expert Group.

Two main areas of concern have been identified that may not be adequately considered by the current regulatory process. Firstly, that these substances have the potential to contaminate groundwater drinking water sources. Secondly, that these substances have the potential to travel to areas far from the point of release and may eventually reach environmental concentrations that could result in adverse environmental effects. A common concern across both aspects is that the chemicals remain in the water column, and may be extremely difficult to treat or remove. This results in an expectation of gradually increasing water concentration if emissions continue, and due to the spread, effective ubiquity in the water column. A number of projects are already on-going on the first point, so this work focuses solely on the second concern.

This report explores the environmental assessment of highly persistent chemicals with low bioaccumulation potential, using modelling of specific example substances which are known to be very persistent. Moreover, whether a ‘cut-off’ point can be potentially set to define whether to use a risk assessment or a hazard-based approach. The concept is important for determining and prioritising the potential hazard and risk management of such chemicals, particularly perfluorinated alkyl substances (PFAS).

The report is divided into discrete tasks, which are connected, these are as follows.

- Capability of available regulatory models
 - To assess, using the model EUSES, if such very persistent substances can be effectively modelled and if results of assessments at different spatial scales facilitate understanding of the accumulation of these substances to high levels over time.
- Alternative approaches

- To evaluate if a limited set of other fate and distribution models have the potential to be useful in the context of assessing the fate of very persistent substances.
- Modelling of GenX
 - Which model is best to apply to a substance to understand its fate and distribution at different spatial scales, using a real substance data set.
- Modelling of Perfluorohexanoic acid (PFHxA)
 - Applying the appropriate model to a similar substance but with a more diverse use pattern.
- Results of regulatory interventions on these substances
 - Considering the consequences of reductions or cessations in releases and the time taken for concentrations to reduce at different spatial scales, which could inform the use of such assessments in the regulatory context.

Each of these tasks is reported in detail in turn in this report.

2 Capability of available regulatory models

2.1 Background

This task focused on the capabilities of the EUSES model to investigate the effects of persistence on the estimated concentrations and masses at the regional, continental and global scales. The EUSES model is a commonly used tool for the risk assessment of chemicals within Europe and is closely aligned with the methods for risk assessment used under UK REACH.

Note: The following analysis is based on EUSES v2.1.2. A more recent version of EUSES (v2.2.0) is also available, however, several 'bugs' are evident within v2.2.0 and so EUSES v.2.1.2 was chosen as the preferred version for use in this report. The parameters are identical in both EUSES v2.1.2 and v2.2.0

2.2 Steady state models within EUSES

The EUSES program contains various steady-state distribution models representing different geographical scales. The important parameters in these distribution models are summarised in Table 2.1.

The linkages between the various steady-state models within EUSES and their respective default assumptions are important in understanding the EUSES model outputs in terms of their relevance for persistent substances.

Firstly, in order for a model to reach steady-state there must necessarily be both inflow of chemical into the model and removal of chemical from the model. Steady-state is reached once the overall rate of removal of the chemical equals the overall rate of input. Without a removal mechanism, the concentration of a chemical would keep on increasing indefinitely with continued input into the model and would never reach a steady-state.

The removal of a chemical from the model can be either by degradation of the chemical or by other processes. For EUSES, these other processes include outflow from one model to another (e.g. from the regional model to the continental model) or processes that are considered to permanently remove the chemical from the environment being considered (e.g. deep burial, soil erosion etc.). For very persistent substances, these latter, non-chemical related properties of the model can dominate the overall removal of the substance and the time to steady-state.

In order to exemplify the interplay between the substance properties, the model assumptions about removal, and the time to steady-state, a series of EUSES runs have been carried out.

Table 2.1 Steady-state distribution model parameters within EUSES

Parameter	Regional model	Continental model	Global moderate model	Global arctic model	Global tropic model
Area (km ²)	4×10 ⁴	7.04×10 ⁶ (including regional)	8.5×10 ⁷ (including continental and regional)	4.25×10 ⁷	1.275×10 ⁸
Temperature (°C)	12	12	12	-10	25
Residence time of air (d)	0.687	9.05	30.2	22.3	38.6
Residence time of freshwater (d)	43.3	172	2.69×10 ³ (for water)	5.84×10 ³ (for water)	1.09×10 ⁴ (for water)
Residence time of seawater (d)	4.64	365			
Net sedimentation rate for freshwater (mm/yr)	2.8	2.75	2.8×10 ⁻³	2.0×10 ⁻³	2.0×10 ⁻³
Net sedimentation rate for seawater (mm/yr)	1.53	6.69×10 ⁻³			
Sediment mixing depth (m)	0.03	0.03	0.03	0.03	0.03
Mixing depth of soil (m)	0.05 (natural soil) 0.2 (industrial soil) 0.05 (industrial/urban soil)	0.05 (natural soil) 0.2 (industrial soil) 0.05 (industrial/urban soil)	0.05	0.05	0.05
Soil erosion rate (mm/yr)	0.03	0.03	0.03	0.03	0.03

It is helpful to the analysis to visualise a simplified diagram of the models within EUSES (the example is for the Regional model but is equally relevant to the Continental and Global models within EUSES) as shown in Figure 2.1.

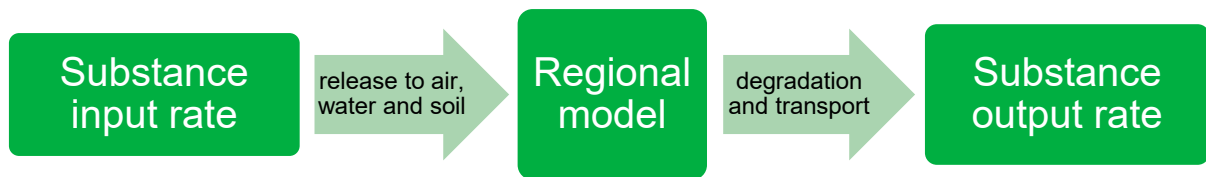


Figure 2.1 Simplified diagram of the EUSES Regional model

In this simplified approach the various inputs (e.g. via air, water and sewage sludge) are considered as a single input and the various removal processes (e.g. degradation, transport to the Continental model etc.) are considered as a single output process. In such a system, ‘steady-state’ is reached when the substance input rate is equal to the substance output rate.

Using this approach the steady-state mass of the substance in the Regional model can be expressed in terms of the mass of substance released into the regional model and the mass of substance removed (by all processes) from the regional model as follows.

$$\begin{aligned} & \text{Rate of mass increase in the regional model } \left(\frac{kg}{d} \right) \\ & = \text{rate of mass input } \left(\frac{kg}{d} \right) - \text{rate of mass removal } \left(\frac{kg}{d} \right) \end{aligned}$$

Steady-state is reached once the rate of mass increase in the regional model = 0. At this point the following holds:

$$\text{Rate of mass input } \left(\frac{kg}{d} \right) = \text{rate of mass removal } \left(\frac{kg}{d} \right)$$

Assuming that a) there is a constant rate of mass input and b) the rate of mass removal is an overall first order process with a rate constant of k (with units of d⁻¹), this can be rewritten as follows.

$$\text{Rate of mass input } \left(\frac{kg}{d} \right) = k \times \text{mass at steady state (kg)}$$

The mass at steady-state (kg) can be obtained from the EUSES output (see Appendix B for an example). Therefore, for a given constant input rate the overall k can easily be estimated. The time to 95% steady-state, hence the time to which 95% of the predicted steady-state concentration will be reached, can

then be estimated using the following equations (assuming an overall first order removal process).

$$k = \frac{\text{rate of mass input}}{\text{mass at steady state}}$$

$$0.95 = 1 - e^{-kt}$$

$$t_{95} = \frac{-\ln(0.05)}{k} = \frac{3.0}{k}$$

where t = time (days)

t_{95} = time to 95% of steady-state

k = overall first order removal rate constant (d^{-1})

rate of mass input = total daily release of substance into model (kg/d)

mass at steady-state = steady-state mass calculated by EUSES

Although the use of this simplified approach does not give information on the actual processes that are dominant in the removal of the substance from the Regional model, it does allow useful information on the time to steady-state to be estimated.

In theory the same approach could be applied to the other steady-state models in EUSES. In practice this is limited as it is not possible to determine the exact chemical inflows into the various models. However, in cases where there is only direct input via water, air or soil into the Regional model it is possible to carry out such calculations at the Regional scale, EU-scale (sum of Regional and Continental scales) and also the overall system (sum of Regional, Continental, Global: Moderate, Global: Arctic and Global:Tropic) scale.

For cases where there is direct input via water, air or soil into both the Regional and Continental model, it is possible to carry out similar calculations based on the total daily release of the substance into both models (i.e. the sum of the daily regional and continental release of the substance), and the steady-state masses calculated by EUSES at the EU-scale (sum of Regional and Continental Scales) and the overall system (sum of Regional, Continental, Global: Moderate, Global: Arctic and Global:Tropic) scale.

Example calculations for GenX have been undertaken assuming a hypothetical release rate of 1 kg/day via either surface water, air or soil, into the Regional model (see section 4.2 for GenX chemical and environmental fate properties used). The results are summarised in Table 2.2.

Table 2.2 Example calculations for GenX using EUSES

Model scale	Release rate 1 kg/day		
	to surface water	to air	to soil
Steady-state mass – Regional	48 kg	105 kg	141 kg
Steady-state mass – Continental	2,120 kg	1,100 kg	1,060 kg
Steady-state mass – Global: Moderate	9.8×10^4 kg	5.1×10^4 kg	4.9×10^4 kg
Steady-state mass – Global: Arctic	6.4×10^4 kg	3.3×10^4 kg	3.2×10^4 kg
Steady-state mass – Global Tropic	2.2×10^5 kg	1.1×10^5 kg	1.1×10^5 kg
Total steady-state mass (all scales)	3.8×10^5 kg	2.0×10^5 kg	1.9×10^5 kg
Estimated time to 95% steady-state – Regional	144 days	314 days	424 days
Estimated time to 95% steady-state – EU-scale (Regional + Continental)	6.51×10^3 days	3.62×10^3 days	$3,60 \times 10^3$ days
Estimated time to 95% steady-state – Whole system	1.14×10^6 days	5.93×10^5 days	5.71×10^5 days

For comparison, similar calculations have been undertaken for a substance with the same physico-chemical properties as GenX but assuming that the degradation half-lives in water, sediment and soil either correspond to those in the REACH P-criterion (Table 2.3) or vP-criterion (Table 2.4). The purpose of these calculations is to demonstrate the differences between a substance that is essentially not degradable in the environment and those that are slowly degraded but are still considered to be persistent or very persistent within the meaning of the PBT- and vPvB-criteria.

Table 2.3 Example calculations for a substance with the same physico-chemical properties as GenX assuming a half-lives in water, sediment and soil corresponding to the P-criterion

Model scale	Release rate 1 kg/day		
	to surface water	to air	to soil
Steady-state mass – Regional	27 kg	61 kg	78 kg
Steady-state mass – Continental	38 kg	15 kg	11 kg
Steady-state mass – Global: Moderate	8.8 kg	3.3 kg	2.6 kg
Steady-state mass – Global: Arctic	0.46 kg	0.17 kg	0.14 kg
Steady-state mass – Global Tropic	0.056 kg	0.021 kg	0.017 kg
Total steady-state mass (all scales)	75 kg	79 kg	92 kg
Estimated time to 95% steady-state – Regional	82 days	182 days	234 days
Estimated time to 95% steady-state – EU-scale (Regional + Continental)	196 days	225 days	268 days
Estimated time to 95% steady-state – Whole system	224 days	236 days	276 days

Table 2.4 Example calculations for a substance with the same physico-chemical properties as GenX assuming a half-lives in water, sediment and soil corresponding to the vP-criterion

Model scale	Release rate 1 kg/day		
	to surface water	to air	to soil
Steady-state mass – Regional	32 kg	70 kg	92 kg
Steady-state mass – Continental	44 kg	18 kg	15 kg
Steady-state mass – Global: Moderate	10 kg	4.2 kg	3.5 kg
Steady-state mass – Global: Arctic	0.52 kg	0.22 kg	0.18 kg
Steady-state mass – Global Tropic	0.066 kg	0.027 kg	0.023 kg
Total steady-state mass (all scales)	87 kg	93 kg	111 kg
Estimated time to 95% steady-state – Regional	96 days	211 days	275 days
Estimated time to 95% steady-state – EU-scale (Regional + Continental)	229 days	266 days	321 days
Estimated time to 95% steady-state – Whole system	261 days	279 days	332 days

These theoretical calculations show that GenX itself is estimated to reach 95% steady-state reasonably quickly at the regional scale (around 144-424 days in the example, see Table 2.2) but will take much longer to reach 95% steady-state at the EU-scale (3.60×10^3 to 6.51×10^3 days (9.9 to 18 years)) and in the whole system when global scale modelling is included (5.71×10^5 to 1.14×10^6 days (1,560 to 3,120 years)). The relatively short time to 95% steady-state at the regional scale can be explained by the fact that GenX in the water phase will be transported from the regional model into the continental and global models as a result of water transport and the relatively short residence time of water in the regional model (43.3 days for freshwater and 4.64 days for seawater; see Table 2.1) compared with the global models (2.69×10^3 to 1.09×10^4 days (7.4 to 29.9 years)) for water; see Table 2.1). Since GenX is assumed to be highly persistent (essentially no biodegradation occurs) the time to 95% steady-state is dominated

by the physical removal processes (in this case the residence time of water in the system).

This can be contrasted with a substance with the same physico-chemical properties as GenX but which degrades at the half-lives corresponding to the REACH P- and vP-criteria (Table 2.3 and Table 2.4). For these examples, the time to 95%-steady-state in the regional model is shorter than, but similar to, that for GenX (82-234 days for P- and 96-275 days for vP- compared with 144-424 for GenX itself) but are several orders of magnitude shorter than from GenX when the whole system is considered (224-276 days for P- and 261-332 days for vP- compared with 5.71×10^5 to 1.14×10^6 days). In these cases the slow, but measurable, biodegradation rate assumed, dominates the time to 95% steady-state at the global scale, and contributes to (but does not dominate) the time to 95% steady-state at the regional scale.

The time to 95% steady-state at both the regional and global scale is potentially an important consideration for persistent substances. A short time to 95% steady-state indicates that:

1. further build up of the concentration (or mass) of the substance in the environment would not be expected to occur over more extended time scales and,
2. a reduction in emission rate (or a cessation of emission) would lead to a relatively rapid reduction in the concentration in the environment.

Conversely a very long time to 95% steady-state indicates that:

1. the concentrations would be predicted to keep increasing for many years once release to the environment has started and,
2. the concentration would only reduce very slowly following a reduction or cessation of emission.

2.3 Is it theoretically possible for concentrations at points far from source of release to exceed the predicted local exposure concentrations?

This is an important point to consider for highly persistent substances as it relates to the confidence that Regulators and risk assessors may have in a quantitative risk assessment carried out under UK REACH (for example using the EUSES model). Quantitative risk assessments are based on a comparison of the predicted environmental concentration (PEC) with the predicted no effect concentration (PNEC). This comparison is also known as the risk characterisation ratio (RCR). A $PEC/PNEC < 1$ is taken to show that the risk is adequately controlled.

For substances that are extremely persistent but which are not bioaccumulative, it has been argued that over extended time periods there is the potential for environmental concentrations far from source to increase to the point at which adverse effects may occur.

The risk assessments carried out under UK REACH using the EUSES model are based on PEC/PNEC comparisons at a local scale and a regional scale. The local scale is taken to be the immediate vicinity of a source of release and the regional scale is taken to be an area with an above average level of industrial activity occurs. The regional PECs act as the “industrial background” concentrations for the local PEC estimations. It is therefore important to understand whether the local and regional risk assessment carried out under REACH is likely to be protective of the wider environment for these types of substances.

There are two aspects that need to be considered.

1. Will the local concentrations predicted always be higher than the predicted regional concentrations?
2. Will the regional concentrations predicted always be higher than the predicted continental concentrations and the predicted concentrations in the Global Moderate, Global Arctic and Global Tropic models within EUSES?

These are considered in detail below.

2.3.1 Local versus regional concentrations

A key part of the methodology implemented in the EUSES model is that, in general, the predicted regional concentrations act as a background concentration (i.e. are added to) for the predicted local concentrations. Thus, at first sight, it might be expected that the predicted local concentrations will always be higher than the predicted regional concentrations. However, this is not always the case owing to the way the regional background concentrations are taken into account for some environmental compartments. The relevant details of the equations used to add-in the regional background concentrations are discussed below (the equations are taken from ECHA Guidance R.16 (ECHA, 2016); the same method is implemented in EUSES).

For freshwater (surface water) or marine water

$$PEC_{local_{water}} = C_{local_{water}} + PEC_{regional_{water}}$$

Where: $PEC_{local_{water}}$ = Predicted local concentration in surface water (mg/l).

$PEC_{local_{water}}$ = Local concentration in surface water during a release episode (mg/l).

$PEC_{regional_{water}}$ = Predicted regional concentration in surface water (mg/l).

In this case, as the regional PEC is directly included in local PEC there should be no situations where the regional PEC is higher than the local PEC.

The situation with marine water is the same as for surface water whereby the regional concentration in marine water is directly added in to the local PEC for marine water.

For freshwater sediment or marine sediment

The local PEC for sediment is calculated directly for the $PEC_{local_{water}}$ using the following equation.

$$PEC_{local_{sediment}} = \frac{K_{susp-water}}{RHO_{susp}} \times PEC_{local_{water}} \times 1000$$

Where: $PEC_{local_{water}}$ = Predicted local concentration in surface water (mg/l).

$K_{susp-water}$ = Suspended matter-water partition coefficient (m^3/m^3).

RHO_{susp} = Bulk density of wet suspended matter = 1,150 kg/m^3 .

$PEC_{local_{sediment}}$ = Predicted local concentration in sediment (mg/kg wet weight (ww)).

The important points to note are:

- The regional concentration input to the local sediment concentration is accounted for by the $PEC_{regional_{water}}$ (as this contributes to the $PEC_{local_{water}}$) rather than the $PEC_{regional_{sediment}}$.
- In the current context the predicted regional concentrations are steady-state concentrations and it is theoretically possible for substances to build-up in the regional sediment compartment over time so that the $PEC_{regional_{sediment}}$ becomes higher than the $PEC_{local_{sediment}}$.

The extent to which this is possible is substance and use pattern specific as the regional concentration in sediment depends on the properties of the substance and the total release of the substance into the regional environment compared with the local release for any one exposure scenario. An example to demonstrate this is shown below (Table 2.5). The example is based on a lifecycle with a

manufacturing step (with a relatively low environmental release) and an industrial use (with a relatively high environmental release).

Table 2.5 Example calculations showing the possibility of PEC_{regional} exceeding PEC_{local} for sediment and marine sediment. Scenarios where the regional PEC is greater than the local PEC are shaded.

Substance property	Value assumed	
Molecular weight	250 g/mol	
Melting point	-40°C	
Vapour pressure	1×10 ⁻³ Pa at 25°C	
Water solubility	0.01 mg/l at 25°C	
Log K _{ow}	5	
Biodegradability	Not readily biodegradable	
Exposure scenario	Local	Regional
1) Manufacture – local releases	2.74×10 ⁻⁴ kg/day to waste water and 2.74×10 ⁻⁴ to air over 365 days	2.74×10 ⁻⁴ kg/day to waste water and 2.74×10 ⁻⁴ to air
2) Industrial use	137 kg/day to waste water and 137 kg/day to air over 365 days	137 kg/day to waste water and 137 kg/day to air
PECs	Local	Regional
1) Manufacture – PEC in surface water	2.16×10 ⁻⁴ mg/l	2.09×10 ⁻⁴ mg/l
1) Manufacture – PEC in marine water	1.87×10 ⁻⁵ mg/l	1.79×10 ⁻⁵ mg/l
1) Manufacture – PEC in freshwater sediment	0.0198 mg/kg ww	0.0335 mg/kg ww
1) Manufacture – PEC in marine sediment	1.71×10 ⁻³ mg/kg ww	2.49×10 ⁻³ mg/kg ww
2) Industrial use – PEC in surface water	3.8 mg/l (exceeds solubility)	2.09×10 ⁻⁴ mg/l
2) Industrial use – PEC in marine water	0.38 mg/l (exceeds solubility)	1.79×10 ⁻⁵ mg/l
2) Industrial use – PEC in freshwater sediment	351 mg/kg ww	0.0335 mg/kg ww
2) Industrial use – PEC in marine sediment	35.1 mg/kg ww	2.49×10 ⁻³ mg/kg ww

The example calculations shown in Table 2.5 demonstrate that for the manufacture scenario the local PECs in sediment and marine sediment are lower than the regional PECs in sediment and marine sediment (see grey cells in Table 2.5) even though this is not the case for the water concentrations. Such situations are very substance and use-pattern dependent but are most likely to arise in

situations where the substance being assessed adsorbs strongly to sediment and the release to the environment from one lifecycle step is much lower than the release from one or more other lifecycle steps.

For Soil

The local PECs estimated are estimated using the following equations.

$$PEC_{local\ soil} = C_{local\ soil} + PEC_{regional\ natural\ soil}$$

Where: $PEC_{local\ soil}$ = Predicted local concentration in soil (mg/kg).
These are estimated for agricultural soil averaged of 30 days, agricultural soil averaged over 180 days and grassland.

$C_{local\ soil}$ = Local concentration in soil (mg/kg).

$PEC_{regional\ natural\ soil}$ = Predicted regional concentration in natural soil (mg/kg)

In this case the regional concentration in natural soil is accounted for in the local PECs for agricultural soil and grassland. Therefore, similar to the case for sediments, it is possible that the regional concentration in agricultural soil will be higher than that in natural soil and this may then translate in the predicted regional concentration in agricultural soil being higher than the predicted local concentration in agricultural soil (depending on the substance properties and the relative balance between the local release for a specific exposure scenario and the total regional release). This is demonstrated in Table 2.6 for the same substance and exposure scenarios as used above for sediment (see Table 2.5).

Table 2.6 Example calculations showing the possibility of PEC_{regional} exceeding PEC_{local} for soil. Scenarios where the regional PEC is greater than the local PEC are shaded.

PECs	Local	Regional
1) Manufacture – PEC in agricultural soil averaged over 30 days	0.0204 mg/kg ww	0.102 mg/kg ww
1) Manufacture – PEC in agricultural soil average over 180 days	0.0204 mg/kg ww	0.102 mg/kg ww
1) Manufacture – PEC in grassland	0.0194	Not applicable
1) Manufacture – PEC in natural soil	Not applicable	0.0108 mg/kg ww
2) Industrial use – PEC in agricultural soil averaged over 30 days	766 mg/kg ww	0.102 mg/kg ww
2) Industrial use – PEC in agricultural soil average over 180 days	766 mg/kg ww	0.102 mg/kg ww
2) Industrial use – PEC in grassland	289 mg/kg ww	Not applicable
2) Industrial use – PEC in natural soil	Not applicable	0.0108 mg/kg ww

As can be seen (see grey cells in Table 2.6 above), the predicted local concentration in the agricultural soil is around five times lower than the predicted regional concentration in agricultural soil for the manufacture scenario.

For Air

The local concentration in air is estimated using the following equation.

$$PEC_{local,air,ann} = C_{local,air,ann} + PEC_{regional,air}$$

Where: $PEC_{local,air,ann}$ = Predicted annual average local concentration in air (mg/m^3).

$C_{local,air,ann}$ = Annual average concentration in air 100 m from a point source of release (mg/m^3).

$PEC_{regional,air}$ = Predicted regional concentration in air (mg/m^3).

Similar to the case for water, local PEC in air automatically incorporates the regional air concentration and so the local PEC will always be higher than the regional PEC.

2.3.2 Regional concentrations versus continental and global concentrations

It is difficult to fully test if the regional concentrations will always be higher than the continental or global concentrations for every situation. The EUSES model allows releases to occur directly into both the regional and continental model and then allows transport to occur between the regional and continental model and the continental and global models. It is not possible in EUSES to input releases directly into the global models.

Within these limitations of the EUSES input, it is possible to test two extreme situations. Firstly, there is direct release into the regional model only and secondly there is direct release into the continental model. The results of such an analysis are summarised in Table 2.7.

As can be seen for the scenario with direct release to the regional model, concentrations are highest in the regional compartments, lower in the continental compartments and lowest in the global compartments.

However, the predicted continental concentration in freshwater, freshwater sediment, soil and air is higher than the predicted regional concentrations for the scenario with direct release to the continental model (see grey cells in Table 2.7 below). Global concentrations are still predicted to be lower than both the regional and continental values.

It is difficult to comment on the extent to which these findings are generally applicable to all substances and use patterns as it is not possible to test all possible combinations of input data.

Table 2.7 Example calculations comparing the regional, continental and global concentrations predicted by EUSES. Scenarios where the predicted continental or global concentration is higher than the predicted regional concentration are shaded grey. The global models do not distinguish between marine and freshwater or agricultural and natural soil.

Substance property		Value assumed					
Molecular weight	250 g/mol						
Melting point	-40°C						
Vapour pressure	1×10 ⁻³ Pa at 25°C						
Water solubility	0.01 mg/l at 25°C						
Log Kow	5						
Biodegradability	Not readily biodegradable						
PECs scenario 1 (release 10 kg/day to air and waste water in the regional model)	Surface water (mg/l)	Marine water (mg/l)	Freshwater sediment (mg/kg ww)	Marine sediment (mg/kg ww)	Agricultural soil (mg/kg ww)	Natural soil (mg/kg ww)	Air (mg/m ³)
Regional PEC	1.52×10 ⁻⁵	1.31×10 ⁻⁶	2.44×10 ⁻³	1.81×10 ⁻⁴	7.44×10 ⁻³	1.38×10 ⁻³	3.19×10 ⁻⁷
Continental PEC	6.74×10 ⁻⁸	6.13×10 ⁻⁹	1.08×10 ⁻⁵	8.50×10 ⁻⁷	9.06×10 ⁻⁵	9.13×10 ⁻⁵	2.12×10 ⁻⁸
Global: moderate PEC	3.47×10 ⁻⁹		4.81×10 ⁻⁷		2.80×10 ⁻⁵		6.49×10 ⁻⁹
Global: arctic PEC	4.01×10 ⁻⁹		5.55×10 ⁻⁷		4.46×10 ⁻⁵		4.31×10 ⁻⁹
Global: tropic PEC	2.46×10 ⁻⁹		3.41×10 ⁻⁷		1.40×10 ⁻⁵		6.79×10 ⁻⁹
PECs scenario 2 (release 10 kg/day to air and waste water in the continental model)	Surface water (mg/l)	Marine water (mg/l)	Freshwater sediment (mg/kg ww)	Marine sediment (mg/kg ww)	Agricultural soil (mg/kg ww)	Natural soil (mg/kg ww)	Air (mg/m ³)
Regional PEC	9.53×10 ⁻⁸	1.41×10 ⁻⁸	1.53×10 ⁻⁵	1.95×10 ⁻⁶	9.28×10 ⁻⁵	9.36×10 ⁻⁵	2.17×10 ⁻⁸
Continental PEC	2.64×10 ⁻⁷	6.03×10 ⁻⁹	4.23×10 ⁻⁵	8.36×10 ⁻⁷	1.64×10 ⁻⁴	9.47×10 ⁻⁵	2.20×10 ⁻⁸

Global: moderate PEC	3.51×10^{-9}	4.86×10^{-7}	2.84×10^{-5}	6.59×10^{-9}
Global: arctic PEC	4.06×10^{-9}	5.63×10^{-7}	4.52×10^{-5}	4.37×10^{-9}
Global: tropic PEC	2.49×10^{-9}	3.45×10^{-7}	1.42×10^{-5}	6.85×10^{-9}

2.3.3 Summary

The analysis carried out shows that in some cases the predicted regional concentration (PEC_{regional}) can exceed the predicted local concentration (PEC_{local}) for sediment and soil. The extent to which this occurs depends upon the substance properties and the relative release rate for a specific local scenario compared with the total regional release of the substance. However, regional water concentrations will always be equal to or lower than local water concentrations due to the model design of EUSES. This is especially important in the assessment of persistent and mobile compounds that are expected to remain in the water phase.

It is important to note that all the information necessary to check for these issues is readily available from the EUSES output and it is straight forward to carry out the following specific checks:

- Check if the PEC_{regional} for sediment, marine sediment and agricultural soil is greater than the respective PEC_{local}s.
 - This may indicate that the local PEC/PNEC ratios may not be sufficiently protective of the regional environment.
- Check if the continental PECs are greater than the regional PECs in all compartments.
 - This may indicate that the regional PEC/PNEC ratios may not be sufficiently protective of the build-up of the substance at a continental (e.g. Europe-wide) scale.
- Check if the global PECs (e.g. from the Global: Moderate, Global: Arctic and Global: Tropic models) are higher than either the regional PECs or continental PECs in all compartments.
 - This may indicate that the local and regional PEC/PNEC ratios may not be sufficiently protective of the long-term build-up of the substance in the wider global environment.

When the local PECs > regional PECs > continental PECs > global PECs, this provides reassurance that the PEC/PNEC ratios based on the local and regional PECs are protective of the wider global environment as well as the local environment.

3 Alternative approaches

3.1 Background

Two models have been identified by the Environment Agency as being cited in academic and regulatory assessments as potentially useful for investigating the environmental behaviour of persistent chemicals. These are the following (with relevant URL for where the model is obtained):

- MUST model (https://www.ime.fraunhofer.de/en/Research_Divisions/business_fields/AE_BR/Businessareas_AE/Software_E/MUST.html).
- GloboPOP model (<https://www.utsc.utoronto.ca/labs/wania/downloads/>).

This Section provides an overview of these two models and their utility for use in further modelling of PFAS (carried out in Section 4 and 5).

In addition a simple spreadsheet model developed by Crookes and Fisk (2018) was also considered in the later modelling (see Section 4.4.3). The AQUATOX v.3.2 model (<https://www.epa.gov/ceam/aquatox>) was investigated but it proved difficult to apply readily to the general situations modelled. Such models are more appropriate to site-specific assessments where the local hydrological conditions are well defined. No other suitable models were located for use in the subsequent modelling.

3.2 MUST model

The Multimedia Stock Pollution Tool (MUST) is a freely available software developed by the Fraunhofer Institute. MUST is a dynamic modelling tool which calculates the expected concentration (so called 'pollution stock') in the environmental compartments air, water, soil, sediment, suspended sediment and biota given a defined and time-dependent emission scenario. The user can define the time dependence of the release pattern. The tool estimates overall half-lives for the disappearance (DT_{50}) (i.e. movement of the substance outside the dimensions of the Environment) and degradation ($DegT_{50}$). In addition, time dependent (Mackay IV) and steady-state distributions (Mackay III) are calculated.

The model comes with two pre-set 'Environments' (EU Regional and EU Continental) and both Environments are made up of several compartments, i.e. air, water, sediment, soil and biota. Information on various parameters of the environments and compartments are included in the model (see Figure 3.1). The parameters of the regional and continental environments are based on the

parameters from the regional and continental scales in EUSES. However, these scales are connected in EUSES (i.e. substances can be transferred from the regional scale to the continental scale), but they are separate environments in the MUST model (i.e. no flux from one environment into the other).

Multimedia Stock Pollution Tool (MUST) 1.0

Program ?

Environment Substance Emission

Scenario EU regional

Parameter	Unit	Value
Height of the atmosphere	km	1
Area	km ²	40400
Water fraction	%	4
Water depth	m	4.75
Soil depth	cm	10
Sediment depth	cm	3
Fraction of susp. sediment	ppm	15
Fraction of biota	ppm	100
Soil density	kg/L	1.7
Soil org. carbon content	%	2
Sediment org. carbon content	%	5
Susp. sediment org. carbon content	%	10
Temperature	K	285
Residence time air	d	0.7
Residence time water	d	40
Average connection percentage to STP	%	80

Figure 3.1 Screenshot from the MUST model displaying the parameters of the included environments exemplified for the EU regional environment

Chemical property and environmental fate data for 17 substances are included in the MUST model (see Figure 3.2). These 17 substances are: HBCDD, DecaBDE, Dechlorane Plus, anthracene, benzo[a]pyrene, pyrene, DDT, lindane, PFOA, PFOS, PFNA, PFDA, D4, D5, bisphenol A, nonylphenol and dimethylpropylphenol. The model does not contain GenX or PFHxA. Substances can be added, however this cannot be done directly in the model. Additional substances need to be added to the database, which is saved in the SQLite file (i.e. C:\MUST\Data\StockPoll.sqlite). Changes can be made to the sqlite file with programs such as DB Browser for SQLite (<https://sqlitebrowser.org/>). The model requires substance specific physico-chemical properties including molecular weight, partition coefficients (octanol-water (K_{ow}), air-water (K_{aw})), Henry's Law constant, BCF and reaction half-lives (air, soil, water, sediment, suspended matter and biota) (see Figure 3.2).

In a similar way of adding/editing substances, new environments can be added to the model or parameters of existing environments can be changed by accessing them in the SQLite file.

Multimedia Stock Pollution Tool (MUST) 1.0

Program ?

Environment Substance Emission

Substance HBCDD

Parameter	Unit	Value
Molar_mass	g/mol	641.7
LogKow	-	5.63
LogKaw	-	-3.6
Henry	Pa m ³ /mol	0.75
KOC	L/kg	175000
BCF	-	18100
DT50_air	d	3.2
DT50_water	d	1000000
DT50_soil	d	120
DT50_sed	d	214
DT50_susp	d	1000000
DT50_biota	d	1000000

Figure 3.2 Screenshot from the MUST model displaying the chemical properties and environmental fate parameters included for the 17 substances exemplified with HBCDD.

Besides selecting the environment and substance, emission data can be entered with releases to the various compartments (air, water, soil, sediment, suspended sediment and biota) for different time points. There is an option (selected by check box) to include sewage treatment plant (STP) in the assessment, which is based on the SimpleTreat model (<https://www.rivm.nl/en/soil-and-water/simpletreat>). No further information on the fate of a substance in the STP (i.e. distribution to air, water, sludge and percent degraded) is provided in the model.

The output provided by the model comprises various charts covering the time period for which there is emissions data entered, including:

- emissions of the substance to the various compartments.
- steady-state fraction of the substance for the various compartments. This can be displayed for each of the years for which emission data was entered.
- changes in the mass of the substance (or concentration) in the various compartments over time.
- disappearance of the substance from the various compartments due to degradation and export.

A full report can be saved as a text file containing all the details from the assessment.

There are several limitations of the model for the current project, which are summarised below:

- In the regional environment, no distinction is made between surface water and marine water compartments. For the continental environment, only freshwater is included, no marine water compartment.
- The regional and continental environments are not linked as they are in EUSES, therefore there is no flux from one environment into the other.
- The model is lacking a global environment, for example moderate, Arctic and tropical environments which are included in EUSES.
- Total emissions to a compartment need to be entered, therefore, if emissions are based on multiple use scenarios, these need to be combined.
- STP doesn't consider volatilisation of the substance to air, only releases to sludge and water.
- No groundwater compartment is included in the model.

For the purpose of this project, the MUST model is a useful tool. As it is a level IV non-steady-state, dynamic mode, it allows investigation of changes in concentrations of a substance over time as a result of changes in emissions. This type of modelling is required for modelling for GenX (see Section 4) and PFHxA (see Section 5).

3.3 GloboPOP model

GloboPOP is an environmental fate model that has been developed for persistent organic pollutants (POPs) by Frank Wania and Donald Mackay (<https://www.utoronto.ca/~wania/downloads2.html>). It is a zonally averaged multi-media model describing the global fate of POPs on the time scale of decades. The model predicts concentrations or amounts in air, water (freshwater and marine) sediment, soil and fish (freshwater and marine).

The model requires substance specific physico-chemical properties including molecular weight, partition coefficients (octanol-water (K_{ow}), air-water (K_{aw}) and octanol-air (K_{oa})) and reaction half-lives (air, soil, water and sediment) (see Figure 3.3). As the model estimates the distribution of the substance at a global scale at different temperatures, values of 'Energy of phase transfer' are required for the partition coefficient and values for activation energies for the reaction half-lives in order to estimate values for these parameters at different temperatures. The model doesn't estimate values for any of the input parameters if data are not available.

Chemical Properties X

Chemical Name **PCB-28** Molecular mass (g/mol) 257.54

Equilibrium Partitioning between Air, Water and Octanol

Partition Coefficients at 25°C (dimensionless)		Energies of Phase Transfer in J/mol	
log K octanol-water	5.66	ΔU octanol-water	-26200
log K air-water	-1.91	ΔU air-water	52300
log K octanol air	7.85	ΔU octanol-air	-78500

Reaction Half Lives

	air	uncult. soil	agri. soil	fresh water	sea water	fw sediment
half-life at 25 °C in h		10000	10000	5500	5500	17000
activation energy in J/mol	10000	30000	30000	30000	30000	30000
	1.04E-12	reaction rate of vapour with OH in cm ² /(molecules.s)				

Default Emission Parameters

fraction emitted into a compartment in %

air	agri-soil	fresh water
100	0	0

seasonality of emissions

amplitude as fraction of mean 0

month of maximum emission JAN v

DB Operations

New Chemical	Help
Save	Print
Save As	Cancel
Delete	OK

Figure 3.3 GloboPOP chemical properties input screen exemplified with PCB-28

The distribution of a substance is modelled globally over ten latitudinal zones (N-Polar, N-Boreal, N-Temperate, N-Subtropic, N-Tropic, S-Tropic, S-Subtropic, S-Temperate, S-Subpolar, S-Polar). Default setting of these zones (e.g., dimensions, temperatures, etc.) can be changed if needed. Emissions to air, water and soil over time can be defined to each of these zones.

The output of the model includes temporal trends of the substance concentrations or amounts in any of the environmental compartments for each of the zones. It also provides information on emissions, degradation/deposition/volatilisation rates in different compartments.

There are several limitations for the use of GloboPOP for determining the environmental distribution of PFAS such as GenX:

- Physical-chemical properties: As mentioned above, input data are needed on partition coefficients and half-lives of the substance as well as additional data in order to extrapolate these parameters to different temperatures. These types of data are not available and are difficult to estimate. For example the GloboPOP requires the energies of phase transfer and the authors are not aware of methods for estimating these values for PFAS.

- There are upper and lower limits for the partition coefficient at which the model operates. For example, entering log K_{ow} values <-4.3 will crash the model. The reported log K_{ow} value for GenX is -8.97.
- Releases are distributed globally by the model, so emissions from a single point source (as is the case for GenX in this project) are diluted globally resulting in very low concentrations (even in the zone where emissions take place). The model doesn't provide concentrations in e.g. an EU regional scale.
- Software is rather old (released in 2000) and required some workarounds to install. Saving results files also seems problematic.

These limitations mean that the GloboPOP model has not been considered further for the modelling of GenX (see Section 4) or PFHxA (see Section 5).

4 Modelling of GenX

4.1 Background

GenX (2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid, its salts and its acyl halides, covering any of their individual isomers and combinations thereof) is a perfluoroalkyl substance that is highly persistent but has a low bioaccumulation potential. The use pattern of Gen-X is well defined (it is used in processing at one EU site) and the time point at which its use commenced is also known. Subsequently, it has been detected at decreasing latitudes in the North Sea over time (ECHA, 2019b).

The possible modelling solutions which can be used to predict the spread of GenX in the environment over different spatial and temporal scales have been considered.

4.2 Chemical and environmental fate properties of GenX

The important chemical and environmental fate properties of GenX are summarised in Table 4.1. These are taken mainly from the GenX SVHC support document (ECHA, 2019b) and have not been reviewed in detail.

Table 4.1 Physico-chemical properties of GenX

Property	Value	Unit	Note	Reference
Molecular weight	329	g/mol	Mol.wt of the anion	
Solubility	1000	g/L	@ 20°C	GenX SVHC document (ECHA, 2019b)
Vapour pressure	0.017	Pa	@ 20°C	GenX SVHC document (ECHA, 2019b)
Log Kow	2.58		Not reported if this is a measured or estimated value	GenX SVHC document (ECHA, 2019b)
Log Koc soil	1.08		Based on measured data	GenX SVHC document (2019b)
Koc	230			Estimated by EUSES (based on Kow)
Henry's Law constant	4.06×10^{-6}	Pa m ³ /mol	@ 20°C	GenX SVHC document (2019b)

4.3 Tonnage and release estimates

GenX has been used as a perfluorooctanoic acid (PFOA) replacement in the production of fluoropolymers at a fluorochemical production plant in the Netherlands, since 2012. A Netherlands government department report stated that for 2017 a total of 50 tonnes were used at the site with a release factor of 1% to air and 4% to water (ILT, 2018). Release factors are based on mass balance data from Chemours whereby 54.5% of the used GenX is incinerated, 40% is recycled, 4% is released to water and 1% is released to air. Another Netherlands governmental report (from RIVM) stated air emissions over the 2012-2015 period and using the 2017 release factors, total tonnage and emissions to water were calculated (de Kort *et al.*, 2019). For 2019, information on emissions to air and water were published by the production company (Chemours). An overview of the annual tonnages used at the site and emissions to air and water can be found in Table 4.2. Data for 2016 and 2018 were not found.

Table 4.2 Available data on GenX tonnage used at the site in the Netherlands and emissions to air and water

Year	Tonnage used	Release factor to air	Emissions to air (kg)	Release factor to water	Emissions to water (kg)
2012	20.7 ^e	0.01 ^d	207 ^a	0.04 ^d	828 ^e
2013	31.9 ^e	0.01 ^d	319 ^a	0.04 ^d	1276 ^e
2014	41.7 ^e	0.01 ^d	417 ^a	0.04 ^d	1668 ^e
2015	31.5 ^e	0.01 ^d	315 ^a	0.04 ^d	1260 ^e
2016	No data available				
2017	50 ^b	0.01 ^b	500	0.04 ^b	2000
2018	No data available				
2019		- ^f	346.5 ^c	- ^f	0.28 ^c
Total			2105		7032

- Notes:
- a) Source: <https://www.rivm.nl/bibliotheek/rapporten/2019-0083.pdf>
 - b) Source: <https://www.ilent.nl/documenten/rapporten/2018/06/08/afvalstromen-van-chemours>
 - c) Source: <https://radar.assets.avrotros.nl/editorial/Documenten/20201002%2C%20Vragen%20Radar%20%26%20antwoorden%20Chemours.pdf>
 - d) Read-across data from 2017
 - e) Tonnage used and emissions to water are estimated using the reported emissions to air and the release factors to air and water.
 - f) Since 2017 releases to air and water were reduced, therefore release factors from 2017 are no longer valid.

Monitoring data in surface water are also available for GenX in the EU, some of which were obtained from downstream of the GenX processing site in the Netherlands. The available data are summarised in Table 4.3.

Table 4.3 Summary of available monitoring data for GenX in water. Values in brackets are between the method detection limit (MDL) and the method quantification limit (MQL).

Year	Location	Comment	Concentration (ng/L)	Reference
2013	Netherlands	Upstream of plant	<0.5 - 0.75	Heydebreck <i>et al.</i> , 2015b
		Downstream of plant	<0.5 – 91	Heydebreck <i>et al.</i> , 2015b
		Other sites	<0.5	Heydebreck <i>et al.</i> , 2015b
2013	Germany	Rhine	nd - 107.6	Heydebreck <i>et al.</i> , 2015b
		Elbe	nd	Heydebreck <i>et al.</i> , 2015b
		North Sea (German coast)	nd - 3.70	Heydebreck <i>et al.</i> , 2015b
2014	Norway/Iceland	Norwegian Sea	0.178 to 0.500	ECHA, 2019b
		East Iceland Current	<0.023	ECHA, 2019b
2016	Netherlands	Upstream of plant	<0.2 – 22	Gebbink <i>et al.</i> , 2017
		Upstream of plant	0.59 - 2.0	Pan <i>et al.</i> , 2018
		Downstream of plant	1.7 – 812	Gebbink <i>et al.</i> , 2017
		Other sites	<0.2	Gebbink <i>et al.</i> , 2017
		Other sites	0.66 - 1.5	Pan <i>et al.</i> , 2018
2016	United Kingdom	River Thames	0.70 - 1.58	Pan <i>et al.</i> , 2018
2016	Sweden	Lake Malaren	0.88 - 2.68	Pan <i>et al.</i> , 2018
2016	Germany	River Rhine	0.59 - 1.98	Pan <i>et al.</i> , 2018
2016/2017	Germany	Bight	0.92-2.5	Joerss <i>et al.</i> , 2019
		Elbe river	(0.070) ^a -1.5	Joerss <i>et al.</i> , 2019

Year	Location	Comment	Concentration (ng/L)	Reference
		Baltic Sea	(0.032)-0.082	Joerss <i>et al.</i> , 2019
		Oder lagoon	(0.028)-(0.037)	Joerss <i>et al.</i> , 2019
2017	Netherlands	Upstream of plant	<1	Versteegh and de Voogt, 2017
		Upstream of plant	<6	Rijkswaterstaat, 2017
		Downstream of plant	1 – 128	Versteegh and de Voogt, 2017
		Downstream of plant	1.6	RIWA-Rijn, 2018
		Downstream of plant	<12 – 102	Rijkswaterstaat, 2017
		Other sites	<1 – 47	Versteegh and de Voogt, 2017
		Other sites	<6 – 35	Rijkswaterstaat, 2017
2018	Netherlands	Upstream of plant	<10	RIWA-Rijn, 2019
		Downstream of plant	0.11 – 0.67	RIWA-Rijn, 2019
		Other sites	<20 – 6800 ^a	van Bentum <i>et al.</i> , 2018
		Other sites	<0.1 – 1.1	RIWA-Rijn, 2019
2018	Marine/Arctic	North Sea	0.052 - 0.120	Joerss <i>et al.</i> , 2020
		Norwegian sea	(0.019) - 0.033	Joerss <i>et al.</i> , 2020
		Greenland sea	<MDL - 0.026	Joerss <i>et al.</i> , 2020
		Arctic - Fram Strait	(0.014) - 0.045	Joerss <i>et al.</i> , 2020
		Arctic - Fram Strait	(0.015) - 0.070	Joerss <i>et al.</i> , 2020

a) A point source was responsible for the high concentration measured.

4.4 Exposure scenarios

The environmental distribution of GenX as a result of multiple year emissions was assessed using the MUST model (see Section 3.2). The model contains two default Environments, i.e. EU Regional and EU Continental. Details on the parameters of the Environments (or scales) are provided in Table 4.4.

Table 4.4 Parameters of Regional and Continental scales in MUST

Parameter	Unit	EU Regional	EU Continental
Height of the atmosphere	km	1.0	1.0
Area	km ²	4.04×10 ⁴	3,560,000
Water fraction	%	4.0	3.0
Water depth	m	4.75	3.0
Soil depth	cm	10.0	10.0
Sediment depth	cm	3.0	3.0
Fraction of susp. sediment	ppm	15.0	15.0
Fraction of biota	ppm	100.0	100.0
Soil density	kg/L	1.7	1.7
Soil org. carbon content	%	2.0	2.0
Sediment org. carbon content	%	5.0	5.0
Susp. sediment org. carbon content	%	10.0	10.0
Temperature	K	285.0	285.0
Residence time air	D	0.7	9.05
Residence time water	D	40.0	172.0
Average connection percentage to STP	%	80.0	80.0

The MUST model includes an option of including waste water treatment (sewage treatment plant 'STP') in the assessment (by selecting a check box). The distribution of the substance within a STP is based on SimpleTreat model. The model does not display any details on the STP distribution, but by estimating the distribution in a standalone version of SimpleTreat 4 the distribution would be 99.57% to water, 9.9×10⁻⁶% to air and 0.43% to sludge.

There are upper and lower limits for some property values beyond which the model does not work, e.g., Koc values of 12 were reported for soil, but this number seems too low. A value of 230 (generated as default value in EUSES 2.1.2) was used instead. Table 4.5 shows all the property values used for the MUST modelling for the assessment done for this present report.

Table 4.5 Physical-chemical and environmental fate properties of GenX used in the MUST model. DT₅₀ is the time for 50% degradation/metabolism to occur.

Property	Unit	Value
Molar mass	g/mol	329
Log Kow (octanol-water partition coefficient)	-	2.58
Log Kaw (air-water partition coefficient)	-	-8.97
Henry's law constant	Pa m ³ /mol	2.56×10 ⁻⁶
K _{OC} (organic carbon-water partition coefficient)	L/kg	230
BCF (bioconcentration factor)	L/kg	3
DT ₅₀ air*	D	20.57
DT ₅₀ water**	D	1,000,000
DT ₅₀ soil**	D	1,000,000
DT ₅₀ sediment**	D	1,000,000
DT ₅₀ suspended sediment**	D	1,000,000
DT ₅₀ biota***	D	1

Note:

* Data taken from GenX SVHC document (ECHA, 2019b)

** Data taken as read-across from other PFAS included in the MUST model (PFOS, PFOA, PFNA, PFDA).

*** Data taken from Hassell *et al.* (2020)

4.4.1 Exposure scenario based on reported releases

The environmental distribution of GenX based on the releases to air and water over the period of 2012-2019 was estimated using the EU Regional environment in the MUST model (emission to air and water can be found in Table 4.2).

In the regional scale of the model, the GenX mass present in the water compartment follows the emission pattern, whereas the mass in the soil compartment is increasing during the 2012-2019 period (Figure 4.1). The presence of GenX in soil originates largely from sludge application on soil (~89%) and to a lesser extent from atmospheric deposition (~11%).

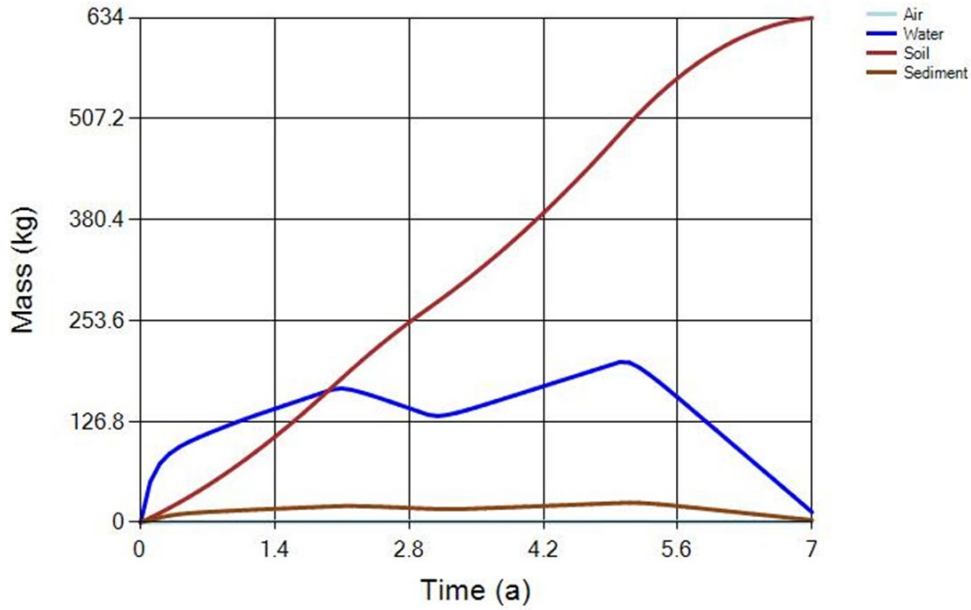


Figure 4.1 GenX distribution to air, water, sediment and soil (in kg) in the regional model based on 2012-2019 releases (this graph is a standard output from MUST). Note that time ‘0’ on the x-axis is 2012 and ‘7’ is 2019.

The highest surface water concentration (in 2017) is estimated to be 2.6×10^{-5} mg/L (26 ng/L), whereas the soil concentration in 2019 is estimated to be 9.7×10^{-5} mg/kg (0.097 ng/g). GenX concentrations in surface water in the Netherlands are generally reported below the estimated concentration of 26 ng/L although concentrations >26 ng/L were reported (sometimes linked to local point sources of contamination) (Gebbinck and van Leeuwen, 2020).

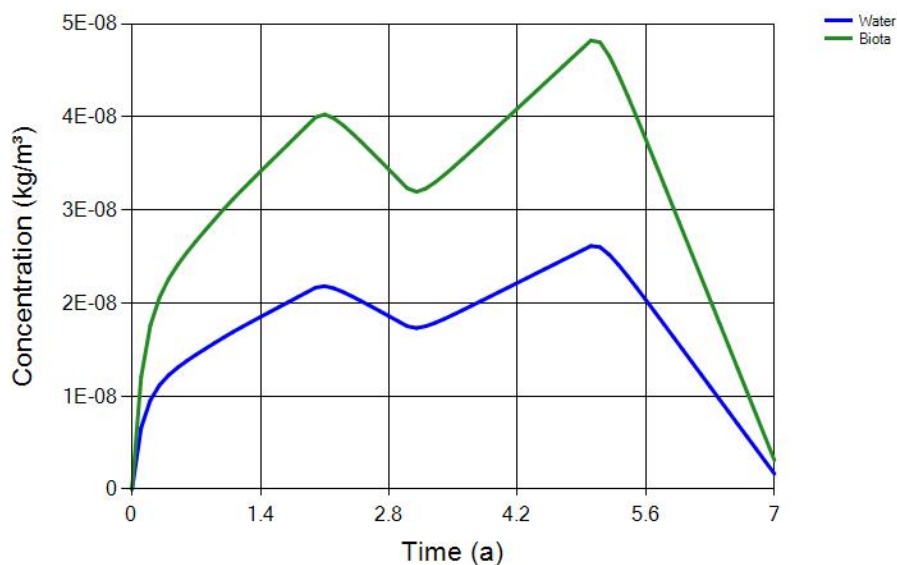


Figure 4.2 GenX concentration in water and biota in the regional model as a result of 2012-2019 releases (this graph is a standard output from MUST). Note that time ‘0’ on the x-axis is 2012 and ‘7’ is 2019

The GenX concentration in biota during the 2012-2019 period follows the trend of the water concentration and is estimated to reach 480 ng/g in 2017 (Figure 4.2). Fish monitoring data in the Netherlands are very limited. GenX was detected in muscle tissue from a single carp in a small lake known to have local GenX contamination (collected in 2018) at 0.0047 mg/kg (4.7 ng/g) (ECHA, 2019b).

The production site has made efforts to reduce emissions since 2017 as can be seen with low emissions to water in 2019. The effect of a post 2019 phase-out (i.e. zero emission to water and air) on the presence of GenX in environmental compartments was investigated. As can be seen in Figure 4.3, the amount of GenX in the water compartment decreases rapidly. Post phase-out, the concentration in soil remains stable as there is no soil degradation of GenX and the model also assumes no export of GenX from the soil compartment (this is the case for both the regional and continental environments).

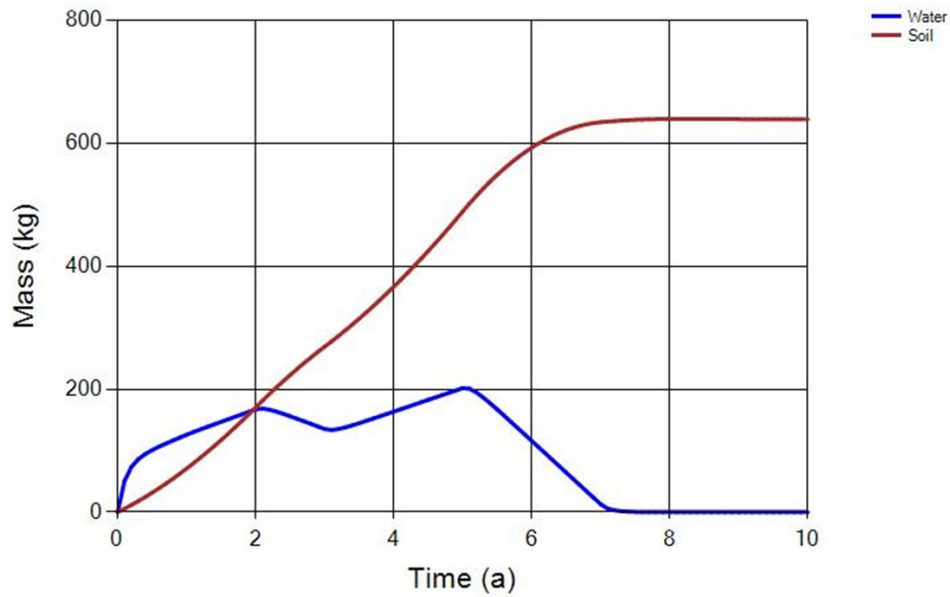


Figure 4.3 GenX distribution to water and soil (in kg) in the regional model based on 2012-2019 releases followed by 3 years of zero emissions to air and water (this graph is a standard output from MUST).

Assuming the same emission pattern as described above followed by a several year phase-out of GenX releases, a similar pattern is observed in the continental environment, although the time taken for the water concentrations to reduce to near zero is slightly longer than for the regional environment (Figure 4.4). This reduction is due to export out of the continental environment. As described for the regional environment, the soil concentrations remain stable as there is no degradation and no export is assumed by the model.

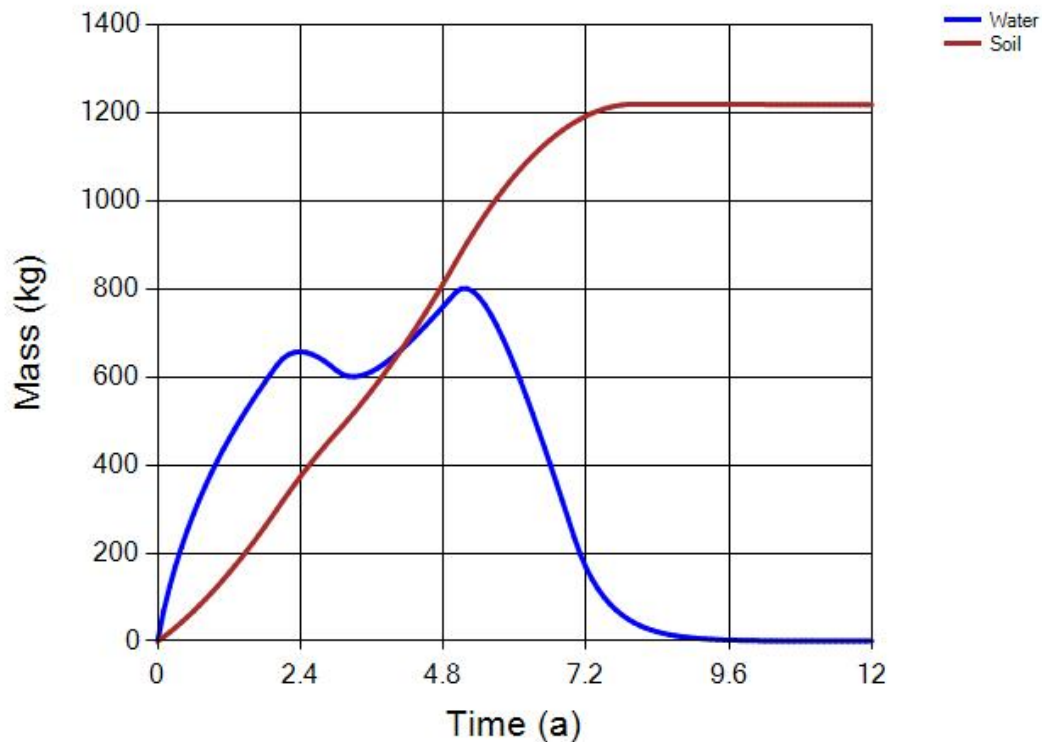


Figure 4.4 GenX distribution to water and soil (in kg) in the continental model based on 2012-2019 releases followed by 5 years of zero emissions to air and water (this graph is a standard output from MUST).

4.4.2 Local and regional modelling of GenX with EUSES

The releases from the GenX processing site have also been investigated using EUSES using the physico-chemical and fate input parameters in Table 4.5. The resulting local and regional predicted environmental concentrations (PECs) are shown in Figure 4.5 and Figure 4.6. The calculations are based on the estimated yearly release estimates for the site and take into account the flow rate of the sewage treatment plant. The default dilution factors of 10 for freshwater and 100 for marine have been assumed.

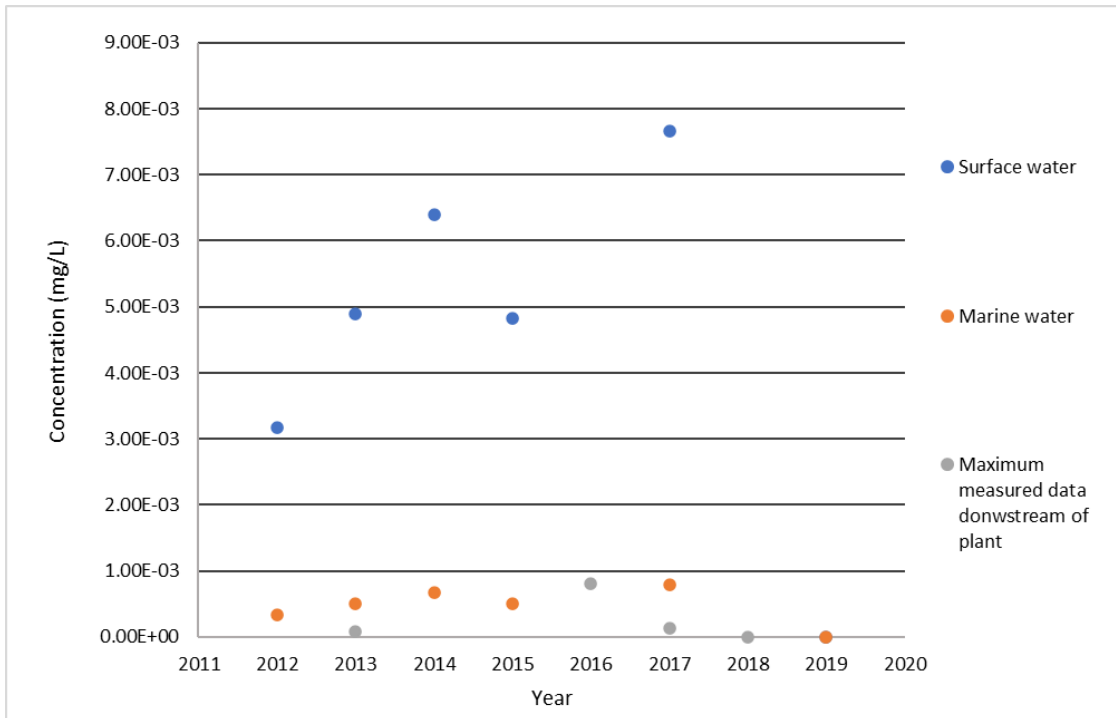


Figure 4.5 Local PECs for the GenX processing site

The local PECs in surface water range from around 3 $\mu\text{g/L}$ in 2012 up to around 8 $\mu\text{g/L}$ in 2017, and mirror the increase in the estimated release to water from the site over those years. Based on the 2019 release rate, the local PEC would be around $7 \times 10^{-3} \mu\text{g/L}$.

The local PECs in marine water follow a similar trend to the freshwater but are approximately 10 times lower (resulting from the higher dilution factor assumed for marine water compared to freshwater) increasing from around 0.3 $\mu\text{g/L}$ in 2012 to around 0.8 in 2017 and then falling to $7 \times 10^{-4} \mu\text{g/L}$ in 2019.

The available monitoring data measured downstream of the GenX processing site are also shown in Figure 9. The measured data range downstream of the site varies between 0.11 and 812 ng/L (1.1×10^{-4} to 0.81 $\mu\text{g/L}$; see Table 4.3). These are around a factor of 10 lower than the predicted concentration in freshwater but of a similar order to those estimated in marine water. The local PECs estimated using EUSES assume a dilution factor of 10 for freshwater and 100 for marine water (the EUSES defaults); the actual dilution at the site is not known but the discrepancy between the measured data and the predicted data could be explained if the dilution factor at the site was around 100 rather than 10.

The measured data for the North Sea in 2018 are in the range 0.052 to 0.12 ng/l (see Table 4.3). These compare to the predicted regional PEC for marine water of 0.7 ng/l for 2019.

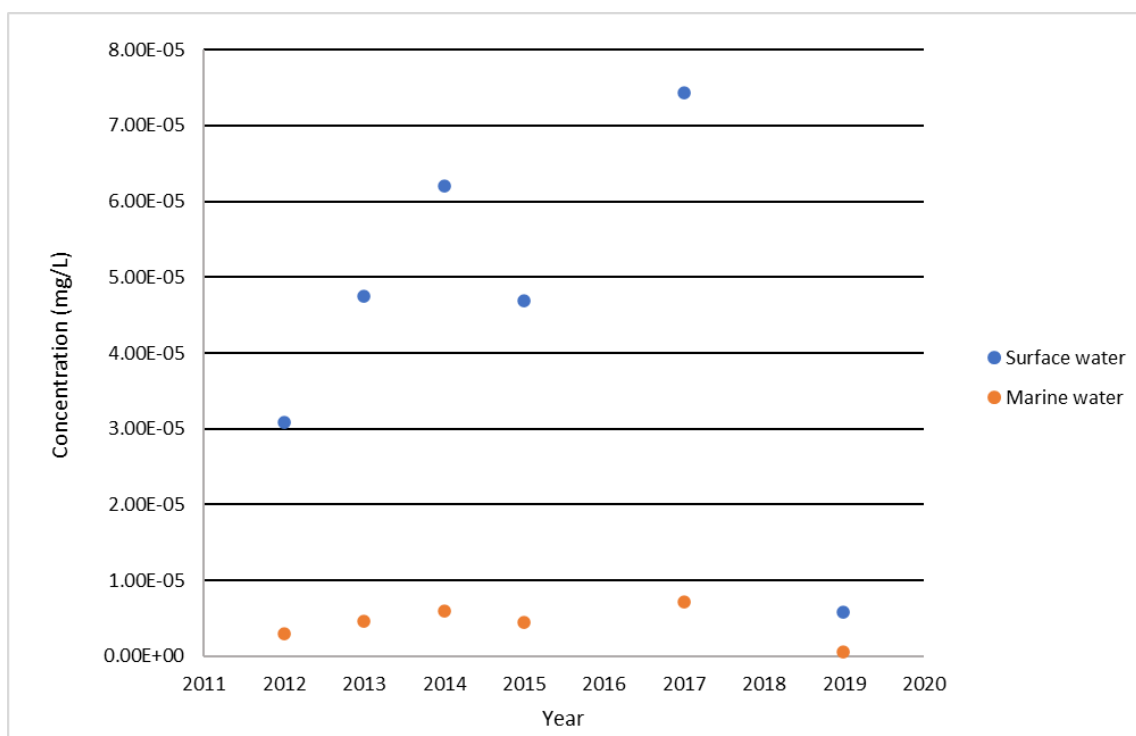


Figure 4.6 Regional PECs for the GenX processing site

The local model within EUSES assumes essentially immediate mixing and equilibrium between the water and sediment phase, and so the local PECs respond instantly to changes of emission rate.

The regional model within EUSES is a steady-state model and for a given release, the achievement of steady-state requires time (i.e. the concentrations gradually build up until the steady-state concentration is reached). Unfortunately, EUSES does not provide any information on the time to steady-state. However, as discussed in Section 2 it is possible to estimate this time to steady-state indirectly.

The steady-state regional PECs show an increasing trend with the increasing emission rate to water between 2012 and 2017 and then decline in 2019 (see Figure 4.6. The regional PEC in surface water is predicted to increase from around 0.03 $\mu\text{g/L}$ in 2012 to 0.07 $\mu\text{g/L}$ in 2017, falling to $6 \times 10^{-3} \mu\text{g/L}$ in 2019. The regional PEC in marine water is predicted to increase from around $3 \times 10^{-3} \mu\text{g/L}$ in 2012 to $7 \times 10^{-3} \mu\text{g/L}$ in 2017, falling to $6 \times 10^{-4} \mu\text{g/L}$ in 2019.

The available measured data from around the EU are summarised in Table 4.3. The levels measured in freshwaters not directly influenced by specific point sources are in the general range <0.1 to 108 ng/L ($<1 \times 10^{-4}$ to $0.1 \mu\text{g/L}$). These are generally in the same range as the regional surface water concentrations predicted using EUSES. The measured data in marine water from around the EU (Table 4.3) are in the range not detected to 3.7 ng/L (not detected to $3.7 \times 10^{-3} \mu\text{g/L}$).

ng/l). Again, these are of a similar concentration to those predicted in regional marine water using EUSES.

Using the approach outlined in Section 2, the time to 95% steady-state in the regional model has been estimated based on each yearly release amount. The results are summarised in Table 4.6.

Table 4.6 Estimated time to 95% steady-state from EUSES modelling (days)

Model scale	2012	2013	2014	2015	2017	2019
Estimated time to 95% steady-state – Regional	179	180	180	179	179	314
Estimated time to 95% steady-state – EU-scale (Regional + Continental)	5.91×10^3	5.92×10^3	5.91×10^3	5.92×10^3	5.92×10^3	3.63×10^6
Estimated time to 95% steady-state – Whole system	1.03×10^6	1.03×10^6	1.03×10^6	1.03×10^6	1.03×10^6	5.95×10^5

These estimates show that at a regional scale 95% steady-state concentrations will be achieved reasonably rapidly (<1 year). However, GenX is predicted to build up in the environment at the global scale over extended periods of time (>1000 years to reach 95% steady-state). An explanation for the relatively short time to 95% steady-state at the regional level is that the transport of substance from the region into the continental/global environment is likely to be the dominant removal process from the regional environment for highly persistent substances that occur main in the water phase such as GenX.

4.4.3 Simplified mass-balance model approach

Crookes and Fisk (2018) used a simplified one-compartment mass-balance model to explore the relationship between persistence of a substance and the concentrations in biota. A similar model has also been used by Fisk and Disley (2014) to investigate dynamic modelling of persistence in environmental compartments.

For the current task, the model used in Crookes and Fisk (2018) has been used to approximate to the regional water compartment using the default regional water compartment sizes from the EUSES model. These are summarised in

Table 4.7. In this simplified form the model assumes that the substance is primarily in the water phase, which is a reasonable assumption for GenX.

The simple mass-balance model requires a first order “loss” rate constant from the regional water compartment. This includes all processes that can lead to loss from the regional compartment including both degradation and flow out of the compartment. As discussed in Section 4.4.2 (using the method outlined in Section 2.2), the estimated time to 95% steady-state for GenX in the regional compartment is around 180-314 days. Assuming an overall first-order loss process, these are equivalent to half-lives of around 40-70 days. For the simple modelling used here a half-life of 70 days has been assumed

Table 4.7 Regional water compartment size assumed in the simplified mass-balance model

Parameter	Value assumed	Comment
Area of land + rivers	40,000 km ²	EUSES default
Fraction of freshwater	0.03	EUSES default
Area of freshwater	1.20×10 ⁹ m ²	Calculated from above
Depth of freshwater	3 m	EUSES default
Volume of freshwater	3.60×10 ⁹ m ³	Calculated from above
Area of seawater	400 km ²	EUSES default
Depth of seawater	10 m	EUSES default
Volume of seawater	4.00×10 ⁹ m ³	Calculated from above
Total water volume (freshwater + seawater)	7.60×10⁹ m³	Calculated from above

The simplified model has been applied to the GenX releases to water for the years 2012 to 2019. The resulting predicted regional concentrations showing the build-up over time are given in Figure 4.7.

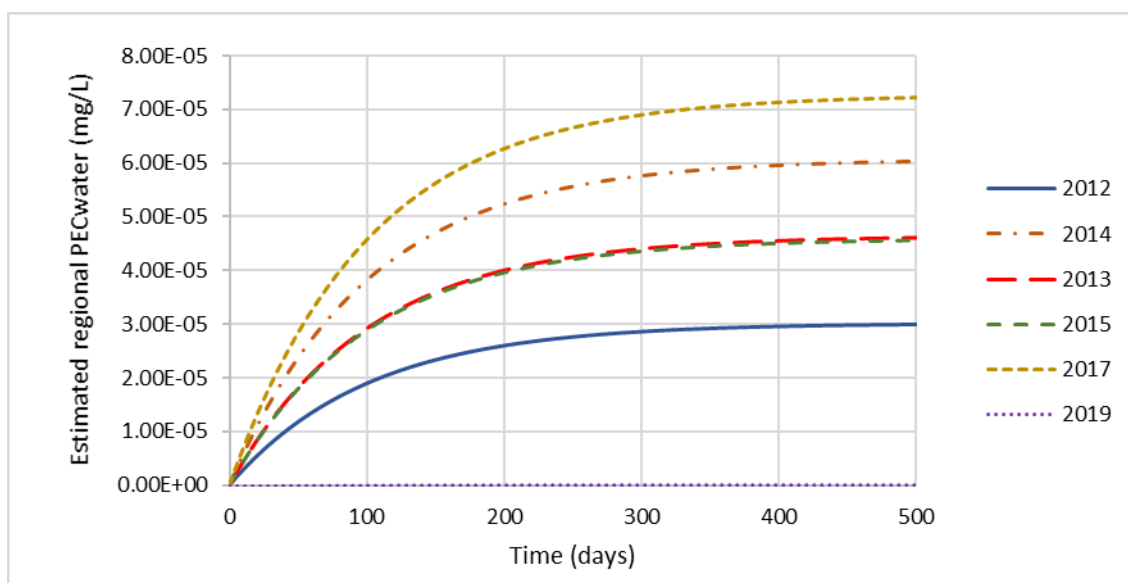


Figure 4.7 Predicted regional water concentrations using the simplified one-compartment box model

As can be seen from Figure 4.7, the predicted concentrations are estimated to reach steady-state within one year at the regional level.

It is important to note that the regional PECs estimated using this approach do not include any continental ‘background’, although the transport (loss) to the continental and global scales is accounted for. This is different to the regional PECs obtained using EUSES itself (see Section 4.4.2) where the continental background is included automatically in the predicted regional PECs. Furthermore, for the simple model used here, the freshwater and marine water volumes have been combined whereas in EUSES these are treated separately. Thus the PECs estimated in Figure 4.7 are similar, but not identical to, those estimated by EUSES itself in Figure 4.6. For example, using EUSES the steady-state regional concentration for 2017 is estimated to be 7.44×10^{-5} mg/l in surface water and 7.21×10^{-6} mg/l in seawater compared to around 7.27×10^{-5} mg/l in water using the simple one-compartment model. Despite these limitations, the simplified model is still considered to be useful to investigate the timescales for steady-state to be achieved.

Using this simple model, it is also possible to investigate the effect of the year-by-year fluctuations in the release to the environment. This is shown in Figure 4.8. For this analysis, the yearly release figures given in Table 4.2 are averaged over the year; for years where release figures are missing, the figure for the preceding year has been assumed. Figure 4.8 indicates that regional concentration would be expected to respond reasonably rapidly (i.e. within 1-2 years) to a change in release rate.

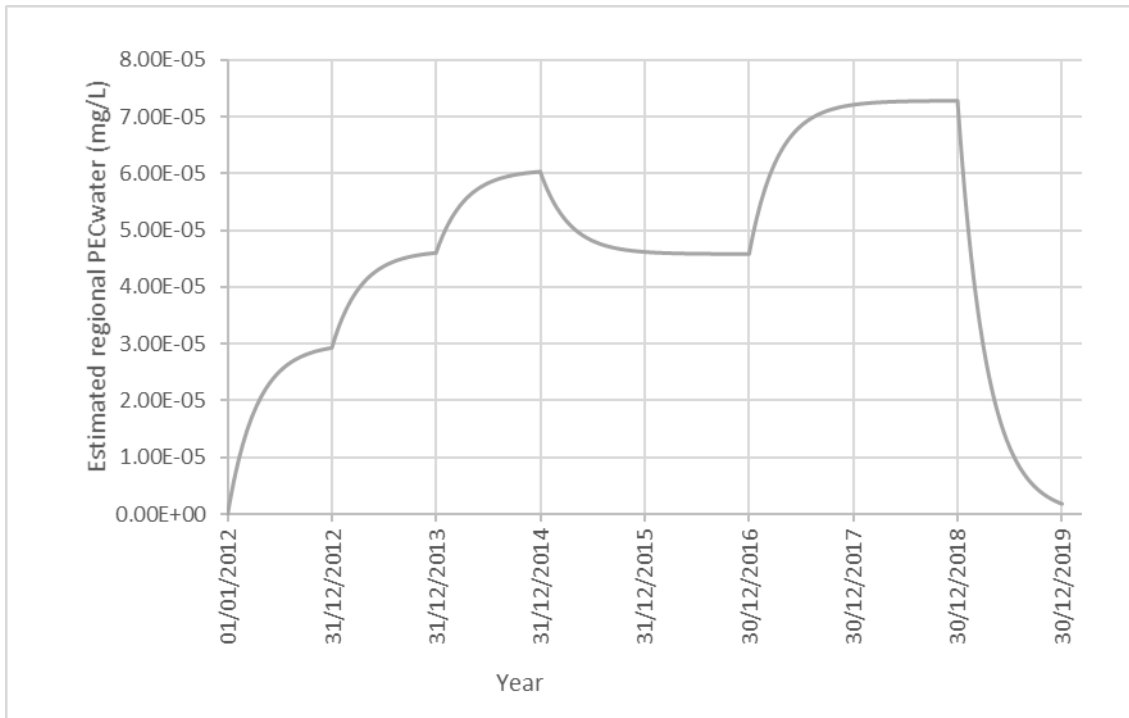


Figure 4.8 Effect of year-by-year fluctuations in the release rate on the estimated regional PEC in water

The concentration in biota (e.g. fish) can also be estimated using the simple box model. The bioconcentration factor (BCF) is the ratio of the concentration of a chemical in an organism (e.g. fish) divided by the concentration in the exposure medium (e.g. water) at steady-state. The BCF can also be defined kinetically based on the rate constants for uptake from water and depuration from the organism. If the kinetics and uptake and depuration are known, these can be taken into account in addition to the BCF. However, for GenX the kinetics are unknown and a simple rapid equilibrium between the concentration fish and concentration in water is assumed using the BCF of 3 L/kg. The resulting predicted concentration in fish is shown in Figure 4.9.

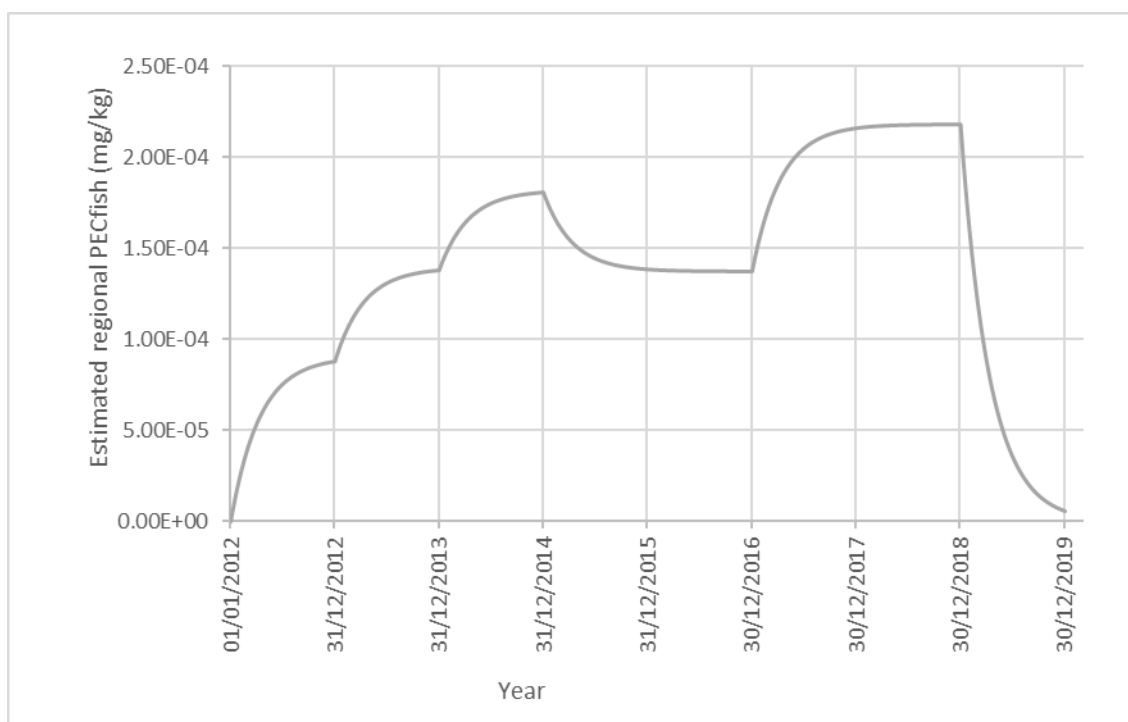


Figure 4.9 Effect of year-by-year fluctuations in the release rate on the estimated regional concentration in fish using a BCF of 3 L/kg

4.4.4 Hypothetical exposure scenarios

Estimation of release rates to achieve a target concentration

One way that it may be possible to consider the level of concern posed by a substance is to calculate the time it would take, or the emission rate that would be required, for a substance to reach a particular concentration in an environmental compartment.

Using the MUST model, hypothetical scenarios are created in order to estimate the extent of releases needed to reach certain target concentrations in surface water (i.e. 1 ng/L, 10 ng/L, 100 ng/L ... 1 mg/L).

Releases are only set to water (fixed for a five year period) as deposition from air releases contribute <1% of the mass being present in water. The assessment includes the STP. Emissions needed to reach target concentrations were estimated in the regional and continental environments of the MUST model (Table 4.8 and Table 4.9).

At the regional scale, an emission to water of 75 kg/y would be needed in order to reach a surface water concentration of 1 ng/L, 750 kg/y to reach 10 ng/L and ultimately 7.5×10^7 kg/y to reach 1 mg/L (Table 4.8). Emission to water required to obtain target concentration in surface water and biota in the regional scale of the MUST model.). The corresponding estimated concentrations in biota

would vary between 0.018 mg/kg (with a release of 75 kg/y to water) to 18,000 mg/kg (with a release of 7.5×10^7 kg/y to water).

The time to reach steady GenX concentrations in surface water and biota is <1 year at the regional scale.

Table 4.8 Emission to water required to obtain target concentration in surface water and biota in the regional scale of the MUST model.

Target concentration in surface water ($\mu\text{g/L}$)	Emissions to water (kg/y)	Concentration in biota (mg/kg)
0.001	7.5×10^1	0.018
0.01	7.5×10^2	0.18
0.1	7.5×10^3	1.8
1	7.5×10^4	18
10	7.5×10^5	180
100	7.5×10^6	1800
1000	7.5×10^7	18000

At the continental scale, an emission to water of 730 kg/y would be needed in order to reach a surface water concentration of 1 ng/L, 7300 kg/y to reach 10 ng/L and ultimately 7.3×10^8 kg/y to reach 1 mg/L (Table 4.9). The corresponding estimated concentrations in biota would vary between 0.18 mg/kg (with a release of 730 kg/y to water) to 180,000 mg/kg (with a release of 7.3×10^8 kg/y to water).

The time to reach steady GenX concentrations in surface water and biota is approximately three years at the continental scale.

Table 4.9 Emission to water required to obtain target concentration in surface water and biota in the continental scale of the MUST model.

Target concentration in surface water ($\mu\text{g/L}$)	Emissions to water (kg/y)	Concentration in biota (mg/kg)
0.001	7.3×10^2	0.18
0.01	7.3×10^3	1.8
0.1	7.3×10^4	18
1	7.3×10^5	180
10	7.3×10^6	1800
100	7.3×10^7	18000
1000	7.3×10^8	180000

The Netherlands authority RIVM has set a water quality limit for GenX in surface water at 0.118 µg/L (Smit, 2018). In order to reach that concentration in surface water in the regional and continental scales, approximately 8.6×10^3 and 8.5×10^4 kg/y, respectively, would need to be emitted to water. At the regional scale, this annual amount released to water is >4 times higher than the highest reported emissions to water (in 2017; see Table 4.2).

Consideration of distance to achieve a specific concentration

The concentrations in the environment depend upon the release rate of the substance to the environment, the distance of the monitoring point from the point of release and the time between the release occurring and the concentration being determined. The effect of different emission rates on the concentration have been considered in the previous example. This example considers the time and distance aspects.

In many respects, time and distance are interrelated. For example, increased dilution generally occurs with distance from a point of release, and the time taken to travel that distance also increases. At the same time, concentrations of substances can build up over time at points distant from the source of release.

The consequence of this is that at distances close to a source of release the concentrations are expected to be the highest (as the lowest dilution occurs and removal processes such as degradation have had only limited time to occur). These local concentrations are expected to establish rapidly and reflect the local dilution conditions. Furthermore these local concentrations are expected to be relatively constant over time provided the release rate does not change, but to rapidly change in response to a change in the release rate. Thus, for situations local to a point of release at a given release rate, the distance at which a specific concentration is reached is dependent in large part on the local dilution. This means that it is difficult to set a “standard” or “generic” distance at which a specific concentration will be reached. For a release into a river, for example, the dilution factor in the river would be expected to increase the further downstream from the source and so the distance depends upon the specific properties of the receiving water. The concentrations would be expected to be highest immediately downstream from the discharge point and then decrease with increasing distance downstream.

At larger scales (regional, continental, global), the available models considered effectively estimate an “average” concentration over the scale considered. Therefore the concentrations relate to an area (e.g. region, continent, arctic etc.) rather than a specific point in that area. This means that it is difficult to predict a concentration at a specific compliance point more distant from a point source of release e.g. a specific point in the marine environment.

4.5 Summary

The modelling work carried out suggests that local and regional concentrations of GenX are expected to respond quickly to changes in emission, with steady-state predicted to be achieved typically <1 year. The main driving forces for the predicted concentrations at a local (and regional) scale are a) the release rate to the environment, b) the local and regional dilutions and c) the residence time of water within the system being considered. This means that the ability to reliably predict concentrations of GenX at a regional scale depend on the assumed properties of the receiving environment. In this respect the uncertainty in the predicted local and regional concentrations for highly persistent substance are not significantly different to any other substance.

The predicted concentrations in biota (e.g. fish) follow a similar trend to the concentration in water. This assumes a rapid steady-state is established between the fish and the concentration in water. The kinetics of uptake and depuration from biota for GenX is not known, and so the effect of these kinetics on the time trends of the predicted concentrations in biota could not be investigated.

At larger modelling scales (e.g. global scale) the modelling carried out suggests that long timescales are needed for GenX to reach steady-state. The pattern for the predicted steady state concentrations of GenX based on the release scenario assumed is Local PECs > regional PECs > continental PECs > global PECs.

5 Modelling of PFHxA

5.1 Background

This task involved modelling concentrations of perfluorohexanoic acid (PFHxA) in the environment. PFHxA has a much more complex use pattern than GenX and it is formed as a degradation product from many other perfluoroalkyl substances. This complexity means that the actual amounts of PFHxA released to the environment are uncertain. The purpose of the modelling of PFHxA therefore is to explore time trends in the possible build-up over time of PFHxA in a semi-quantitative approach using example scenarios. It is not an attempt to accurately predict the actual concentrations of PFHxA in the environment. The results should therefore be seen in this context.

5.2 Chemical and environmental fate properties

The chemical and environmental fate properties relevant to PFHxA are summarised in Table 5.1. Data are presented both for ammonium undecafluorohexanoate, which is representative of the anionic form of PFHxA and of the fully protonated PFHxA (acid form). At the pHs typically encountered in the environment, PFHxA will exist predominantly in the anionic form. Both sets of properties are considered in the analysis in Section 5.4 so that the difference in the predicted behaviour of the two forms can be compared. The data are taken mainly from the ECHA Restriction Report (ECHA, 2019c).

Table 5.1 Chemical and environmental fate properties relevant to PFHxA.

Property	Value for ammonium undecafluorohexanoate	Value for PFHxA (acid form)	Reference
Molecular weight	314.05 g/mol*	314.05 g/mol	
Melting point	>135°C (decomposes)	12-14°C	ECHA, 2019c
Boiling point	>135°C (decomposes)	157	ECHA, 2019c
Solubility	57.61 g/L (at 20°C)	15.7 g/L (ambient temperature; assumed to be 25°C)	ECHA, 2019c
Vapour pressure	4.47×10 ⁻³ Pa (at 25°C)	264 Pa (at 25°C)	ECHA, 2019c
Log Kow	1.5	4.06	ECHA, 2019c
Log Koc soil	1.63	No data	ECHA, 2019c
Koc	42.7	No data	ECHA, 2019c
Henry's Law constant	2.44×10 ⁻⁵ Pa m ³ /mol	5.28 Pa m ³ /mol	ECHA, 2019c
BCF	3.162	No data	PFA
Half -life in air	20.57 days**	20.57 days	ECHA, 2019c
Half-life in water, soil and sediment	Assumed to be not degradable***	Assumed to be not degradable***	

* Relates to the anion. ** Data for PFHxA (acid form) assumed to be the same for the anion. *** In EUSES minimum degradation half-lives of 5×10⁵days in water, 1×10⁷days in sediment and 1×10⁶ days in soil (all at 12°C) is automatically included by default for these substances.

5.3 Tonnage and release estimates

An estimate of the amount of PFHxA release to the environment is available in PFHxA Annex XV Restriction Report (ECHA, 2019c). This is based on an estimate of the amounts of substances with C6 perfluorinated side chains (PFHxA-precursor substances) that are used and released in the EU and assuming that these precursor substances degrade reasonably rapidly in the environment, releasing PFHxA. It was estimated that around 1,000 to 5,000 tonnes/year of PFHxA could be release into the EU environment as a degradation product of these precursor substances and, that without restriction, around 10,000 to 50,000 tonnes of PFHxA would have been released to the EU environment within the next 20 years.

5.4 Exposure scenarios

5.4.1 MUST modelling

The MUST modelling has been undertaken assuming a yearly release of between 1,000 and 5,000 tonnes of PFHxA into the EU environment. The actual environmental compartment(s) to which this release initially occurs is unknown but, given the properties of the anionic form of PFHxA, it is likely to ultimately be to water. For the analysis here it has been assumed that either 1,000 to 5,000 tonnes/year of PFHxA is released in turn to air, waste water or soil. The water concentration is modelled for each of these scenarios using the regional and continental environments of the MUST model (Table 5.2). All scenarios were run using the properties of the ammonium undecafluorohexanoate (anionic form) and PFHxA (acid form).

Table 5.2 PFHxA concentrations in Regional and Continental water estimated by MUST.

Emission compartment	Emission (kg/y)	Water concentration (mg/L)	
		ammonium undecafluorohexanoate (anionic form)	PFHxA (acid form)
Regional environment			
Air	1000	9.0×10^{-8}	1.5×10^{-8}
Air	5000	4.5×10^{-7}	7.8×10^{-8}
Water	1000	1.4×10^{-5}	2.8×10^{-6}
Water	5000	7.0×10^{-5}	1.4×10^{-5}
Soil	1000	- ^a	1.6×10^{-8}
Soil	5000	- ^a	8.0×10^{-8}
Continental environment			
Air	1000	5.4×10^{-8}	2.3×10^{-9}
Air	5000	2.7×10^{-7}	1.2×10^{-8}
Water	1000	1.4×10^{-6}	5.5×10^{-8}
Water	5000	7.2×10^{-6}	2.8×10^{-7}
Soil	1000	- ^a	2.3×10^{-9}
Soil	5000	- ^a	1.2×10^{-8}

^a Water concentrations did not reach steady-state, even after 100 years of emissions and are therefore not reported.

Emissions of PFHxA to water resulted in the highest water concentration compared to the scenarios where PFHxA is released to air or soil. Water concentrations of ammonium undecafluorohexanoate are estimated to be approximately five times higher compared to water concentrations of the acid of PFHxA in the regional environment, while in the continental environment the concentrations of ammonium undecafluorohexanoate were approximately 24 times higher than the water concentrations of the acid of PFHxA.

For all scenarios, steady-state concentrations in water were reached within one year, with the exception of the scenario where ammonium undecafluorohexanoate was released to the soil compartment. In this scenario, concentrations were increasing in the water compartment, even after 100 years of emissions.

Assuming releases to water only (as a worst case scenario), emissions are estimated that are needed to reach target concentrations (1 ng/L, 10 ng/L, etc) in the water compartment (Table 5.3).

Table 5.3 Emission to water required to obtain target PFHxA concentrations in water in the regional scale of the MUST model

Target concentration in surface water (µg/L)	Emissions to water (kg/y)	
	ammonium undecafluorohexanoate	PFHxA (acid form)
0.001	7.2E+01	3.5E+02
0.01	7.2E+02	3.5E+03
0.1	7.2E+03	3.5E+04
1	7.2E+04	3.5E+05
10	7.2E+05	3.5E+06
100	7.2E+06	3.5E+07
1000	7.2E+07	3.5E+08

At the regional scale, an emission to water of 72 kg/y of ammonium undecafluorohexanoate would be needed in order to reach a water concentration of 1 ng/L, 720 kg/y to reach 10 ng/L and ultimately 7.2×10^7 kg/y to reach 1 mg/L (Table 5.3). For the acid form of PFHxA, 350 kg/y would need to be emitted to water in order to reach a water concentration of 1 ng/L, 3500 kg/y for 10 ng/L and ultimately 3.5×10^8 kg/y to reach 1 mg/L.

5.4.2 EUSES modelling

The EUSES modelling has been undertaken assuming a yearly release of between 1,000 and 5,000 tonnes of PFHxA into the EU environment. The actual environmental compartment(s) to which this release initially occurs is unknown but, given the properties of the anionic form of PFHxA, it is likely to ultimately be to water. For the analysis here it has been assumed that either 1,000 to 5,000 tonnes/year of PFHxA is released in turn to air, waste water or soil. In addition, the analysis has also considered the effects of different proportions of the total release into the regional and continental models within in EUSES. The different scenarios considered are summarised in Table 5.4. Each scenario was run using the properties of the ammonium undecafluorohexanoate (anionic form) and PFHxA (acid form).

Table 5.4 EUSES scenarios considered for PFHxA modelling

Scenario	Total release (tonnes/year)	Total daily release (kg/day) ^a	Regional fraction	Continental fraction	Regional release (kg/day)	Continental release (kg/d)
A	1,000	2,740	0.1	0.9	274	2,466
B	1,000	2,740	1	0	2,740	0
C	5,000	13,699	0.1	0.9	1,370	12,329
D	5,000	13,699	1	0	13,699	0

Note: a) Assuming release on 365 days/year.

The regional, continental and global PECs in water obtained by EUSES modelling are summarised in Appendix A. Example plots for the release to waste water are shown in Figure 5.1. For the global models, only the global: arctic concentrations are shown; the concentrations predicted in the global: moderate and global:tropic models are similar to these).

The results of this analysis show that for both substances and all scenarios, the highest PECs in water are obtained in the regional model with the continental PECs being lower. The global PECs are generally of a similar order of magnitude to, but in all cases lower, than the continental PECs.

For the anionic form, the highest concentrations in regional surface water result, as would be expected, from Scenario D which has the highest regional release. Similarly the highest continental concentrations result from Scenario C which has the highest continental release.

At a global scale, both Scenario C and Scenario D lead to the highest predicted concentrations for the anionic form; both these scenarios have the same overall

total release to the environment and differ only in how this is distributed between the regional and continental models. Following release to waste water and soil the global concentrations in water obtained in Scenario C and D are generally similar but some small differences in the predicted water concentrations obtained in Scenario C and D are evident at the global scale following release to air, indicating the compartment of release is important to the overall modelling results.

The acid form generally shows an overall similar pattern as the anionic form, although some small differences are evident for example the continental PEC in marine water is highest for Scenario D rather than Scenario C following release via air. This may reflect the higher vapour pressure and/or higher log Kow of the acid form compared with the anionic form.

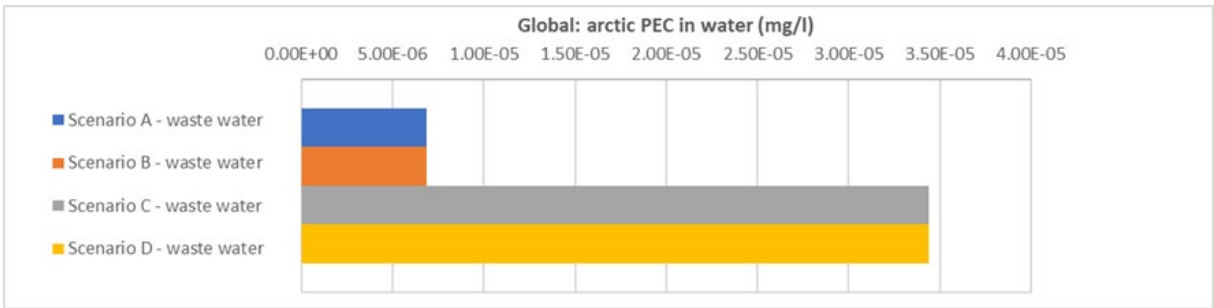
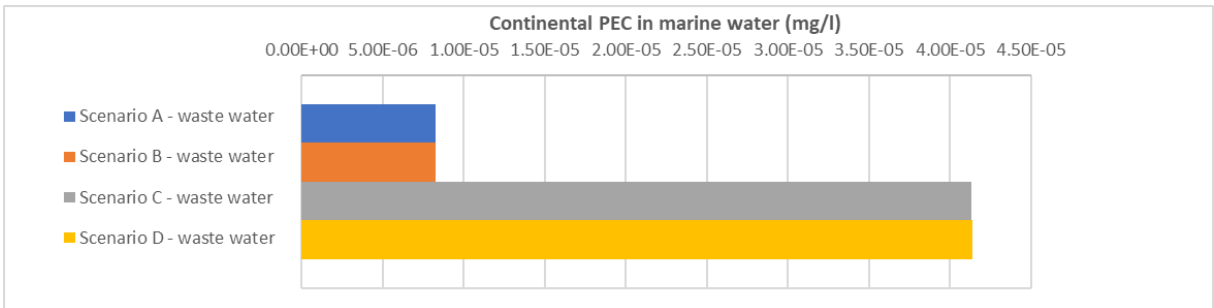
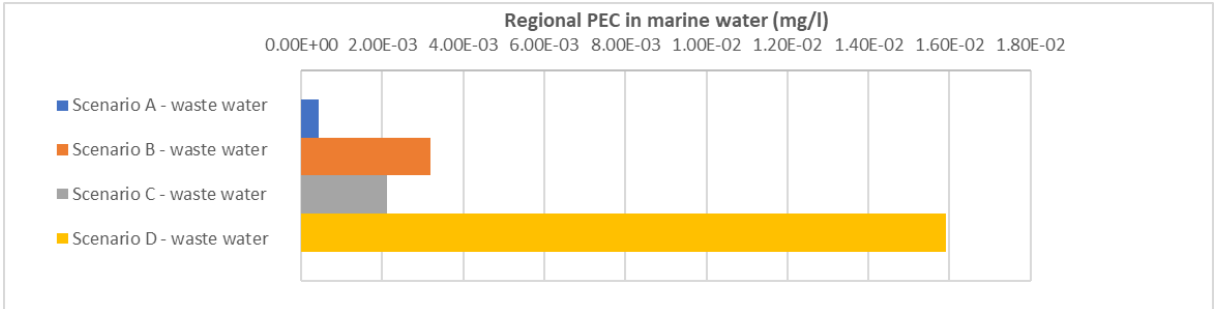
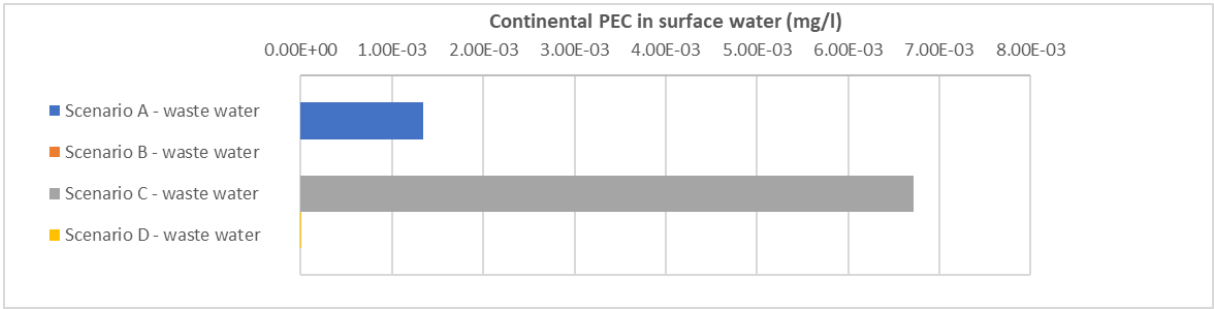
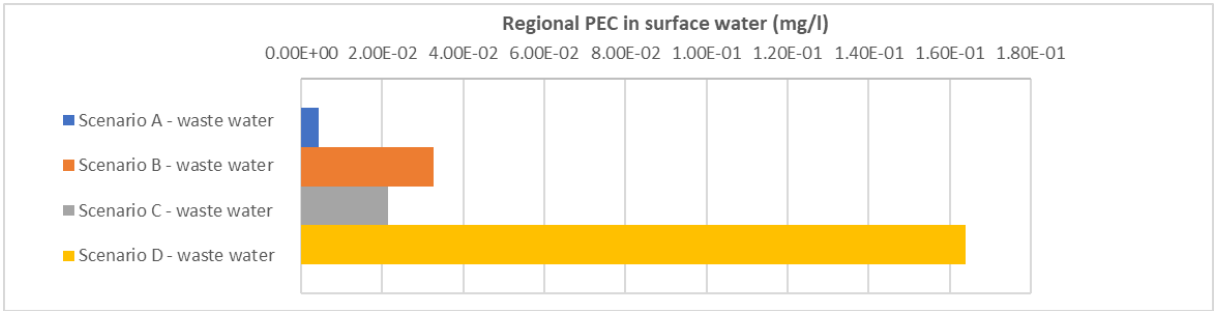


Figure 5.1 PECs in surface water for ammonium undecafluorohexanoate (anionic form) following release to waste water.

The steady-state masses predicted in EUSES for the four scenarios are summarised in Figure 5.2 for ammonium undecafluorohexanoate (anionic form) and Figure 5.3 for PFHxA (acid form).

As would be expected, the steady-state masses are highest for Scenario C and D, which have the highest overall release rate. For the anionic form (Figure 5.2) the majority of the steady-state mass resides in the global compartments, and the distribution of the steady-state mass is broadly similar between the three assumptions over the compartment of initial release (waste water, air and soil). The total steady-state mass is highest when the release is assumed to be initially to waste water.

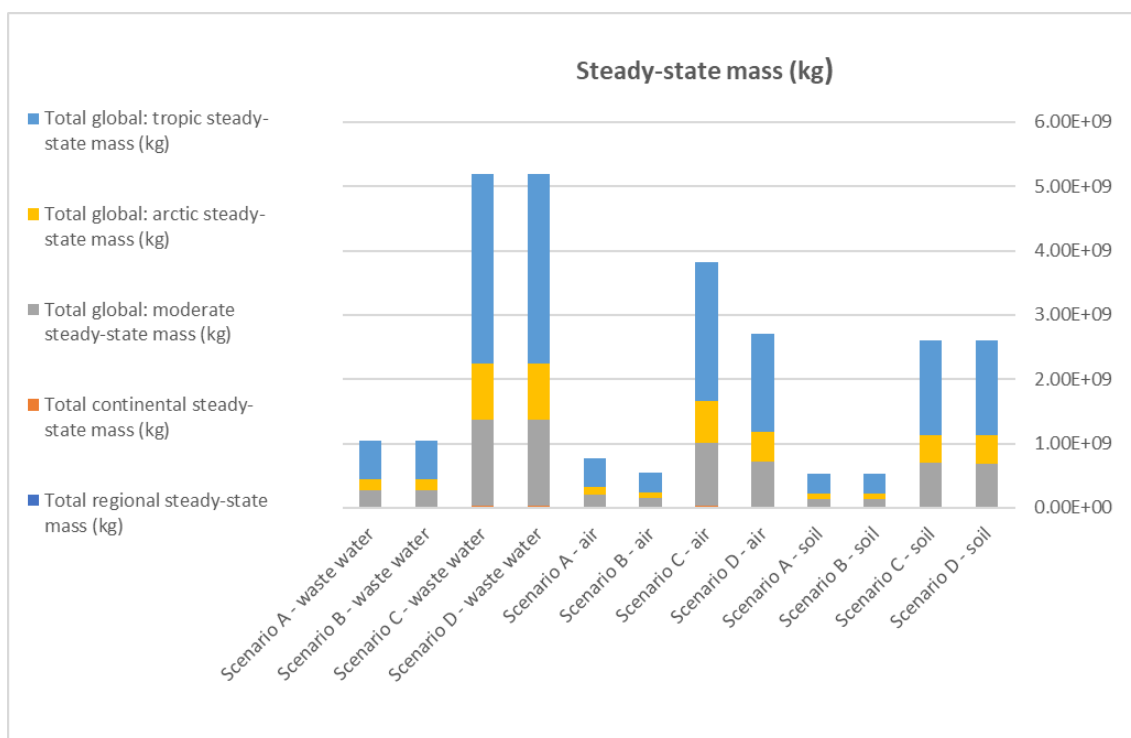


Figure 5.2 Predicted steady-state masses for ammonium undecafluorohexanoate (anionic form)

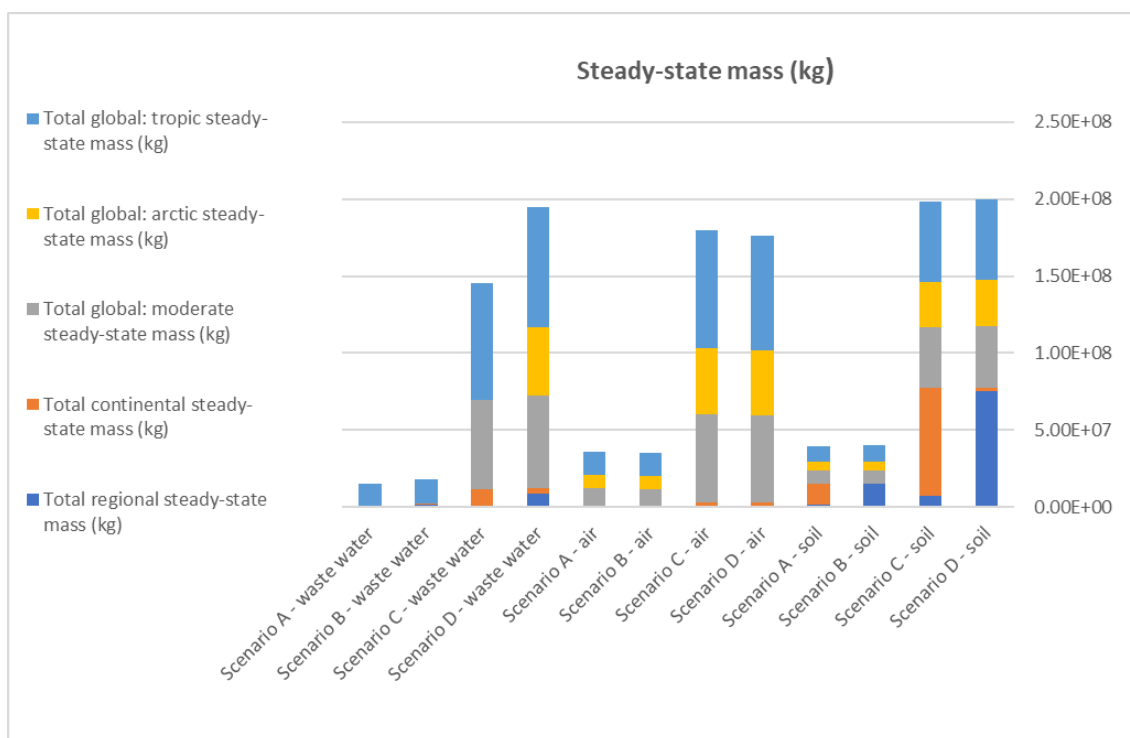


Figure 5.3 Predicted steady-state masses for PFHxA (acid form)

The modelling for the acid form (Figure 5.3) shows a different pattern to the anionic form. The highest steady-state masses for the acid form result from initial release to the soil compartment and there is also a significant contribution from the regional and continental compartments to the total steady-state mass.

These differences between the acid form and the anionic form can also be seen in the estimated time to 95% steady-state in Table 5.5 (estimated using the method given in Section 2.2). This shows that the time to 95% steady-state in the regional model is around 10 times shorter for the anionic form than the acid form, whereas the time to 95% steady-state in the whole model system is 10-20 times longer for the anionic form than the acid form. This suggests that the anionic form is transported from regional and continental areas to global areas more readily than the acid form. This may result from the higher log Kow assumed for the acid form compared with the anionic form, meaning that higher adsorption onto to sediment/soil is predicted for the acid form than the anionic form with a resulting reduction in transport potential. It is also interesting to note that the time to 95% steady-state is dependent upon the assumed compartment for the release (e.g. air, water or soil).

Table 5.5 Estimated time to 95% steady-state from EUSES steady-state masses

Scenario	Assumed compartment of release	Model scale	Estimated time to 95% steady-state (days)	
			Anionic form	Acid form
A	Waste water	Regional	194	1,944
		EU (Regional + Continental)	6,815	2,604
		Total system	1,135,158	41,177
	Air	Regional	721	29
		EU (Regional + Continental)	5,140	636
		Total system	834,997	39,290
	Agricultural soil	Regional	1,021	16,448
		EU (Regional + Continental)	4,342	16,941
		Total system	569,388	43,459
B	Waste water	Regional	150	1,941
		EU (Regional + Continental)	6,491	2,688
		Total system	1,136,481	42,699
	Air	Regional	709	20
		EU (Regional + Continental)	4,017	643
		Total system	593,429	38,615
	Agricultural soil	Regional	998	16,446
		EU (Regional + Continental)	4,174	16,918
		Total system	570,046	43,749
C	Waste water	Regional	195	1,947
		EU (Regional + Continental)	6,841	2,610
		Total system	1,138,434	41,258
	Air	Regional	721	29
		EU (Regional + Continental)	5,159	640
		Total system	839,588	39,446
	Agricultural soil	Regional	1,022	16,492
		EU (Regional + Continental)	4,356	16,962
		Total system	573,006	43,589
D	Waste water	Regional	150	1,937
		EU (Regional + Continental)	6,480	2,684
		Total system	1,138,003	42,651
	Air	Regional	709	20
		EU (Regional + Continental)	4,017	643
		Total system	592,225	38,615
	Agricultural soil	Regional	1,000	16,490
		EU (Regional + Continental)	4,176	16,962
		Total system	571,580	43,771

5.5 Summary

The modelling carried out on PFHxA shows, similar to the case with GenX, that steady-state at the regional level is predicted to be reached relatively quickly (e.g. < 1 year) for the anionic form (the predominant form likely to be present in the environment) following release to water. There is some uncertainty over the

amounts of PFHxA released into the environment and so it has not been possible to model known time trends in the yearly release. Again, similar to the case with GenX, steady-state is predicted to be reached only slowly at the global scale. The following are also evident from the modelling carried out.

- The time to steady-state depends on the compartment to which the release is assumed to occur (e.g. water, air or soil).
- Steady-state is predicted to be reached more rapidly at the regional scale compared with the global scale.
- The differences in the properties between the anionic and acid form of PFHxA lead to differences in the predicted times to steady-state.
 - The anionic form is predicted to reach steady-state more rapidly than the acid form at the regional and EU level but more slowly than the acid form when the total system is considered.
 - In the current scenarios considered, these differences may relate to the different assumptions over the properties of the substance, notably the higher adsorption to sediment and soils assumed for the acid form compared with the anionic form. This suggests that a good understanding of the properties of the substance is important when considering these types of PFAS.

The ultimate steady-state concentrations achieved are dependent upon the release rates to each compartment along with the time to steady state. This means that it is difficult to draw generic conclusions. The dependence of the modelling upon the release amounts, compartments of initial release and substance properties means that a substance-by-substance approach is needed.

6 Results of regulatory interventions on these substances

6.1 Background

This task considers whether the models available are able to predict how long it will take for concentrations to decrease if emissions are reduced or ceased or whether any rules of thumb can be made based on substance half-life to estimate the rate of removal if emissions cease.

6.2 Discussion

The time taken for a given concentration to decrease following a reduction or cessation in emissions is dependent upon the overall loss or removal rate from the environment of interest. As discussed in Section 2.2 it is possible to estimate an approximate overall removal rate constant from the EUSES model at different scales (e.g. regional or global). Assuming that the loss follows overall first-order kinetics, and that the method used in Section 2.2 gives a reasonable approximation to the overall loss rate constant, it is then possible to estimate the approximate time for concentrations to fall to approximately 50% of their original value (half-life) using the following equation.

$$\text{half-life} = \frac{\ln(2)}{k} = \frac{0.693}{k}$$

Where: half-life = time taken for concentration to fall to 50% of starting value (days).

k = approximate first order removal rate constant (days⁻¹).

As an example, the estimated half-lives following cessation of emissions to water for GenX are shown in Table 6.1. These are based on the example calculations in Section 2.2 (see Table 2.2, Table 2.3 and Table 2.4).

At a regional level, the MUST model can be used directly to investigate the changes in concentration resulting from changes in emission rate or cessation of emissions.

In cases where the substance primarily occurs in one compartment (e.g. water) an approach using simple one-compartment mass-balance model outlined in Section 4.4.3 can be used to investigate the effects of changing emission rates over time on the resulting concentrations at a regional scale for example. This is exemplified in Figure 4.8 for the regional water compartment and in Figure 4.9 for biota (fish).

Table 6.1 Example calculations of half-lives following cessation of emissions to water for GenX using EUSES

Model scale	Estimated half-life following cessation of emissions to water		
	GenX	GenX assuming a half-lives in water, sediment and soil corresponding to the P-criterion	GenX assuming a half-lives in water, sediment and soil corresponding to the vP-criterion
Regional	33.3 days	18.9 days	22.1 days
EU (Regional + Continental)	1.50×10^3 days	45.4 days	52.9 days
Whole system	2.64×10^5 days	51.9 days	60.4 days

The PFAS substances used as examples have a relatively low lipid bioaccumulation potential, based on the fish bioconcentration factor. For these substances the concentration in fish can be estimated using the BCF. The resulting concentration in fish assumes that the substance in the fish is at steady-state with the concentration in water, and that this steady-state is established instantaneously. The kinetics of uptake and depuration by fish is unknown for the substances considered and therefore it is not possible to investigate further any time-trends in the accumulation in biota. Using the assumption of an instantaneous steady-state in the biota (fish), the predicted concentration in biota would be expected to mirror the changes in the concentration in water resulting from changes in emission rates over time. This assumption will hold provided that the rates of uptake and depuration from biota are much faster than the rate of change of concentration in the water resulting from the changes in emission rate.

7 Overall conclusions

It is important to note that all modelling approaches are an approximation to the actual situation in the environment. However, it is possible to obtain useful information from some relatively simple approaches to modelling to inform assessments of the impact of the persistence of a substance.

For the specific PFAS considered here, the modelling carried out indicates that the concentrations at a local scale are expected to be influenced mainly by the local dilutions and flow rates. The default dilution factor of ten currently used under REACH for freshwater environments appears to be conservative for the GenX processing site considered in this report. The local concentrations in water predicted are expected to respond rapidly to changes in release rate or cessation of emission.

At a regional scale, both the MUST model and the analysis carried out using the EUSES model suggest that GenX and the anionic form of PFHxA will reach a 95% steady-state concentration in surface water over a period less than one year. It is expected that changes in concentration following a change in release rate or cessation of emission will occur over a similar timescale. The reason for this is that the transport of substance from the region into the continental/global environment is predicted to be the dominant removal process from the regional environment for highly persistent substances that occur mainly in the water phase. For such substances this transport is predicted to occur relatively rapidly compared to other removal processes (e.g. degradation).

At a global scale, the modelling carried out indicates that for both GenX and PFHxA steady-state will be reached only very slowly, over many tens or hundreds of years. This is consistent with the persistent nature of these substances and the possibility of transport via the water phase. The overall amounts of substance released affect the ultimate steady-state concentration reached, but the time to steady-state is mainly dependent upon the assumed compartments of release rather than the actual amounts released, and the properties of the substance.

The modelling work with PFHxA also investigated the effects of the uncertainty in the physico-chemical properties for this type of substance. The available properties of both the anionic form (which is expected to predominate in the environment) and the acid form have been considered and the estimated time to 95% steady-state in the regional model following release to water is around 10 times longer for the acid form than the anionic form, but at the global scale the estimated time to steady-state is much longer for the anionic form than that acid form, although it was still many tens of thousands of days for the acid form. This suggests that the anionic form is transported from regional and continental areas to global areas more readily than the acid form. This may result from the higher

log K_{ow} assumed for the acid form compared with the anionic form, meaning that higher adsorption onto sediment/soil is predicted for the acid form than the anionic form with a resulting reduction in transport potential. In addition, the modelling with PFHxA indicates that the compartment to which the substance is originally released (e.g. initial release to air versus initial release to water) is also important in the time to 95% steady-state and the resulting concentrations in the environment.

Overall the modelling work with PFAS in this report suggest that steady-state concentrations at a regional level will be attained relatively quickly (order to 1 year) but that a slower build up or reduction in concentration over time may occur at global scales following a change in release rate, or cessation of emission.

It is important to note, however, that the findings for the specific PFAS considered in this report, should not automatically be applied to other persistent substances. The analysis carried out in Section 2.2 shows that a substance with the same physico-chemical properties as GenX but where the half-lives in water are assumed to correspond to those of the REACH P-criterion or vP-criterion have markedly shorter estimated times to 95% steady-state (less than one year at a global scale) than GenX itself, with a correspondingly much reduced global burden and concentration. Again differences are evident resulting from the initially assumed compartment of release. This strongly suggests that a substance-by-substance approach whereby all of the available evidence, including modelling data, uncertainty in the substance properties, degradation rates and release rates, are considered.

The following is concluded from the work carried out in this report.

- The current quantitative (PEC/PNEC) approach to risk assessment at a local and regional scale appears to be equally applicable to highly persistent substances as for non-persistent substances.
- The concentrations at a global scale of highly persistent substance such as GenX and PFHxA, which are expected to occur primarily in the water phase, are predicted to build up over prolonged periods (many tens or hundreds of years).
- For the water phase in EUSES, regional concentrations will always be equal to or lower than local concentrations due to the model design. However, continental concentrations may be higher than local concentrations and this possibility should be checked during the exposure modelling.
- An approximate time to steady-state at a global scale can be estimated from the EUSES model. This is informative in that it allows a distinction to be made between persistent substances for which global steady-state

concentrations are predicted to be reached over relatively short periods of time (e.g. a few years) and those for which global steady-state concentrations are predicted to be reached over prolonged time periods (e.g. 100 years or more).

- The example substances considered have a relatively low bioaccumulation potential based on the fish bioconcentration factor. The kinetics of uptake and depuration by fish is unknown. Assuming that the accumulation occurs rapidly, the concentration in fish can be estimated directly from the concentration in water and will follow the same time-trends as the concentration in water.

A possible way forward for the regulatory hazard and risk assessment for prioritising persistent substances may be to make a distinction, based on modelling results, between those persistent substances that are predicted to reach 95% global steady-state within a shorter period, say up to 10 years, and those that are predicted to reach 95% global steady-state over much longer periods (say 100 years or more), as follows:

- Substances that reach 95% steady-state within a shorter period (e.g. <10 years). These types of persistent substances may be better assessed using a quantitative (PEC/PNEC) approach than a qualitative purely hazard based approach. Only limited build up in remote regions is likely to occur, and the local and regional assessments are likely to be protective of remote regions. In addition, the concentrations in the environment would be expected to decline reasonably rapidly following a cessation or reduction in emission.
- Substances that reach 95% steady-state over longer periods (e.g. >100 years). These types of persistent substances may build up in remote/global regions and the concentrations in such regions would only be expected to decline only slowly following a cessation or reduction in emission. Although a quantitative (PEC/PNEC) approach may be protective, there are added uncertainties over the potential timescales involved. These uncertainties could potentially be addressed by requiring a more conservative assessment (e.g. incorporating higher uncertainty factors within a PEC/PNEC approach) or a more qualitative approach.
- Substances that reach 95% steady-state over intermediate periods (e.g. >10-<100 years). These substances are intermediate between the two scenarios described above, so it is suggested that these are considered on a case-by-case basis. Possible considerations could include the amount of information available on the substance (for example in terms of releases to the environment and the properties of the substance), the uncertainty in the underlying substance data set, the level of toxicity shown by the substance and the bioaccumulation potential.

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List of abbreviations

BCF	Bioconcentration Factor
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
DDT	Dichlorodiphenyltrichloroethane
DecaBDE	Decabromodiphenyl ether
DegT50	Degradation half-life
DT50	Disappearance half-life
ECHA	European Chemicals Agency
EUSES	European Union System for the Evaluation of Substances
GenX	2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propionic acid
HBCDD	Hexabromocyclododecane
K _{aw}	Air-water partition coefficient
K _{oa}	Octanol-air partition coefficient
K _{oc}	Organic carbon-water partition coefficient
K _{ow}	Octanol-water partition coefficient
MDL	Method detection limit
MQL	Method quantification limit
MUST	Multimedia Stock Pollution Tool
PBT	Persistent, bioaccumulative and toxic
PEC	Predicted environmental concentration
PFAS	Perfluorinated alkyl substances
PFDA	Perfluorodecanoic acid
PFHxA	Perfluorohexanoic acid
PFNA	Perfluorononanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctanesulfonic acid
PNEC	Predicted No Effect Concentration
POPs	Persistent Organic Pollutants
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
STP	Sewage Treatment Plant
SVHC	Substances of Very High Concern
vPvB	very Persistent and very Bioaccumulative
ww	wet weight

Appendix A Summary of EUSES modelling for PFHxA

The EUSES modelling has been undertaken assuming a yearly release of between 1,000 and 5,000 tonnes of PFHxA into the EU environment. The actual environmental compartment(s) to which this release initially occurs is unknown but, given the properties of the anionic form of PFHxA, it is likely to ultimately be to water. For the analysis here it has been assumed that either 1,000 to 5,000 tonnes/year of PFHxA is released in turn to air, waste water or soil. In addition, the analysis has also considered the effects of different proportions of the total release into the regional and continental models within in EUSES. The different scenarios considered are summarised in Table A1. Each scenario was run using the properties of the ammonium undecafluorohexanoate (anionic form) and PFHxA (acid form).

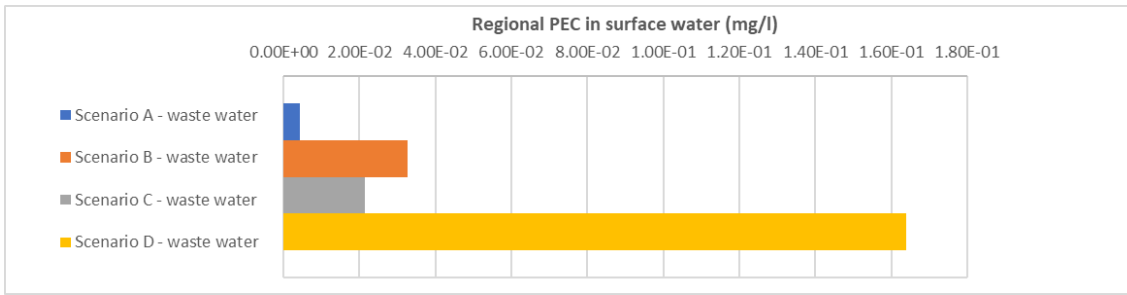
Table A1 EUSES scenarios considered for PFHxA modelling

Scenario	Total release (tonnes/year)	Total daily release (kg/day) ^a	Regional fraction	Continental fraction	Regional release (kg/day)	Continental release (kg/d)
A	1,000	2,740	0.1	0.9	274	2,466
B	1,000	2,740	1	0	2,740	0
C	5,000	13,699	0.1	0.9	1,370	12,329
D	5,000	13,699	1	0	13,699	0

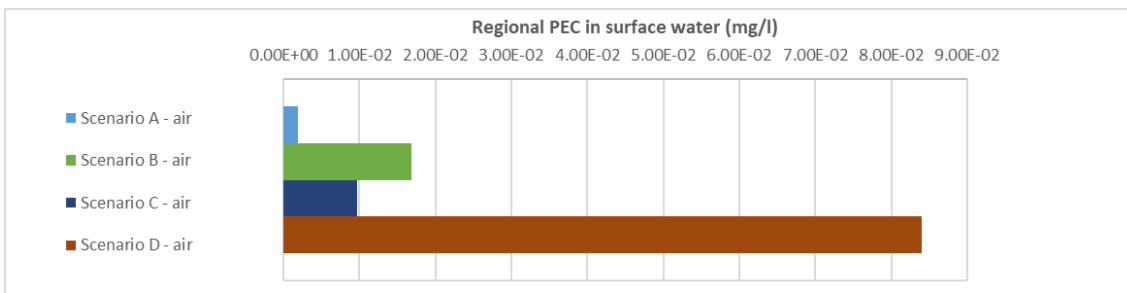
Note: a) Assuming release on 365 days/year.

The regional, continental and global PECs in water obtained by EUSES modelling are summarised Figure A1 to Figure A7 for ammonium undecafluorohexanoate (anionic form) and Figure A8 to Figure A14 for PFHxA (acid form).

a) Release to waste water



b) Release to air



c) Release to soil

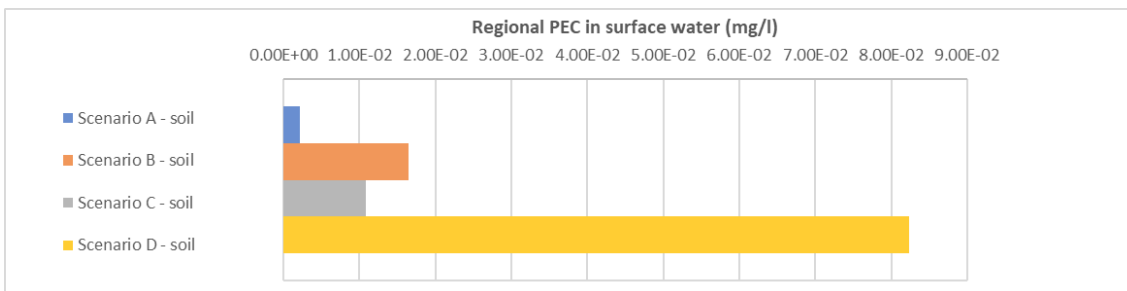
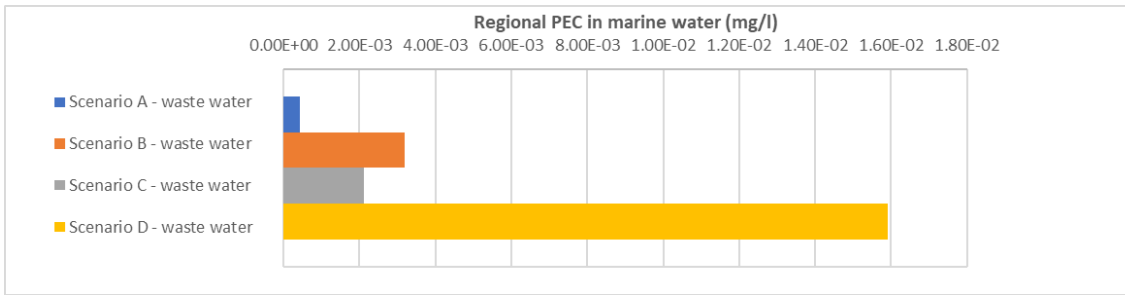
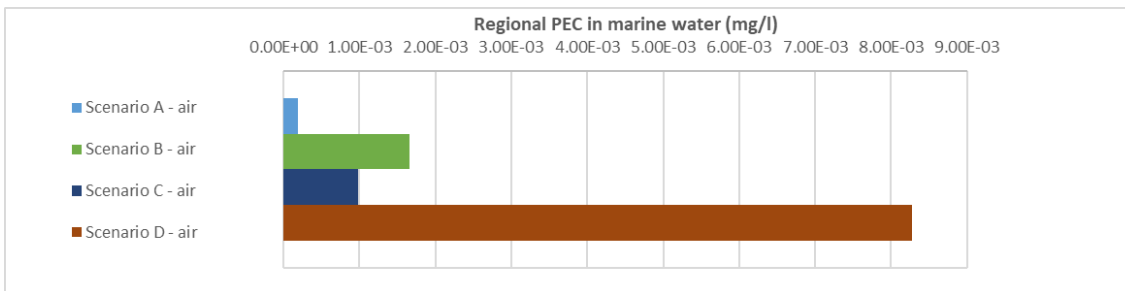


Figure A1 Regional PECs in surface water for ammonium undecafluorohexanoate (anionic form)

a) *Release to waste water*



b) *Release to air*



c) *Release to soil*

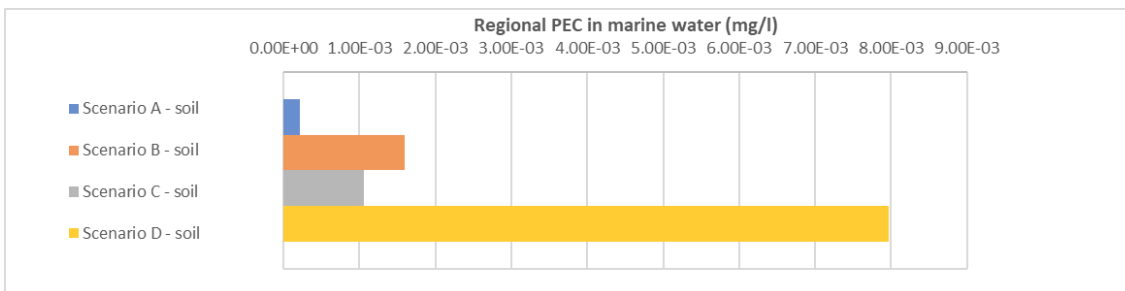
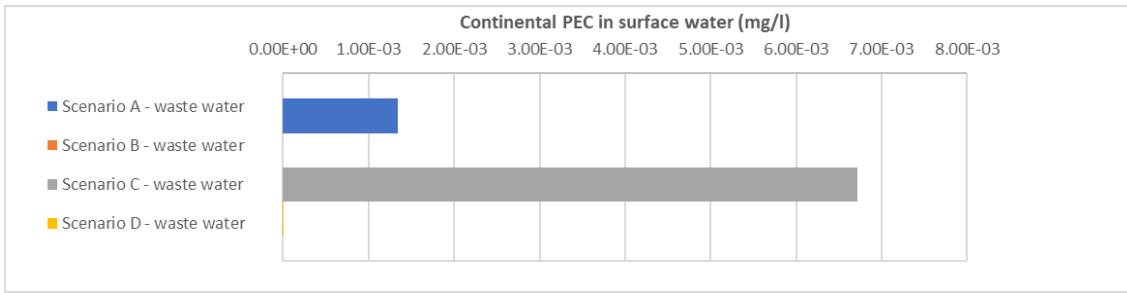
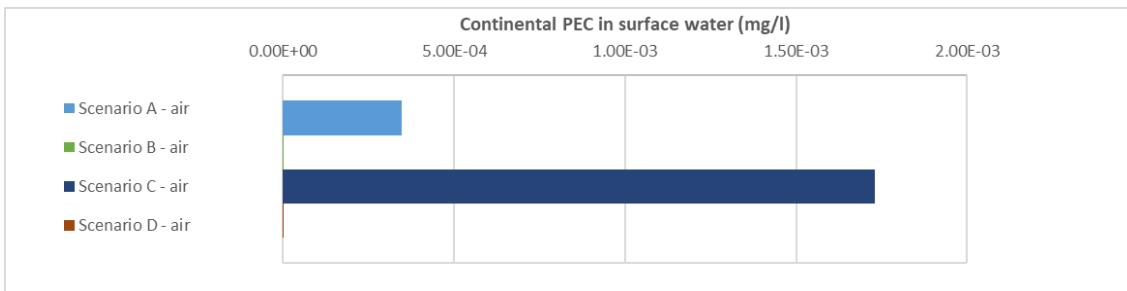


Figure A2 Regional PECs in marine water for ammonium undecafluorohexanoate (anionic form)

a) Release to waste water



b) Release to air



c) Release to soil

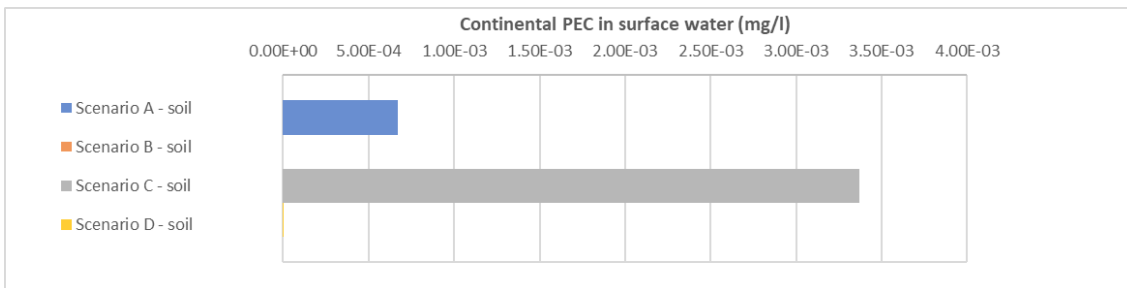
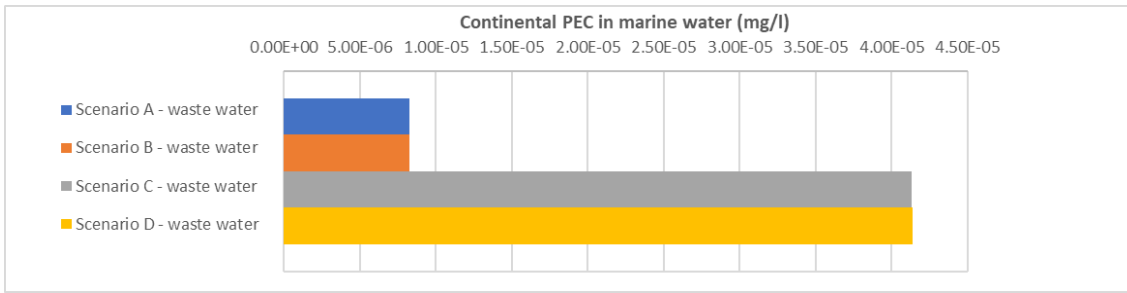
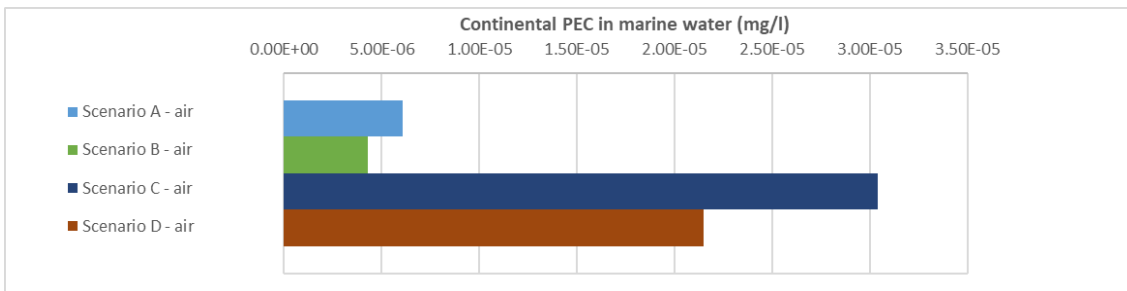


Figure A3 Continental PECs in surface water for ammonium undecafluorohexanoate (anionic form)

a) Release to waste water



b) Release to air



c) Release to soil

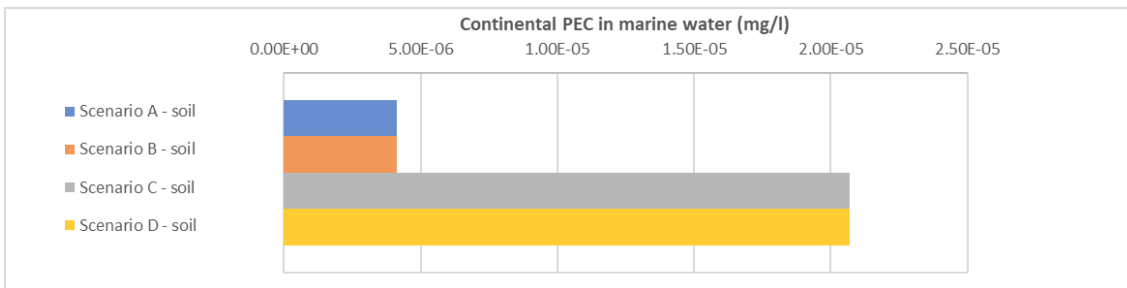
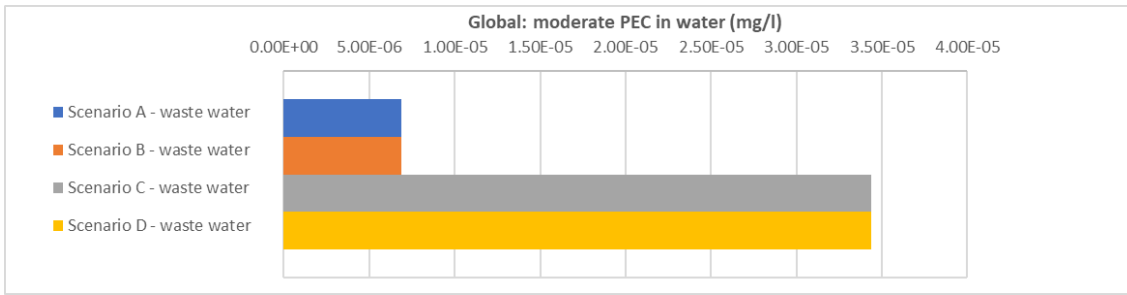
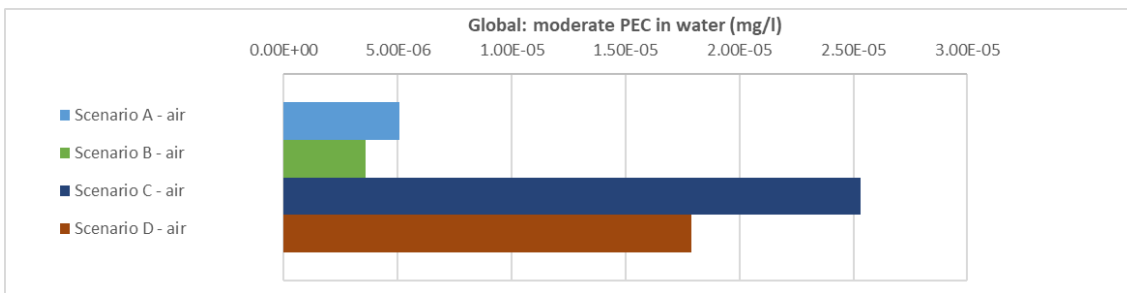


Figure A4 Continental PECs in marine water for ammonium undecafluorohexanoate (anionic form)

a) Release to waste water



b) Release to air



c) Release to soil

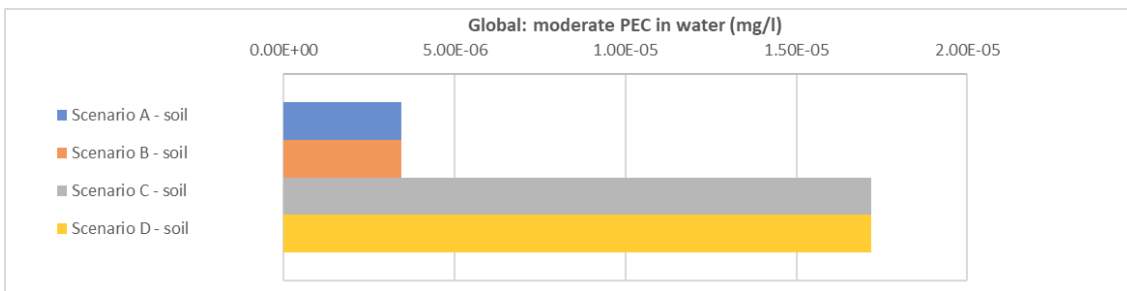
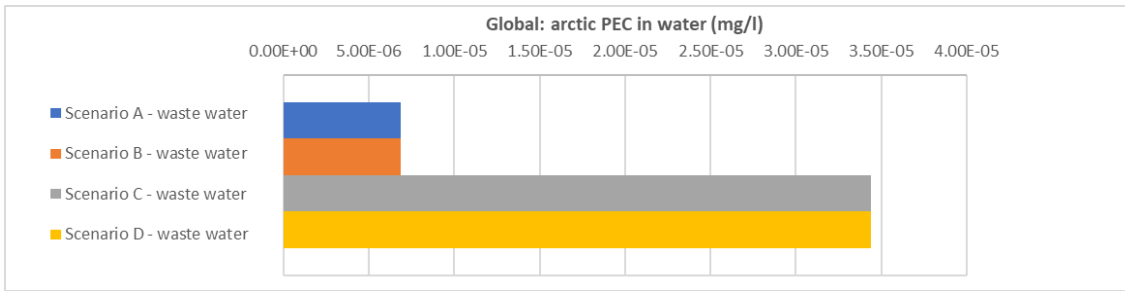
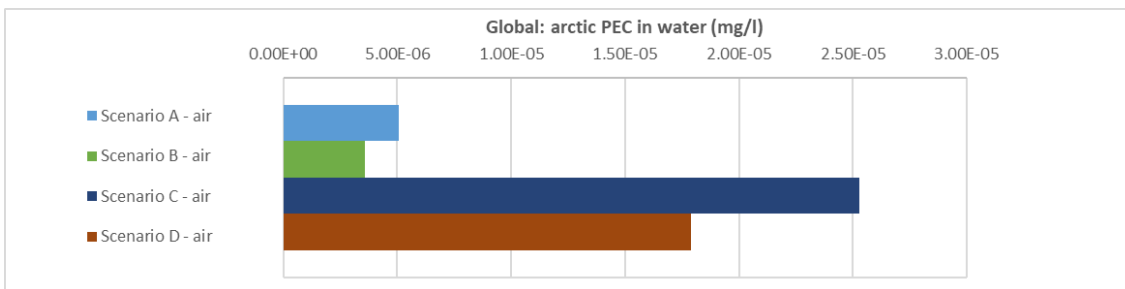


Figure A5 Global: moderate PECs for ammonium undecafluorohexanoate (anionic form)

a) Release to waste water



b) Release to air



c) Release to soil

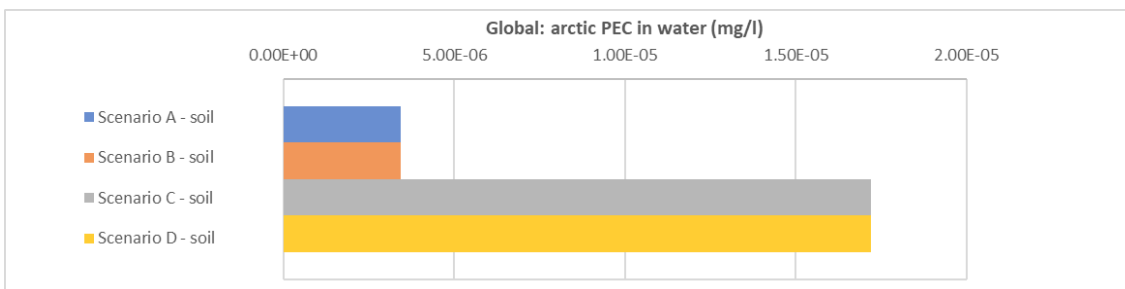
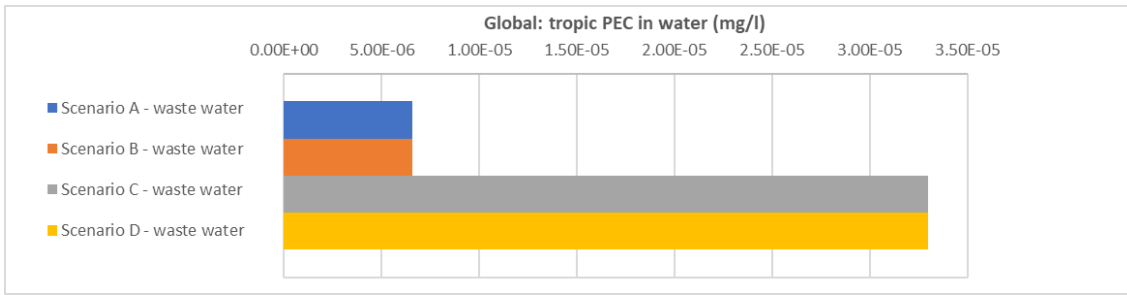
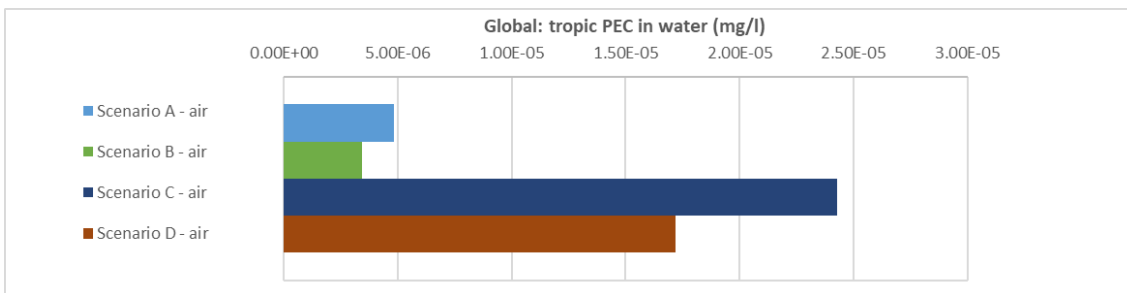


Figure A6 Global: arctic PECs for ammonium undecafluorohexanoate (anionic form)

a) Release to waste water



b) Release to air



c) Release to soil

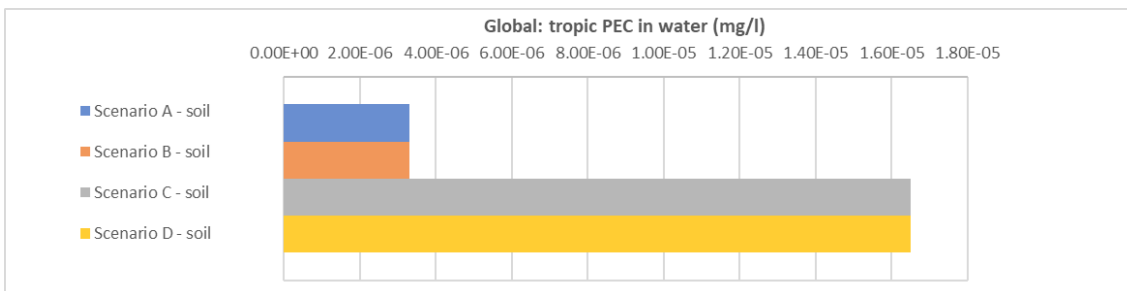
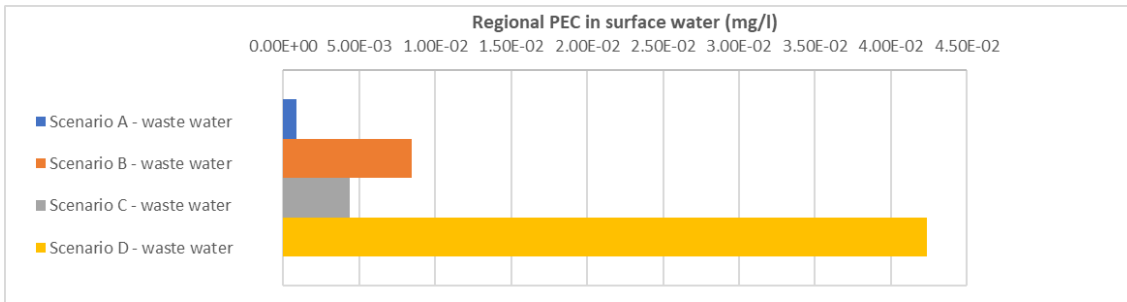
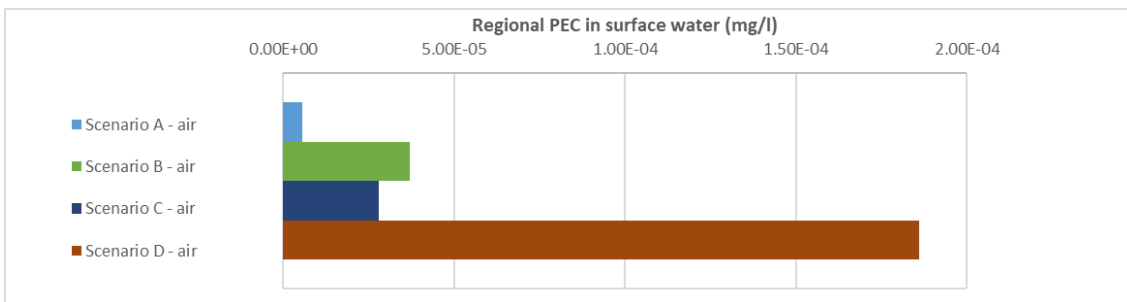


Figure A7 Global: tropic PECs for ammonium undecafluorohexanoate (anionic form)

a) Release to waste water



b) Release to air



c) Release to soil

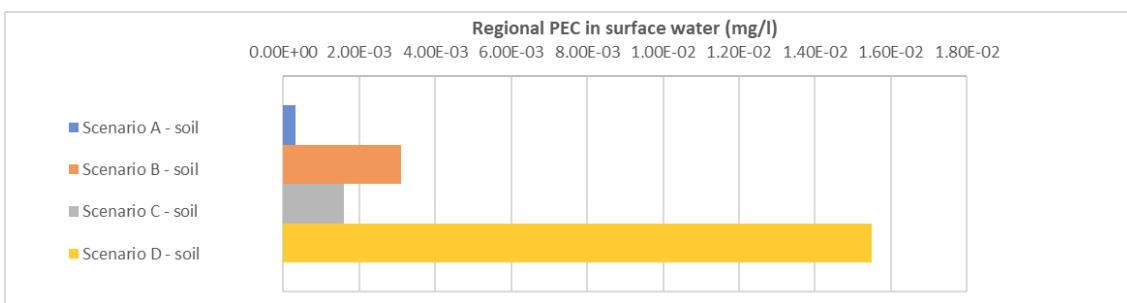
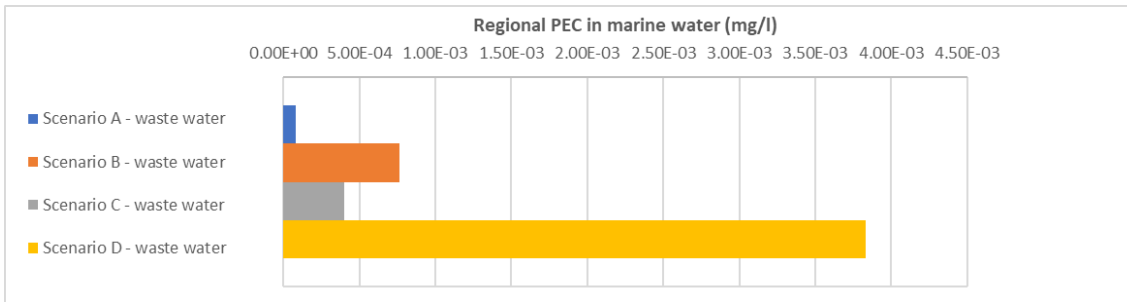
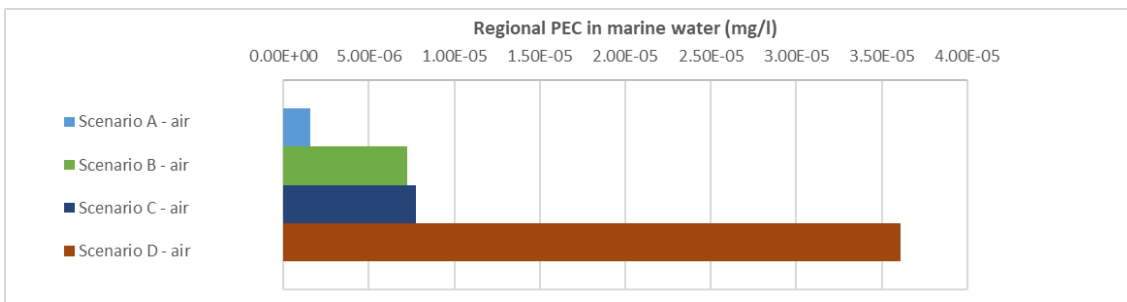


Figure A8 Regional PECs in surface water for PFHxA (acid form)

a) Release to waste water



b) Release to air



c) Release to soil

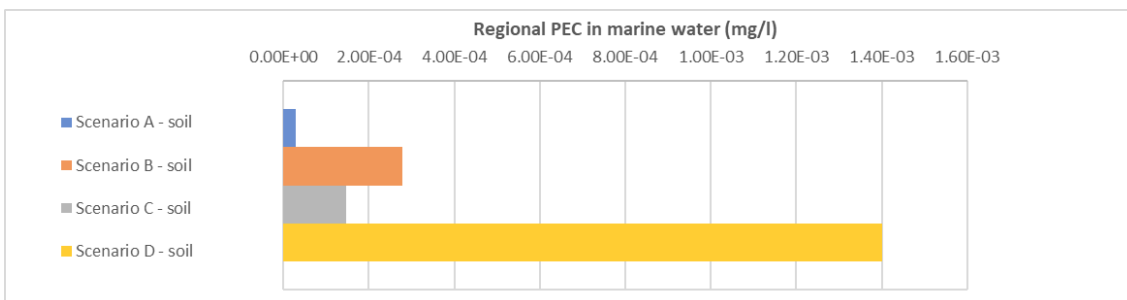
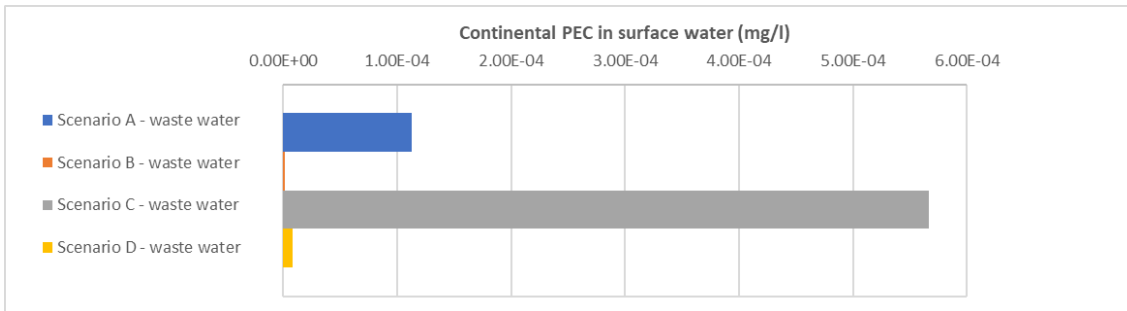
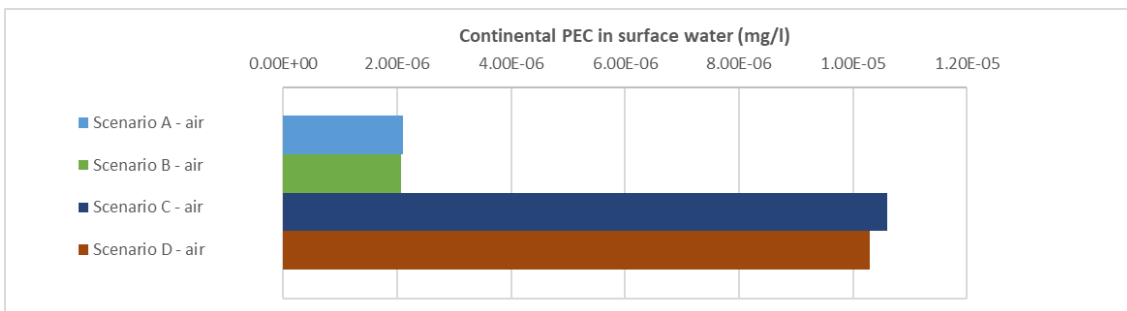


Figure A9 Regional PECs in marine water for PFHxA (acid form)

a) Release to waste water



b) Release to air



c) Release to soil

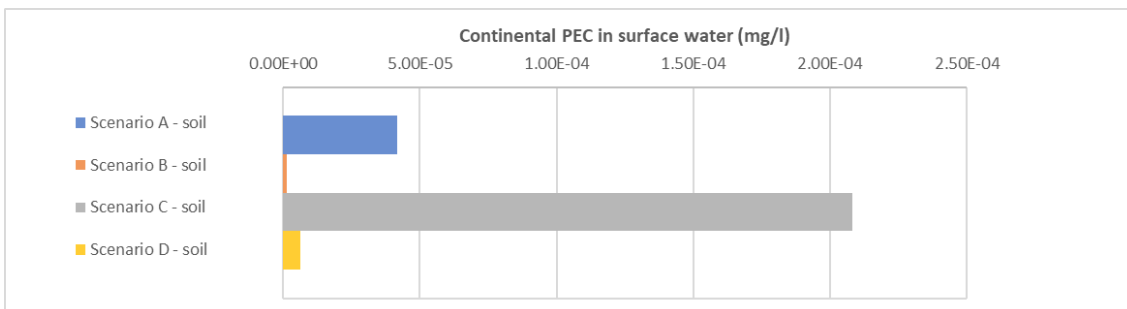
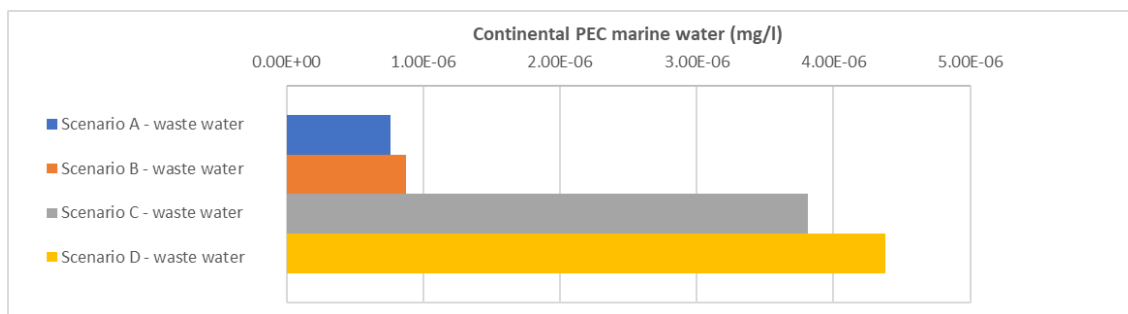
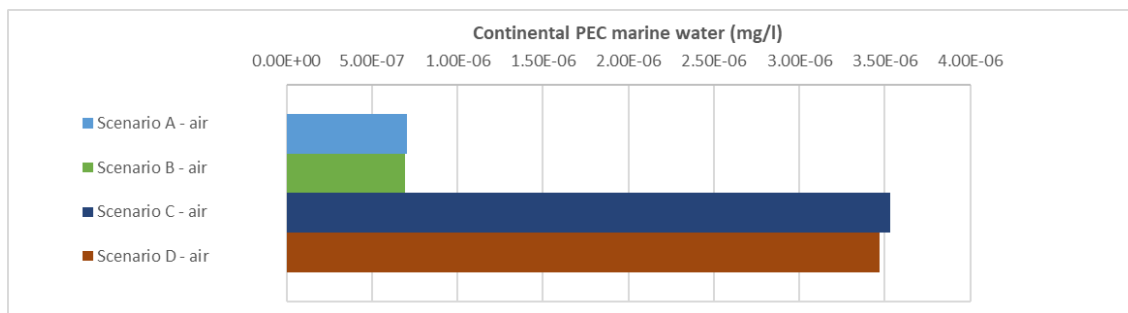


Figure A10 Continental PECs in surface water for PFHxA (acid form)

a) Release to waste water



b) Release to air



c) Release to soil

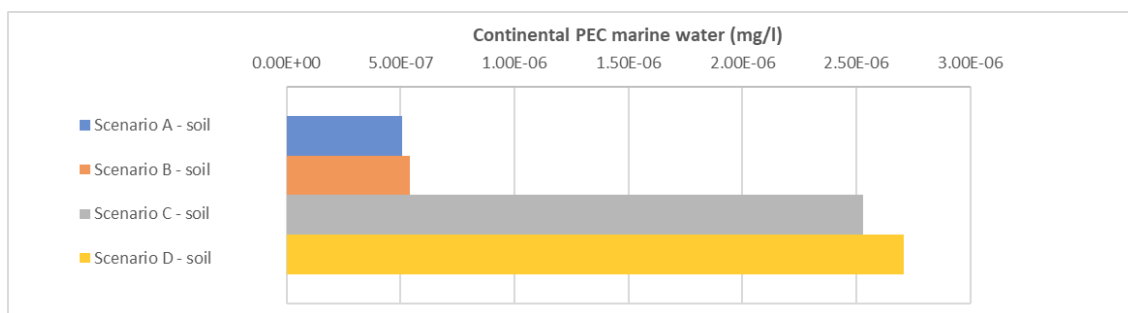
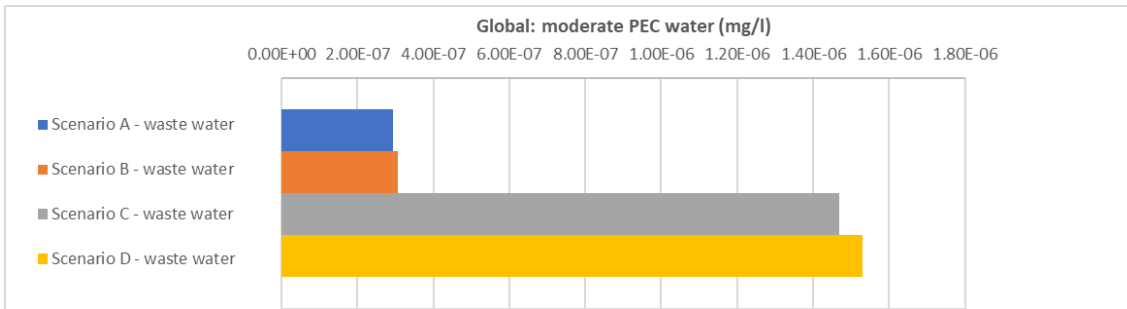
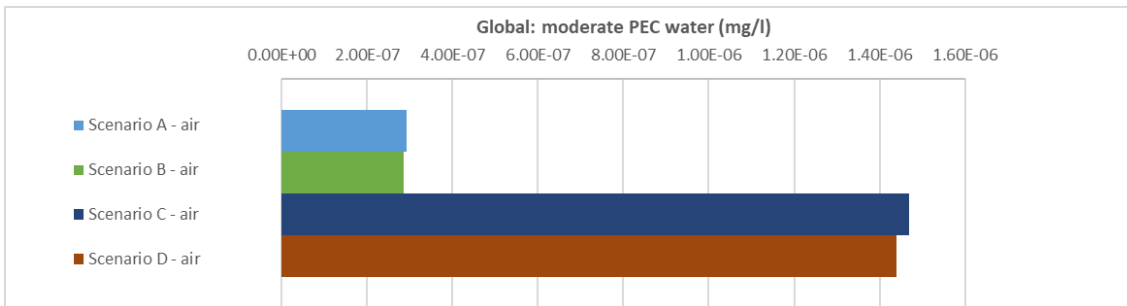


Figure A11 Continental PECs in marine water for PFHxA (acid form)

a) Release to waste water



b) Release to air



c) Release to soil

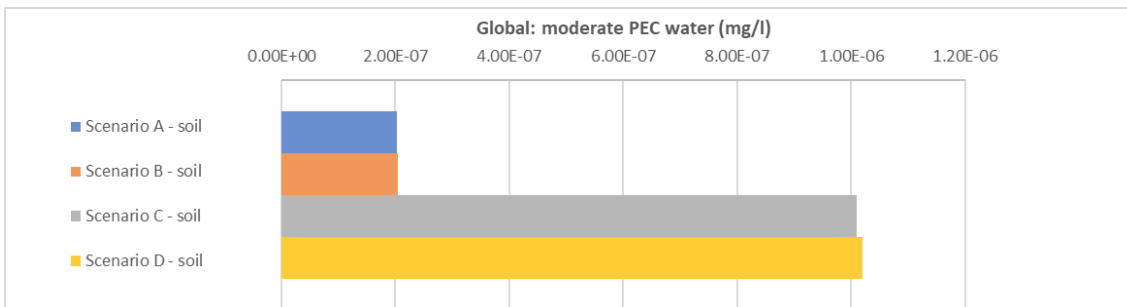
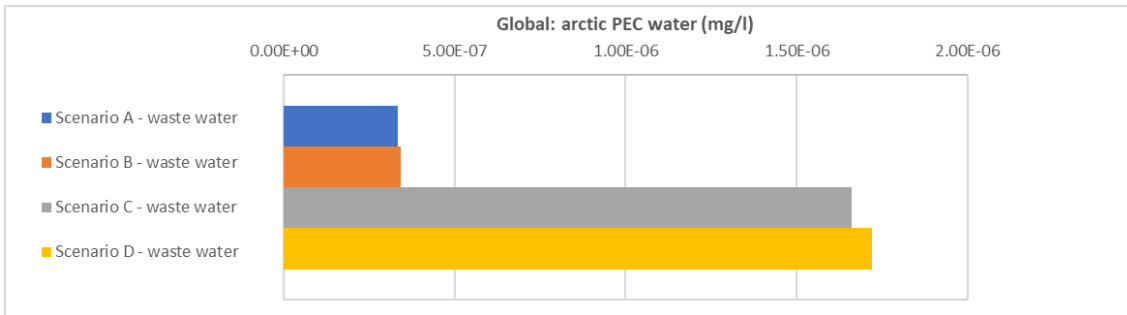
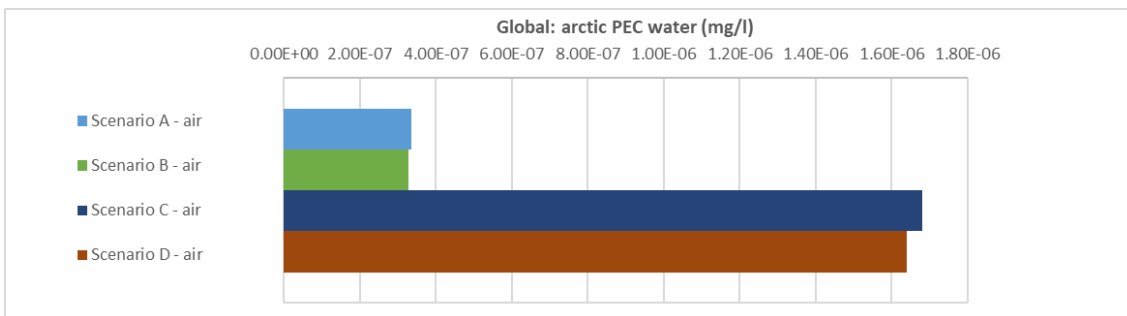


Figure A12 Global: moderate PECs for PFHxA (acid form)

a) Release to waste water



b) Release to air



c) Release to soil

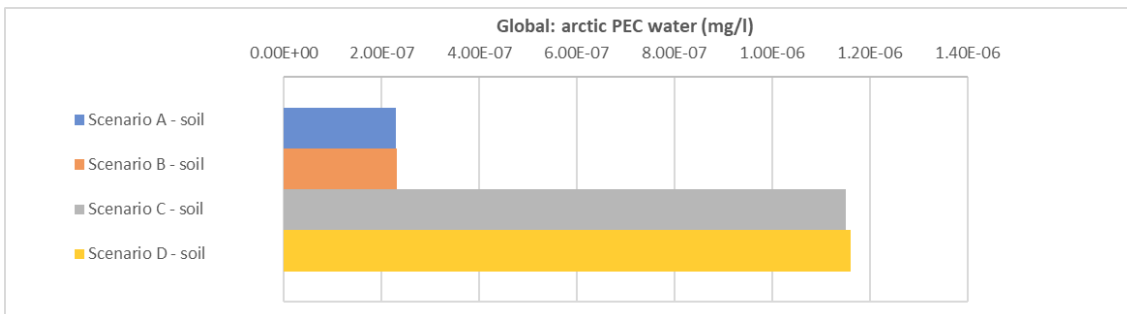
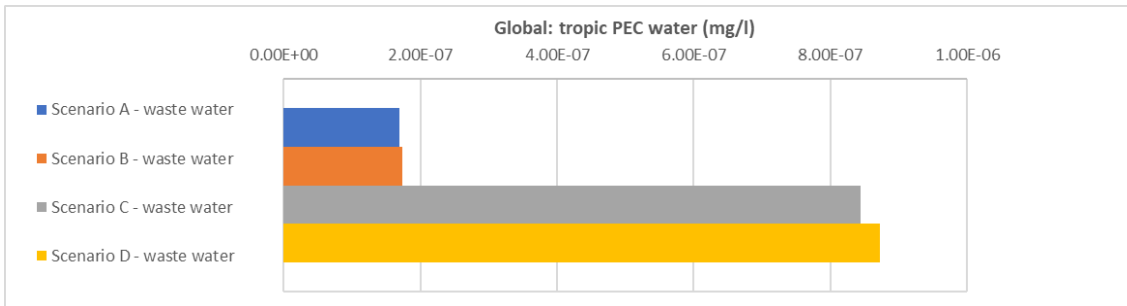
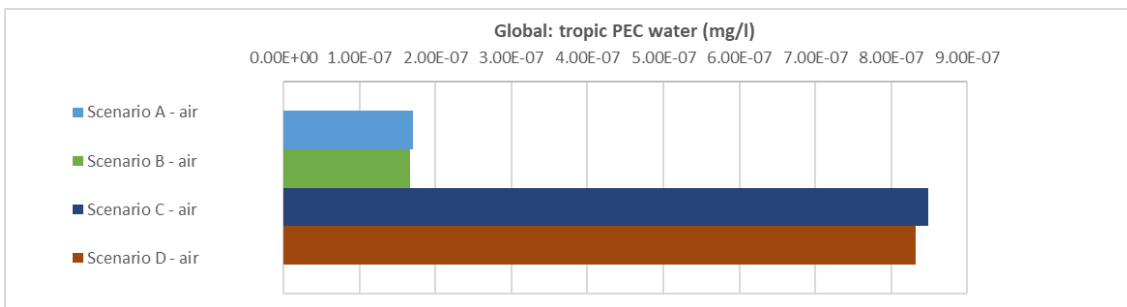


Figure A13 Global: arctic PECs for PFHxA (acid form)

a) *Release to waste water*



b) *Release to air*



c) *Release to soil*

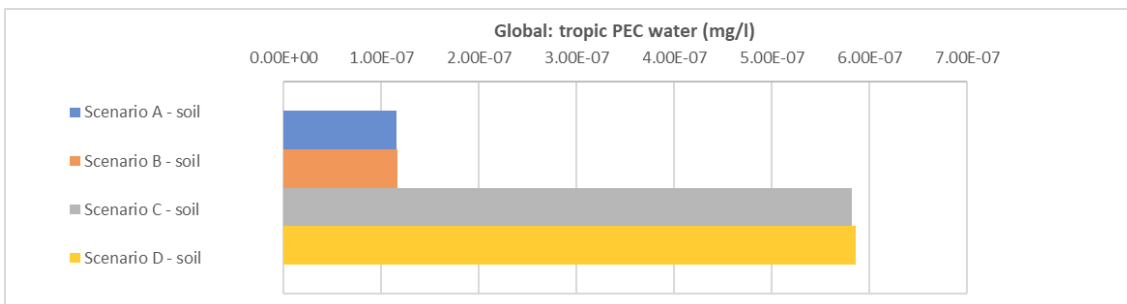


Figure A14 Global: tropic PECs for PFHxA (acid form)

Appendix B Screen shots showing regional, continental and global steady-state masses in EUSES

The following screen shots show examples of the regional, continental and global steady-state masses that are calculated in EUSES. The screen shots correspond to the example calculations for GenX based on a hypothetical release rate of 1 kg/day via surface water into the Regional model (see Table 2.2 in Section 2.2 of the main report).

Screen shot 1: Regional release rate = 1 kg/day via surface water

Category	Medium	Value	Unit	Unit Type
Total regional emission	to air	0	[kg.d-1]	o
	to wastewater	0	[kg.d-1]	o
	to surface water	1	[kg.d-1]	s
	to industrial soil	0	[kg.d-1]	o
	to agricultural soil	0	[kg.d-1]	o
Total continental emission	to air	0	[kg.d-1]	o
	to wastewater	0	[kg.d-1]	o
	to surface water	0	[kg.d-1]	o
	to industrial soil	0	[kg.d-1]	o
	to agricultural soil	0	[kg.d-1]	o

Navigation buttons: **Prev**, **Next**, **Finish**, **Undo**, **Abort**, **Help**

Screen shot 2: Regional, continental and global steady-state masses tab

Regional, continental and global distribution

PECs | Steady-state fractions | **Steady-state masses**

Regional | Continental | Global: moderate | Global: arctic | Global: tropic

Regional PEC in surface water (total)	1.19E-05	[mg.l-1]	<input type="radio"/>
Regional PEC in seawater (total)	1.16E-06	[mg.l-1]	<input type="radio"/>
Regional PEC in surface water (dissolved)	1.19E-05	[mg.l-1]	<input type="radio"/>
Qualitative assessment might be needed (TGD Part II, 5.6)		No	<input type="radio"/>
Regional PEC in seawater (dissolved)	1.16E-06	[mg.l-1]	<input type="radio"/>
Qualitative assessment might be needed (TGD Part II, 5.6)		No	<input type="radio"/>
Regional PEC in air (total)	1.57E-16	[mg.m-3]	<input type="radio"/>
Regional PEC in agricultural soil (total)	6.08E-11	[mg.kgwwt-1]	<input type="radio"/>
Regional PEC in pore water of agricultural soils	1.85E-10	[mg.l-1]	<input type="radio"/>
Regional PEC in natural soil (total)	6.08E-11	[mg.kgwwt-1]	<input type="radio"/>
Regional PEC in industrial soil (total)	6.08E-11	[mg.kgwwt-1]	<input type="radio"/>
Regional PEC in sediment (total)	1.12E-05	[mg.kgwwt-1]	<input type="radio"/>
Regional PEC in seawater sediment (total)	1.11E-06	[mg.kgwwt-1]	<input type="radio"/>

Screen shot 3: Regional steady-state masses

Regional, continental and global distribution

PECs | Steady-state fractions | **Steady-state masses**

Regional | Continental | Global: moderate | Global: arctic | Global: tropic

Steady-state mass in regional freshwater	42.9	[kg]	<input type="radio"/>
Steady-state mass in regional seawater	4.65	[kg]	<input type="radio"/>
Steady-state mass in regional air	6.35E-09	[kg]	<input type="radio"/>
Steady-state mass in regional agricultural soil	4.97E-04	[kg]	<input type="radio"/>
Steady-state mass in regional natural soil	5.59E-05	[kg]	<input type="radio"/>
Steady-state mass in regional industrial soil	2.07E-05	[kg]	<input type="radio"/>
Steady-state mass in regional freshwater sediment	0.465	[kg]	<input type="radio"/>
Steady-state mass in regional seawater sediment	0.0153	[kg]	<input type="radio"/>

Sum of Regional masses = 48 kg

Prev | Next | Finish | Undo | Abort | Help

Screen shot 4: Continental steady-state masses

Regional, continental and global distribution

PECs | Steady-state fractions: Steady-state masses

Regional | **Continental** | Global: moderate | Global: arctic | Global: tropic

Steady-state mass in continental freshwater	2.28E-04	[kg]	<input type="radio"/>
Steady-state mass in continental seawater	2.12E+03	[kg]	<input type="radio"/>
Steady-state mass in continental air	4.56E-09	[kg]	<input type="radio"/>
Steady-state mass in continental agricultural soil	1.8E-04	[kg]	<input type="radio"/>
Steady-state mass in continental natural soil	2.03E-05	[kg]	<input type="radio"/>
Steady-state mass in continental industrial soil	7.52E-06	[kg]	<input type="radio"/>
Steady-state mass in continental freshwater sediment	2.47E-06	[kg]	<input type="radio"/>
Steady-state mass in continental seawater sediment	0.348	[kg]	<input type="radio"/>

Sum of Continental

◀ Prev | ▶ Next | ▶▶ Finish | ↶ Undo | ✖ Abort | ? Help

Screen shot 5: Global: moderate steady-state masses

Regional, continental and global distribution

PECs | Steady-state fractions: Steady-state masses

Regional | Continental | **Global: moderate** | Global: arctic | Global: tropic

Steady-state mass in moderate water	9.82E+04	[kg]	<input type="radio"/>
Steady-state mass in moderate air	4.23E-08	[kg]	<input type="radio"/>
Steady-state mass in moderate soil	6.96E-04	[kg]	<input type="radio"/>
Steady-state mass in moderate sediment	3.22	[kg]	<input type="radio"/>

Sum of Global: moderate masses

Screen shot 6: Global: arctic steady-state masses

Regional, continental and global distribution

PECs | Steady-state fractions: Steady-state masses

Regional | Continental | Global: moderate | **Global: arctic** | Global: tropic

Steady-state mass in arctic water	6.41E+04	[kg]	<input type="checkbox"/>
Steady-state mass in arctic air	5.66E-09	[kg]	<input type="checkbox"/>
Steady-state mass in arctic soil	2.69E-04	[kg]	<input type="checkbox"/>
Steady-state mass in arctic sediment	2.11	[kg]	<input type="checkbox"/>

Sum of Global:
arctic masses =

Screen shot 7: Global: tropic steady-state masses

Regional, continental and global distribution

PECs | Steady-state fractions: Steady-state masses

Regional | Continental | Global: moderate | Global: arctic | **Global: tropic**

Steady-state mass in tropic water	2.16E+05	[kg]	<input type="checkbox"/>
Steady-state mass in tropic air	1.98E-07	[kg]	<input type="checkbox"/>
Steady-state mass in tropic soil	9.86E-04	[kg]	<input type="checkbox"/>
Steady-state mass in tropic sediment	7.08	[kg]	<input type="checkbox"/>

Sum of Global:
tropic masses =

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