Why is High Persistence Alone a Major Cause of Concern?

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Abstract

Persistence is a common hazard criterion for chemicals enshrined in chemical regulation worldwide. In this paper, we argue that the higher the persistence of a chemical, the greater the emphasis that it should be given in chemicals assessment and decision making. We provide case studies for three classes of highly persistent chemicals (chlorofluorocarbons, polychlorinated biphenyls, and per- and polyfluoroalkyl substances) to exemplify problems unique to highly persistent chemicals, despite their otherwise diverse properties. We point out that many well-known historical chemical pollution problems were the result of the release of highly persistent chemicals. Using evaluative modelling calculations, we then demonstrate that if a chemical is highly persistent, its continuous release will lead to continuously increasing contamination irrespective of the chemical’s physical-chemical properties. We argue that these increasing concentrations will result in increasing probabilities of the occurrence of known and unknown effects and that, once adverse effects are identified, it will take decades, centuries or even longer to reverse contamination and therefore effects. Based on our findings we propose that high persistence should be established as a sufficient basis for regulation of a chemical, which we term the “P-sufficient approach”. We argue that regulation on high persistence alone is not over-precautionary given the historical problems that persistent chemicals (and now also polymers) have caused. Regulation of highly persistent chemicals, for example by restriction of emissions, would not only be precautionary, but would serve to prevent poorly reversible future impacts.
1 Introduction

The persistence of organic chemicals has been an important element of chemical hazard assessment for over 40 years\textsuperscript{1–4}. High persistence indicates the potential for long-lasting environmental and human exposure to a chemical that is difficult to control and reverse\textsuperscript{5–7}. The importance of persistence is reflected by the persistence (P) criterion in the PBT (persistence, bioaccumulation potential, toxicity) assessment schemes used under the Stockholm Convention on Persistent Organic Pollutants and in an increasing number of jurisdictions such as Australia, Canada, the EU, Japan, South Korea and the US, and by the “very persistent” (vP) criterion under the EU chemicals regulation, REACH. A review of the historical development of international persistence criteria is provided by Matthies and Beulke (2017)\textsuperscript{8}. Here we suggest that the higher the persistence of a chemical, the greater the emphasis that it should be given in chemicals assessment and decision-making. Specifically, the aim of this work is to provide a transparent and conclusive reasoning why, from a certain point on, the persistence of a chemical indicates such a high level of concern that other criteria are no longer necessary to be assessed in detail in the management of such a chemical.

The focus of this work is on the persistence of organic chemicals. Not covered are inorganic substances such as water and nitrogen (N\textsubscript{2}), salts, mineral substances such as concrete and sand, and metals such as anthropogenically mobilized mercury, cadmium and lead. Some challenges associated with polymers, which are poorly degradable by their very nature, are addressed in the Discussion section.

The particular importance of the persistence of chemicals was already pointed out by Stephenson (1977)\textsuperscript{1} more than 40 years ago:

“On the face of it there appears little reason to be concerned about a material which, even though present in the environment, it not causing any detectable damage. On the other hand, persistent materials, because of this property, will accumulate in the environment for as long as they are released. Since the environment is not effective at cleansing itself of these materials, they will remain for indefinite periods which were not recognized at the time of their original release. The problem could become entirely out of control and it would be extremely difficult if not impossible to do anything about it. Materials which are strongly persistent can accumulate to rather high levels in the environment and effects which would not otherwise be important could become so.”
Since then, this point has been reiterated by several authors every 5–10 years\textsuperscript{2,3,5,7,9–12}. Our final conclusion from all of these analyses is that there may be chemicals whose persistence is so high that it is sufficient alone as a basis for the regulation of these chemicals.

Here we first present conceptual arguments that highlight the meaning of the persistence of chemicals for the occurrence of exposure and, importantly, also risks. We then use results from a multi-compartment environmental fate model to further illustrate these arguments, and finally draw conclusions for the assessment and management of highly persistent chemicals and in particular discuss the “P-sufficient” approach that we introduce here.

**2 Why persistence matters and what it means: the P-sufficient approach**

Persistent chemicals are at the center of many of the most serious cases of environmental contamination in the last 50 years. Examples are polychlorinated biphenyls (PCBs)\textsuperscript{11,13}, chlorofluorocarbons (CFCs)\textsuperscript{14,15}, and per- and polyfluoroalkyl substances (PFASs)\textsuperscript{16}. These cases have been investigated in much detail; in Table 1 we provide an overview of the chemicals’ persistence, production history and the major issues that follow from their persistence. Importantly, the adverse effects caused by persistent chemicals are not limited to health effects in humans and wildlife, but also include physical and chemicals effects such as ozone depletion and global warming.

**Table 1:** Overview of the persistence, production history, and major issues associated with three well-known classes of persistent chemicals. CFCs = chlorofluorocarbons; PCBs = polychlorinated biphenyls; PFASs = per- and polyfluoroalkyl substances; PFAAs = perfluoroalkyl acids; PFOA = perfluorooctanoic acid.

<table>
<thead>
<tr>
<th></th>
<th>CFCs</th>
<th>PCBs</th>
<th>PFASs</th>
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<tbody>
<tr>
<td>persistence</td>
<td>many decades to a century or more in the stratosphere\textsuperscript{17}</td>
<td>years to decades\textsuperscript{18} in terrestrial and aquatic environments</td>
<td>all PFASs are, or ultimately transform into stable substances, often PFAAs. PFAAs degrade slowly in the air\textsuperscript{19} and negligibly in other media\textsuperscript{20–22}</td>
</tr>
<tr>
<td>production history</td>
<td>since the late 1930s\textsuperscript{23}</td>
<td>since 1929\textsuperscript{24}</td>
<td>since the late 1940s\textsuperscript{25}</td>
</tr>
<tr>
<td>First report(s) of presence</td>
<td>CFCs</td>
<td>PCBs</td>
<td>PFASs</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>------</td>
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<td>-------</td>
</tr>
<tr>
<td>mid-1960s early 1970s</td>
<td>late 1960s(^{29,30})</td>
<td>organofluorine fraction discovered in human blood in 1968(^{31}) and in 1976(^{32}) PFOA tentatively identified using NMR</td>
<td></td>
</tr>
<tr>
<td>Start of large-scale investigation</td>
<td>1970s following the discovery of their depletion of stratospheric ozone(^{33})</td>
<td>1970s following the first reports of their presence</td>
<td>2000s after discovery of widespread presence of PFAAs in wildlife(^{14}) and human blood(^{15}).</td>
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</table>

**Major issues associated with the persistence of the chemicals**

<p>| Long-range transport / previously unexpected exposure | the atmospheric lifetime of CFCs is long enough to reach, and be persistent in, the stratosphere(^{28}). | PCBs are globally transported(^{46}) and present everywhere in the global environment, even in regions far away from sources (e.g., Antarctica(^{35}), deep oceans(^{38}) and Arctic biota(^{39})). | PFASs are globally distributed (e.g. in oceans(^{40}) and soils(^{41}), wildlife(^{42}) and human blood(^{43}) including at poles (e.g. Antarctic(^{44})). Short-chain PFAAs are very mobile and can easily pass through drinking water treatment facilities(^{45}). |
| Delayed identification of unexpected effects | More than 40 years after their large-scale production began, CFCs were shown to be depleters of stratospheric ozone(^{33}) and later also found to be potent greenhouse gases(^{46}). | In the late 1960s, it was shown that PCBs bioaccumulate in Baltic food webs(^{38}) and later reproductive effects on seals(^{47}) and white-tailed eagles(^{48}) were observed. In the 1980s, it emerged that PCBs could affect unborn children(^{49-51}). | Exposure to low doses of PFAAs at an early stage of life produces effects not captured by current regulatory testing guidelines (e.g., developmental and immuno-toxicity, endocrine disruption, etc.(^{52})). Consideration of immunotoxicity in health guidelines has reduced the assumed safe levels by orders of magnitude(^{53}). |
| Effectiveness of risk assessments | In 1973, J. Lovelock concluded “that the presence of these compounds constitutes no conceivable hazard”.(^{28}) Stratospheric ozone depletion was an unknown effect at that time. | Risk assessments have been continually refined (health guideline values revised downwards) from the 1920s to the present day as new information on effects emerged(^{4}). | Risk assessments do not reflect the long-term and irreversible exposure to PFASs(^{7,16}). Many PFASs are not considered in risk assessment, and mixture toxicity and non-standard toxicity tests are often neglected. One can therefore expect continual refinement of risk assessments(^{16}). |</p>
<table>
<thead>
<tr>
<th>Effectiveness of Regulatory Actions</th>
<th>CFCs</th>
<th>PCBs</th>
<th>PFASs</th>
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<tr>
<td>International agreement was reached under the Montreal Protocol, which entered into force in 1987. The Montreal Protocol only called for a reduction in emissions of certain damaging CFCs, with later amendments agreeing to their phase-out by 2000. Despite this phase-out, it takes decades for the ozone layer to recover.</td>
<td>Regulatory action began in the late 1970s in some western countries when there was a high level of proof of effects associated with PCBs, but manufacture and use continued elsewhere. Despite their eventual global phase-out, PCBs are still present in many applications and will continue to be major contaminants for decades to come. Levels in soils, sediments and biota decline especially slowly.</td>
<td>Regulatory action can eliminate point source emissions. However, it has no influence on what has already been emitted. Environmental redistribution of PFASs will continue for decades, and background levels will keep increasing. For example, PFOS levels in humans started to decrease after actions by 3M in 2000-2002, but there are no clear trends for environmental and wildlife levels yet.</td>
<td></td>
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<tr>
<th>Technical Implications for Remediation</th>
<th>CFCs</th>
<th>PCBs</th>
<th>PFASs</th>
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<tr>
<td>Stopping emissions was the only way to reduce levels in the troposphere and thus stratosphere, and this was achieved through international treaties.</td>
<td>PCBs can be found in contaminated soils and sediments. The most frequent remediation solutions adopted have been “dig and dump” and “dig and incinerate”, but there are currently new methods emerging.</td>
<td>It is energy-intensive to break the C-F bond to mineralize PFASs. The most effective method for large-scale treatment is through incineration at high temperatures and new advanced mineralization methods are being developed. Short-chain PFASs are too mobile to be concentrated, causing additional challenges in remediation.</td>
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<tr>
<th>Financial Implications for Remediation</th>
<th>CFCs</th>
<th>PCBs</th>
<th>PFASs</th>
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<tr>
<td>CFC replacements were quickly identified (but often have high global warming potential), but some economies were less able to cover the costs of switching to these alternatives. Average destruction costs are estimated to range from $4 to over $6 per kg (for concentrated refrigerant or blowing agent).</td>
<td>The costs of legacy PCB contamination in the European Union have been estimated to be as high as 75.3 billion Euros between 1971 and 2018.</td>
<td>High energy demand means it is very costly to safely dispose of contaminated products and remediate contaminated sites even if technically feasible. Costs of remediation are currently uncertain. The U.S. Air Force estimates that it will cost them $2 billion to clean up PFAS-contaminated water.</td>
<td></td>
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</table>
The cases in Table 1 and others (e.g. PCDD/Fs,\textsuperscript{63–65} brominated flame retardants,\textsuperscript{66–68} organochlorine pesticides,\textsuperscript{69} show that, \textit{empirically}, the particular concerns caused by highly persistent chemicals have been documented in much detail. \textit{Conceptually}, the essence of why high persistence is of outstanding importance in chemicals assessment is perhaps less obvious and it is therefore worth clarifying here. The concern about a chemical in the environment is, of course, related to unwanted effects (of any kind, e.g. toxic effects on wildlife or humans, global warming, ozone depletion, see Table 1) that the chemical may cause. However, as has been learned from many cases in chemical risk assessment (e.g. immunotoxicity of PFASs, endocrine disrupting effects, effects of neonicotinoid pesticides,\textsuperscript{70} adverse effects are difficult to predict and the scientific knowledge about effects will always remain uncertain and, importantly, \textit{incomplete}. This is because the number of possible effects is infinite and it is epistemologically impossible to identify them all. This means that unexpected effects may always occur.

If unexpected effects are caused by a short-lived chemical, it is possible to rapidly cease environmental contamination by restricting or banning its use, which then also means that no additional effects will be caused by that chemical. This is exactly why short-lived chemicals that are released to the environment at high rates should not be called “pseudo-persistent” or “semi-persistent”. In such a case, high levels in the environment are observed, but they are solely caused by continuous and high emissions, not by any type of persistence of the chemical.

In contrast, in the case of highly persistent chemicals, it is not possible to cease environmental contamination within a reasonable time frame by simply restricting or banning their use. Environmental contamination by highly persistent chemicals –and the effects related to this contamination– will continue for years to decades. This poor reversibility of contamination is because highly persistent chemicals are, by definition, difficult to degrade. This directly implies that highly persistent chemicals will require high inputs of energy to remove them from the environment, either through direct application of energy for the destruction of their stable chemical bonds (e.g. incineration) or through methods to remove them from the environment that require substantial energy inputs to drive their separation from contaminated media (e.g. pump and treat: pumping water out of groundwater aquifers and subsequent treatment with various technologies). Examples of the high costs associated with remediation of highly persistent chemicals are provided in Table 1,
above. Importantly, removal or remediation is only feasible for a selection of contamination hotspots, but not for the majority of the environment such as the world’s oceans.

It is **logically incorrect** to say that persistence merely indicates the presence of a chemical in the environment. Persistence indicates an impactful causal relationship that extends into the future: persistent chemicals that are present now will also be present to a certain extent after a considerable number of years (e.g., 25% after 10 years if the degradation half-life is 5 years), and this fact is known already now with 100% certainty. They will undergo (long-range) transport in the environment, and therefore an increasing number of organisms in many ecosystems as well as humans will be exposed, including ones for which this was unexpected such as the Mariana Trench in the case of PCBs. This includes not only chemicals that are volatile and soluble in water, but also low-volatility chemicals with very high octanol-water partition coefficient \(K_{OW}\) and octanol-air partition coefficient \(K_{OA}\), such as deca-BDE and heavy PCBs.

Furthermore, persistence indicates that certain thresholds for causing (often unexpected) effects will be exceeded, and this can also be predicted with 100% certainty. If a substance is persistent, and if emissions continue at a constant rate or increase, the substance will attain higher and higher concentrations in the environment. In this case, the risk quotient (i.e. PEC/PNEC ratio) also increases continuously up to the point that the concentration exceeds the no-effect threshold (see examples given in Section 3, below). In addition, persistence also indicates that a long-lasting cause-effect chain is set into motion by today’s uses and emissions of a persistent chemical. Even if persistent chemicals are present at low concentrations and do not (yet) exceed effect thresholds, they will still be present when, in the future, other chemicals will be emitted so that there will be co-exposure that may cause mixture effects.

In summary, the main concerns with highly persistent chemicals are:

1. The continuous release of highly persistent chemicals will lead to widespread, long-lasting, and increasing contamination.
2. Increasing concentrations will result in increasing probabilities that known and unknown effects occur, individually and/or in a mixture with other substances.
3. Once adverse effects are identified, it will be technically challenging, energy-intensive, and thus costly, to reverse the chemical contamination and therefore the effects. These measures are limited to contamination hotspots, whereas, for most of the environment, no remediation or clean-up will be possible.

In other words, it is not an unsubstantiated concern about the mere presence of a chemical, but it is the much higher likelihood for particularly serious (widespread, long-lasting) adverse effects associated with highly persistent chemicals – effects that have become manifest many times as the historical examples show – that would confer particular importance to persistence as a hazard indicator for triggering management actions. In conclusion, concerns about a chemical are always related to effects, but for highly persistent chemicals, it should not be required that these effects are represented explicitly in the hazard assessment scheme. The hazard assessment of these chemicals should be based solely on their high persistence as a placeholder or proxy for effects.

3 Mass-balance modeling

Here we illustrate the implications of high persistence using a simple multimedia environmental fate model for four example chemicals. The model is a so-called unit-world model with three compartments, one for the global troposphere (height 6000 m, volume $3.06 \cdot 10^{18} \text{ m}^3$), one for the global surface ocean water (depth 100 m, volume $3.62 \cdot 10^{16} \text{ m}^3$), and one for the global surface soil (depth 0.1 m, volume $1.48 \cdot 10^{13} \text{ m}^3$). In each compartment, a first-order degradation process takes place, and in addition, there are three non-degradative losses, diffusion to the stratosphere, settling to deep ocean water, and burial in deep soil.

In total, we modeled four hypothetical chemicals, which differ in their degradation half-lives and $K_{OW}$ values, see Table 2. Here we use the $K_{OW}$ to describe the partitioning of the example chemicals. Although PFAAs are dissociated, i.e. present as anions, at environmental pH, they partition to organic matter similar to hydrophobic organic substances with $\log K_{OW} \sim 2^{73}$. For the ease of calculation, we do not include this aspect in the model calculation because the model results for persistence and concentration-time trends obtained with our example chemicals are qualitatively the same for PFASs. The same degradation half-lives of 2 d (chemicals A and C) and 2000 d (chemicals B and D) were assumed for all three compartments.
A half-life of 2000 d or 5.5 years is long, but not excessively high. Many PFASs have much longer half-lives, namely on the order of decades or centuries.

Table 2: Chemical property data of the four example chemicals.

<table>
<thead>
<tr>
<th>Property</th>
<th>chemical A</th>
<th>chemical B</th>
<th>chemical C</th>
<th>chemical D</th>
</tr>
</thead>
<tbody>
<tr>
<td>log $K_{AW}$</td>
<td>$-1$</td>
<td>$-1$</td>
<td>$-1$</td>
<td>$-1$</td>
</tr>
<tr>
<td>log $K_{OW}$</td>
<td>$2$</td>
<td>$2$</td>
<td>$8$</td>
<td>$8$</td>
</tr>
<tr>
<td>$t_{1/2}$ (d)</td>
<td>$2$</td>
<td>$2000$</td>
<td>$2$</td>
<td>$2000$</td>
</tr>
</tbody>
</table>

For each chemical, we assumed the same constant emission rate to air (100 mol/h) and calculated the concentrations in air, water and soil at steady-state and in a dynamic scenario where the initial concentrations in all media were equal to zero. The absolute value of the emission rate is not relevant here because we compare results of the chemicals relative to one another. The results would be the same with any emission rate.

The main model results are summarized in Table 3; several features of the concentration-time curves of the different chemicals are illustrated in Figure 1.

Table 3: Main model results. Regular font: results from steady-state model. Bold: results from dynamic model.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>chemical A</th>
<th>chemical B</th>
<th>chemical C</th>
<th>chemical D</th>
</tr>
</thead>
<tbody>
<tr>
<td>total inventory (mol)</td>
<td>$6.92 \cdot 10^3$</td>
<td>$4.14 \cdot 10^6$</td>
<td>$6.94 \cdot 10^3$</td>
<td>$3.69 \cdot 10^6$</td>
</tr>
<tr>
<td>$c_A$ (mol/m$^3$)</td>
<td>$2.26 \cdot 10^{-15}$</td>
<td>$1.22 \cdot 10^{-12}$</td>
<td>$2.25 \cdot 10^{-15}$</td>
<td>$3.06 \cdot 10^{-13}$</td>
</tr>
<tr>
<td>$c_W$ (mol/m$^3$)</td>
<td>$4.56 \cdot 10^{-16}$</td>
<td>$1.16 \cdot 10^{-11}$</td>
<td>$5.70 \cdot 10^{-16}$</td>
<td>$2.80 \cdot 10^{-12}$</td>
</tr>
<tr>
<td>$c_S$ (mol/m$^3$)</td>
<td>$1.86 \cdot 10^{-14}$</td>
<td>$1.43 \cdot 10^{-11}$</td>
<td>$1.50 \cdot 10^{-12}$</td>
<td>$1.79 \cdot 10^{-7}$</td>
</tr>
<tr>
<td>fraction in air</td>
<td>$1.0$</td>
<td>$0.9$</td>
<td>$0.99$</td>
<td>$0.25$</td>
</tr>
<tr>
<td>fraction in water</td>
<td>$0$</td>
<td>$0.1$</td>
<td>$0.00$</td>
<td>$0.03$</td>
</tr>
<tr>
<td>fraction in soil</td>
<td>$0$</td>
<td>$0$</td>
<td>$0.01$</td>
<td>$0.72$</td>
</tr>
<tr>
<td>overall persistence (d)</td>
<td>$2.88$</td>
<td>$2.89 \cdot 10^3$</td>
<td>$2.88$</td>
<td>$2.89 \cdot 10^3$</td>
</tr>
<tr>
<td>sum degradation</td>
<td>$99.9$</td>
<td>$59.8$</td>
<td>$99.9$</td>
<td>$53.2$</td>
</tr>
<tr>
<td>losses (mol/h)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sum non-degradation losses (mol/h)</td>
<td>$0.1$</td>
<td>$40.2$</td>
<td>$0.1$</td>
<td>$46.8$</td>
</tr>
<tr>
<td>time to steady-state (d)</td>
<td>$22$ d</td>
<td>$40$ yr</td>
<td>$29$ d</td>
<td>$45$ yr</td>
</tr>
</tbody>
</table>
Figure 1: Concentrations of different model chemicals as a function of time. (i) chemical A with a half-life of 2 days and a log $K_{OW}$ of 2 is present in all three media in appreciable amounts and reaches its steady-state after approximately 0.06 yr. (ii) chemical C with a half-life of 2 days, but a log $K_{OW}$ of 8, reaches its steady-state also after less than 0.1 yr, but is mostly present in the soil. (iii) chemical D with a half-life of 2000 days and a log $K_{OW}$ of 8 reaches its steady-state after approximately 40 years and is mostly present in the soil. (iv) comparison of the concentrations in soil of chemicals C (short half-life) and D (long half-life). After 10 years, the concentration of chemical D is 84,000 times greater than that of chemical C and is still building up, see panel (iii); their release rates are the same.

Important observations are as follows:

An increase in the degradation half-life by a factor of 1000 (from 2 d to 2000 d, chemicals A vs. B and C vs. D) leads to an increase in the time to steady-state by a factor of 570-660 times (from 22-29 d to 40-45 yr). This increase is lower than a factor of 1000 because of the advective losses. These do not scale with the degradation half-lives and, therefore, they become increasingly important if the degradation half-life is longer, see Table 3, degradation losses vs. non-degradation.
losses. Similarly, the increase in the total inventory of chemical in the model system is only around a factor of 550 to 600 because of the increasing effect of the non-degradation losses. Next, the steady-state concentrations in air, water and soil of the highly persistent chemicals (half-life 2000 d) are higher by factors of 136 to $1.19 \cdot 10^5$, compared to the short-lived chemicals. Here it is the influence of the non-degradation losses in combination with different partitioning because of different $K_{OW}$ values that explains why they differ from 1000. Chemical D, for example, is rapidly deposited from the air to soil and water with settling particles and accumulates in the soil, which is caused by its high $K_{OW}$ in combination with the high half-life. Accordingly, the concentration in air of chemical D increases only by a factor of 136 compared to chemical C, but its concentration in soil increases by a factor of $1.19 \cdot 10^5$, which is much more than the increase in the half-lives.

In conclusion, for continuously emitted highly persistent chemicals one can expect the PEC to increase for many years (here: time to steady-state > 40 years) and over this time the PEC/PNEC ratio may well exceed the value of 1 (strong increase in concentrations in water of soil for chemical D, even more than by 1000). Note that these effects are much more pronounced for substances with considerably longer half-lives than the 2000 d assumed here.

An increase in log $K_{OW}$ by 6 log units leads to only a 13–32% increase in the time to steady-state. Although there is a shift of the chemical from air to soil as log $K_{OW}$ increases, this does not largely affect the time to steady state because in the examples presented here all environmental media have the same degradation half-life. For degradable chemicals the half-life often varies markedly between environmental media, but in the case of highly persistent chemicals such as PFASs the half-lives are long in all media. Therefore, in the case of highly persistent chemicals, the partitioning properties (e.g. $K_{OW}$) are not important for controlling the overall persistence of a chemical in the environment.

PFAAs are a class of chemicals that have extremely long degradation half-lives in all media and it is therefore interesting to compare their environmental behaviour with our modelling results. A steady-state condition was never reached for PFAAs because production continually increased between 1950 and 2000 until action to reduce emissions was taken. Even if emissions had levelled off at their production peak in the late 1990s, our modeling results imply that environmental levels would have continued to increase for many decades afterwards. Since action to reduce
emissions of PFAAs commenced, starting in 2000–2002, there has been no evidence of consistent declines of any PFAA in the environment or biota.\textsuperscript{59} Perfluoroalkyl carboxylic acids with nine or more carbons continue to increase in human blood even after measures to reduce their emissions were introduced.\textsuperscript{59}

\section*{4 Discussion and recommendations}

\textbf{Model-derived findings.} The model results presented above illustrate the important general implications of high persistence: the higher the persistence of a chemical, the longer the time-to-steady state, and the higher the steady-state concentrations. Another important finding from the model results is that the $K_{\text{OW}}$ does not modify these general implications of high persistence. The $K_{\text{OW}}$ does modify the specific properties and environmental distribution/partitioning of a chemical, but if the degradation half-lives are similar in all media, this does not affect the persistence-related findings above. A high $K_{\text{OW}}$ is normally related to a high bioaccumulation factor,\textsuperscript{74} and a high bioaccumulation factor is an additional source of concern, but the fundamental concerns related to high persistence are independent of any bioaccumulation ("B") properties of a chemical. B is not a useful criterion for protecting against poorly reversible effects because the residence time of highly persistence chemicals in the environment is often much greater than their residence time in humans and biota, which means that levels in organisms will be poorly reversible regardless of the magnitude of B.\textsuperscript{7} The irrelevance of environmental partitioning with regard to regulation of highly persistent chemicals is reflected on the regulatory side by two regulatory schemes that both focus on persistent chemicals, in one case with high $K_{\text{OW}}$ (Stockholm Convention on POPs, $K_{\text{OW}}$ cutoff of log $K_{\text{OW}} > 5$)\textsuperscript{75}, and in one case with low $K_{\text{OW}}$ (the proposed PMT scheme, $K_{\text{OW}}$ cutoff of log $K_{\text{OW}} < 4$)\textsuperscript{76}.

\textbf{Policy implications of the findings.} Based on the findings presented above, our general proposal is that, in addition to existing chemical assessment schemes, \textit{high persistence should be established as a sufficient basis for regulation of a chemical}. We call this the “P-sufficient” approach. Current chemical assessment schemes place special emphasis on persistent chemicals only if other hazardous properties, such as bioaccumulation potential and toxicity, are also present and, moreover, persistence is largely ignored in risk assessment. For example, under REACH the identification of a
substance as PBT or vPvB automatically requires the registrant to carry out an estimate of emissions, to identify and implement measures to minimize emissions, to indicate in the safety data sheet (SDS) that the substance is PBT/vPvB, and to communicate measures for minimizing emissions to downstream users via the SDS. However, if a chemical is identified as P or vP, but neither PBT nor vPvB, there is no requirement to estimate and mitigate emissions nor any requirement to consider future continuing emissions in the risk assessment. This is a gap in the current European chemical assessment and management schemes given that, as stated above, the risk quotient will continue to increase for a long time for P and vP chemicals if emissions continue. As far as we know, the same deficiencies exist in all international chemical regulation schemes because high persistence in itself is not used as a trigger for regulation in any jurisdiction.

The P-sufficient approach means that high persistence is sufficient for a chemical to be flagged for subsequent management actions. For example, under REACH, the vP criteria could be used for this purpose. If a chemical exceeds the vP criteria, the P-sufficient approach would imply that this is sufficient to require estimation (and minimization) of emissions as occurs currently for PBT and vPvB chemicals. Furthermore, the implication of vP properties could be that the chemical is listed as a Substance of Very High Concern (SVHC) without any consideration of its other properties (i.e. B and T in the case of PBT, or vB in the case of vPvB).

**Empirical basis for the proposed “P sufficient” approach.** Technically, the P-sufficient approach could be based on the same type of evidence that is currently used for, e.g., the vP assessment under REACH. The substances currently classified as vPvB substances in the EU include, a.o., dechlorane plus, short-chain chlorinated paraffins, UV absorbers, long-chain perfluorocarboxylic acids, PFHxS, musk xylene, and the cyclic volatile methylsiloxanes D4, D5, and D6. A review of the data in the SVHC dossiers of these substances shows that a range of different data have been used for the determination of vP properties. In several cases, simulation tests and field dissipation studies were available (UV absorbers, anthracene oils, short-chain chlorinated paraffins, some of the long-chain perfluorocarboxylic acids). These were often complemented by negative results from tests for ready or inherent biodegradability. In other cases (PFHxS, long-chain PFCAs, D6), read-across from similar chemicals with results from simulation tests for degradation was applied. In
one case (deca-BDE), the formation of highly persistent transformation products was
used as a reason why the substance was classified as vP. In the same way as for the
current vPvB determinations, all these types of data can be used under the P-sufficient
approach. If read-across is not possible, simulation tests or field dissipation studies
may have to be performed, but this can be done under existing test guidelines. The
formation of highly persistent transformation products will also be an important type
of evidence, in particular for many PFASs that have reactive endgroups and will form
– highly persistent – PFAAs in the environment.

The P-sufficient approach and the precautionary principle. As pointed out in
section 2, the concern underlying any chemical hazard assessment is about adverse
effects. In the context of persistence assessments, this is often expressed in such a way
that P seemingly only matters in addition to B and T. This is enshrined in the current
PBT assessment schemes, see above, part 2 of this discussion section, but was already
clearly reflected, for example, in the following quote from an internal 3M document
from the 1980s:77,

“Perhaps the most important conclusion from previous studies is the stability of
fluorochemicals. Although stability is one of the most desirable properties
fluorochemicals possess for many applications, from an environmental
perspective, "stability" connotes "persistence” which can be the cause of
concern especially when coupled with other properties. For example, some
fluorochemicals have a tendency to accumulate in biological tissues. Moreover,
some fluorochemicals have biological activity. This is most seriously
demonstrated by the use of some fluorochemicals as pesticides. This is not to
say that all fluorochemicals accumulate or that all have biological activity. But
taken together, stability, the tendency to bioaccumulate, and biological activity
are a potentially troublesome combination.”

In contrast to this approach, the key point of the P-sufficient approach is that this
evidence of some type of effect should not be required to be demonstrated explicitly
(see the reasoning provided in section 2): because the possible effects cannot be
predicted with sufficient reliability and remain incompletely known or entirely
unknown, P alone should be used as a sufficient indicator that serves as a proxy for
adverse effects. Often, using a proxy of actual impacts as a basis for decision-making
is considered an application of the precautionary principle\textsuperscript{5,78,79}. The precautionary principle states that, “where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation”\textsuperscript{80}.

A problem with the implementation of the precautionary principle has been that the call for action based on limited evidence is often considered over-cautious. However, the empirical evidence that has accumulated over the last decades shows that it is not over-cautious if the use of persistent chemicals is restricted or regulated. When the known cases of highly persistent chemicals are considered, it shows that many of them have caused serious environmental impacts. Accordingly, there is a very high likelihood that additional highly persistent chemicals will also cause some kind of relevant environmental impact. Therefore, regulating highly persistent chemicals on the basis of their persistence alone may well be called an act of \textit{prevention}, not just of precaution. In other words, it is entirely rational and empirically well founded to take very high persistence seriously as a proxy of unwanted environmental impacts and to base preventive action on it.

There are also persistent chemicals that exert relatively low toxicity according to current knowledge, such as trifluoroacetic acid (TFA)\textsuperscript{81}. The point of the P-sufficient approach is exactly that also highly persistent chemicals for which the currently known toxicity is rather low should be flagged and considered for regulation. As outlined above, it is well possible that unwanted effects occur at a large scale if such a chemical enters the environment, is distributed widely, and leads to continuously increasing environmental and human exposure. The evidence available from the last 50 years shows that this is not just a hypothetical possibility, but a highly likely outcome.

Similarly, the P-sufficient approach is also suitable for synthetic polymers, which are (very) poorly degradable by their very nature. Many high molecular weight synthetic polymers have traditionally been treated as of low concern under chemical assessment and management schemes due to their low bioavailability. However, as elaborated above, once released, (unexpected) adverse effects by such highly persistent chemicals may not only be biological effects, but also be physical or chemical effects. In the case of high molecular weight synthetic polymers, an increasing number of wildlife mortality by entanglement or ingestion of marine plastic debris has been observed (e.g., Wilcox et al., 2015\textsuperscript{82}). In addition, they may
break down into many smaller pieces (i.e., microplastics), which is another issue of emerging concern\textsuperscript{83,84}. The P-sufficient approach is also in line with the recent call of classifying plastic waste as hazardous\textsuperscript{85} as well as it being flagged as a planetary boundary threat\textsuperscript{86}.

**Conflicts of Interest**

There are no conflicts of interest to declare.

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