



Cite this: *Environ. Sci.: Processes Impacts*, 2018, 20, 32

Can the Stockholm convention address the spectrum of chemicals currently under regulatory scrutiny? Advocating a more prominent role for modeling in POP screening assessment

Michael S. McLachlan 

Frameworks for chemical regulation are based on the science at the time they were written. Today some regulations are being applied to a much broader spectrum of chemicals than we had knowledge of when the regulations were written. This entails a risk that the regulations are being used outside of their chemical application domain. This question is explored using the POP screening assessment in the Stockholm convention, which was developed 20 years ago. Using perfluorinated alkyl acids (PFAAs) as an example, it is shown that the assessment can lead to false negative conclusions. A second case study using octamethylcyclotetrasiloxane (D4) illustrates that there is also a risk of false positives. The risk for false negative classification of PFAAs is due to the inclusion of a screening criterion – bioaccumulation – that is not a requirement for adverse effects of chemicals in remote regions. For D4 the risk of false positive classification stems from the four screening criteria (persistence, bioaccumulation, long-range transport, and adverse effects) applying to different environmental media/compartments. The major lesson is that applying the POP screening procedure to the broad spectrum of chemicals in modern commerce will require that we rely less on the individual screening criteria and more on the comparison of estimated exposure and the thresholds for effects stipulated in Annex D, paragraph 2 of the convention. Models have an important role to play in this context and should become more strongly integrated into the POP screening process.

Received 9th October 2017
Accepted 6th December 2017

DOI: 10.1039/c7em00473g

rsc.li/espi

Environmental significance

This paper illustrates some limitations of the Stockholm convention, one of the most important tools for regulation of chemicals at the global scale. It shows that the criteria to screen for new POPs can lead to false negative and false positive conclusions when applied to chemicals that lie outside of the chemical domain of the screening procedure. This problem is clearly attributed to breaking down the complex processes of chemical transport, fate and exposure into simple indicators, a strategy which cannot be successful across a wide spectrum of chemicals. Integrated transport, fate and exposure models are advocated as a solution.

Introduction

Frameworks for environmental regulation of chemicals are initiated in response to a societal concern and constructed based on the understanding of contaminant science at the time they are formulated. Some of the regulatory frameworks we are currently working with are more than 20 years old. They were developed based on our experience with a limited set of perhaps several hundred environmental contaminants. Today societal concerns have evolved and we are applying these frameworks to tens of thousands of chemicals with a much broader spectrum of uses, modes of emission, and physical

chemical properties. It is possible that some of these chemicals do not fit within these frameworks, which would imply a higher risk of false positive and false negative regulatory decisions. Borrowing on modeling terminology, we can say that a regulation has a chemical application domain arising from the initial societal concern and rooted in the state of the science at the time of its formulation. Are we adhering to these domains in our efforts to regulate more diverse chemicals? Can our regulatory frameworks for chemicals deal with the diversity of chemicals that we are managing today and intend to regulate tomorrow? The answer to this question has significant consequences for future research needs in contaminant science. In the following this question will be explored using the Stockholm convention on persistent organic pollutants.

Department of Environmental Science and Analytical Chemistry (ACES), Stockholm University, 106 91 Stockholm, Sweden. E-mail: michael.mclachlan@aces.su.se



the convention has no predictive power for environmental exposure in remote regions, since the medium where the chemical is persistent is a medium that only a small portion of the chemical ever reaches. A second reason for the large discrepancy between D4 and PCB 180 is the much higher volatility of D4.¹² The much lower tendency to partition from air to either water or organic carbon (Table 1) means that a much smaller portion of the D4 enters surface media. As a consequence, the criteria that have traditionally been used for characterizing the tendency of a POP to accumulate in remote environments, namely long-range atmospheric transport and persistence in any one surface medium, are not sufficient for D4.

In drafting the screening criteria for the convention, the Criteria Expert Group had the foresight to include stipulations that address this problem. In the text for long-range transport they required evidence for “potential for transfer to a receiving environment”. Models have an important role to play in evaluating this potential, and model-based indicators have been developed for this purpose. Xu and Wania employed two of these indicators in their work, transfer efficiency (calculated by the OECD P_{OV} and LRTP Screening Tool)¹⁶ and the Arctic contamination potential (calculated using the Globo-POP model).¹⁷ Both of these indicated that the transfer to receiving environments is much lower for D4 than for established POPs.¹²

Another interesting issue in assessing D4 is the link between environmental levels and bioaccumulation. Is bioaccumulation relevant if it occurs in a compartment where exposure is low? For classical POPs this question did not arise, as they accumulate in aquatic systems and the bioaccumulation criterion is defined for fish. For D4 in remote regions contaminated *via* long-range transport, concentrations will be highest in the air and much lower in surface media as discussed above. Chemical activities are also expected to be lower in the aquatic environment than in the air since air is the source of the chemical to water and D4 hydrolyses quite rapidly in water. Is bioaccumulation in water breathing organisms relevant for such a chemical? Interestingly, while D4 is bioaccumulative in fish, it does not bioaccumulate in mammals.¹¹ Should D4 therefore be classified as non-bioaccumulative because it does not bioaccumulate in the medium with high exposure? This question can and should be addressed by exposure modeling in which fate models and bioaccumulation models are coupled to produce exposure estimates in different organisms that can be compared. However, while such a comparison would tell us which medium is most relevant for exposure, it would not yield a bioaccumulation metric. Here we are reminded of the question that arose in the discussion of false negative classification: is bioaccumulation a relevant metric for classification of POPs? The D4 example also suggests that we should be looking at exposure directly rather than at a surrogate for exposure (such as BCF in fish).

D4 also adds a new facet to the adverse effects criterion. Adverse effects have only been reported for aquatic organisms, and the threshold above which they have been observed is about $5 \mu\text{g L}^{-1}$. The water solubility of D4 is $56 \mu\text{g L}^{-1}$,¹¹ so the threshold for effects is about 10% of the water solubility. Is it conceivably possible to achieve a concentration in water equal

to 10% of the water solubility in a remote region exposed by atmospheric long-range transport? Even if we saturated the atmosphere with D4 in source regions, would not so much be degraded during atmospheric transport and subsequently *via* hydrolysis in water that it would not be possible to attain a concentration of 10% of the solubility? If this is not possible, can D4 be a POP? This question did not arise for classical POPs as their toxicity thresholds were not close to saturation and their environmental degradation was low compared to D4. To address this question, multimedia fate models are the obvious tool of choice.

For classical POPs the screening criteria are effective at eliciting the potential for adverse effects in remote regions, but this is not the case for D4. The persistence criterion does not predict exposure levels, the long-range transport criterion requires an assessment of deposition to surface media, the bioaccumulation criterion is disconnected from the environmental medium with high exposure and thus does not predict organism exposure, and the exposure threshold for effects, although a low concentration, may not be physically achievable in remote environments. To do a meaningful screening assessment of D4, it is necessary to prepare an estimate of the exposure of susceptible organisms in remote regions and compare this with best estimates of effects. This is possible within the framework of the convention, as Annex D stipulates that the screening evaluation should include a comparison between the measured or estimated exposure and toxicity or ecotoxicity data. Models that link long-range transport, fate in remote regions, and exposure to wildlife and humans would be very helpful for conducting such an evaluation.

As discussed above, reversibility of exposure is an important component of the screening assessment of chemicals, as it is a prerequisite for being able to manage the chemical should adverse effects be identified in the future. Although not specified as a goal in the Stockholm convention, it is implicit in the definition of persistence as a screening criterion. Is the persistence criterion a good indicator of the reversibility of exposure for D4? Xu and Wania simulated the global fate of D4 for a scenario in which emissions were stopped after having been constant for 40 years. The amount of D4 in the global environment decreased by 2.5 orders of magnitude in 6 months.¹² This is consistent with other modeling work showing that hypothetical chemicals with environmental degradation half-lives equal to the REACH thresholds for persistence and partitioning properties similar to D4 will be 95% removed from the environment within 1–2.5 years.¹⁸ Xu and Wania found a slower half-life of 1 year for elimination from sediment, whereby the levels in sediment were largely the result of local emissions to water in their model scenario.¹² As discussed above, D4 accumulation in sediment in remote regions is expected to be lower due to degradation during long-range atmospheric transport and in water before deposition to sediment. Here we again have a potential issue of misalignment of environmental media; the medium where the chemical is persistent may not be the medium where exposure is potentially problematic. This issue was not encountered with classical POPs; it too can be addressed using models.



- 7 Risk profile on PFOS from the POPs Review Committee, <http://chm.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/3309/ctl/Download/mid/10910/Default.aspx?id=65&ObjID=4891>, accessed October 2017.
- 8 Risk profile on PFOA from the POPs Review Committee, <http://chm.pops.int/TheConvention/POPsReviewCommittee/ReportsandDecisions/tabid/3309/ctl/Download/mid/16086/Default.aspx?id=29&ObjID=22593>, accessed October 2017.
- 9 I. T. Cousins, R. Vestergren, Z. Wang, M. Scheringer and M. S. McLachlan, *Environ. Int.*, 2016, **94**, 331–340.
- 10 Guidance for the precautionary protection of raw water destined for drinking water extraction from contaminants regulated under REACH, report of the German Federal Environmental Agency, http://www.fachoeekotoxikologie.de/fileadmin/fachoeekotoxikologie/abgeschlossene_Arbeiten/2016/2_FKZ_371265416_UBA_REPORT-PMT_final-FoBiG.pdf, accessed in October 2017.
- 11 Environmental Risk Assessment Report: Octamethylcyclotetrasiloxane from the UK Environment Agency, https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/290565/scho0309bpqz-e-e.pdf, accessed October 2017.
- 12 S. Xu and F. Wania, *Chemosphere*, 2013, **93**, 835–843.
- 13 Official extract of PBT information for D4 from ECHA, <https://echa.europa.eu/documents/10162/22278e0f-c555-4a9e-a24a-a1529779e2f7>, accessed October 2017.
- 14 I. S. Krogseth, A. Kierkegaard, M. S. McLachlan, K. Breivik, K. M. Hansen and M. Schlabach, *Environ. Sci. Technol.*, 2013, **47**, 502–509.
- 15 M. S. McLachlan, A. Kierkegaard, K. M. Hansen, R. van Egmond, J. H. Christensen and C. A. Skjøth, *Environ. Sci. Technol.*, 2010, **44**, 5365–5370.
- 16 F. Wegmann, L. Cavin, M. MacLeod, M. Scheringer and K. Hungerbühler, *Environ. Model. Software*, 2009, **24**, 228–237.
- 17 F. Wania, *Environ. Sci. Technol.*, 2003, **37**, 1344–1351.
- 18 T. Gouin, *Environ. Sci. Policy*, 2010, **13**, 175–184.

