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Added value of the emissions fractions approach when assessing a chemical's potential for adverse effects as a result of long-range transport†

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It is of considerable interest to identify chemicals which may represent a hazard and risk to environmental and human health in remote areas. The OECD P_{OV} and LRTP Screening Tool ("The Tool") for assessing chemicals for persistence (P) and long-range transport potential (LRTP) has been extensively used for combined P and LRTP assessments in various regulatory contexts, including the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs). The approach in The Tool plots either the Characteristic Travel Distance (CTD, in km), a transport-oriented metric, or the Transfer Efficiency (TE, in %), which calculates the transfer from the atmosphere to surface compartments in a remote region, against overall persistence (P_{OV}). For a chemical to elicit adverse effects in remote areas, it not only needs to be transported and transferred to remote environmental surface media, it also needs to accumulate in these media. The current version of The Tool does not have a metric to quantify this process. We screened a list of >12 000 high production volume chemicals (HPVs) for the potential to be dispersed, transferred, and accumulate in surface media in remote regions using the three corresponding LRTP metrics of the emission fractions approach (EFA; ϕ_1, ϕ_2, ϕ_3), as implemented in a modified version of The Tool. Comparing the outcome of an assessment based on CTD/TE and P_{OV} with the EFA, we find that the latter classifies a larger number of HPVs as having the potential for accumulation in remote regions than is classified as POP-like by the existing approach. In particular, the EFA identifies chemicals capable of accumulating in remote regions without fulfilling the criterion for P_{OV}. The remote accumulation fraction of the EFA is the LRTP assessment metric most suited for the risk assessment stage in Annex E of the SC. Using simpler metrics (such as half-life criteria, P_{OV}, and LRTP–P_{OV} combinations) in a hazard-based assessment according to Annex D is problematic as it may prematurely screen out many of the chemicals with potential for adverse effects as a result of long-range transport.

Environmental significance

The Stockholm Convention (SC) has motivated the development of various models and metrics to assess a chemical's potential for long-range environmental transport (LRT). Using a new set of metrics, referred to as the emission fractions approach (EFA), we explore whether the existing LRT metrics recommended by the OECD align with the needs of the SC. A comparison between the existing metrics and the EFA suggests that the utility of the existing approach is limited in terms of identifying whether a chemical is likely as a result of its LRT to elicit adverse effects. The screening approach explored herein should enable future model applications of regulatory and scientific interest that are not possible using the existing method recommended by the OECD.

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† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3va00189j

1. Introduction

The environmental occurrence of Persistent Organic Pollutants (POPs) and other organic chemicals of emerging concern (CECs) in remote areas such as the Arctic and the Antarctic has received considerable attention. A major concern has been the detection of POPs and CECs in biota, potentially leading to adverse effects on wildlife and human health.[1,2] A prerequisite for significant adverse human health and/or environmental effects occurring as a result of long-range environmental transport (LRT) is the accumulation of a given chemical in surface media of the remote environment.

The key regulatory framework for POPs is the Stockholm Convention (SC), which is a global agreement to protect human health and the environment from chemicals that are persistent (*P*), bioaccumulative (B), toxic (T) and have potential for long-range environmental transport (LRTP) to remote areas.[3] The requirement for an organic CEC to be listed under the SC is that it "is likely as a result of its long-range environmental transport to lead to significant adverse human health and/or environmental effects", *i.e.*, the chemical must not only undergo LRT to remote regions, but it must also accumulate in environmental surface media to an extent sufficient to cause harm.

The number of chemicals which have been recognized as POPs has increased since the SC came into effect, as the SC includes provisions for parties to nominate new chemicals for potential amendment. A nomination process involves simple screening criteria such as an atmospheric half-life in air larger than 2 days for LRTP. The UNECE Convention on long-range transboundary air pollution additionally calls for evidence that the substance has a vapor pressure < 1000 Pa for LRATP.[4] However, these criteria do not offer any information on whether and to what extent a chemical of interest has the potential for accumulation in surface media in a remote region following long-range atmospheric transport (LRAT).

The simplest criteria for *P* under the SC and other regulatory frameworks are based on half-lives in surface media, *i.e.*, the time required for the concentration in an environmental medium of interest to be reduced by 50%. Under the SC, a chemical fulfils the *P* criterion if it has a half-life in water larger than 2 months, and in soil/sediment in excess of 6 months. However, single-media half-life criteria may not be relevant unless the chemical is likely to reside in the media under consideration. For example, the degradation half-life in surface media does not offer relevant information for a highly volatile and inert chemical which is emitted to air, and which does not deposit.

In response to the need for a more comprehensive assessment of LRTP and *P* that takes into account how chemicals distribute in the environment, different mathematical models have been developed, *e.g.*[5–9] The OECD P_{OV} and LRTP Screening Tool for assessing chemicals for *P* and LRTP ("The Tool")[10] is an example of a model designed for screening the environmental hazard potential of chemicals. As an alternative to single-media half-lives, The Tool calculates an overall persistence (P_{OV}) which accounts for the distribution of a chemical across environmental compartments as influenced by the mode of entry into the environment.[11] The two LRTP metrics in The Tool[10] quantify the potential of a chemical for (i) transport from a source to a remote region (CTD – characteristic travel distance[12]) in air or water, and (ii) transfer from the atmosphere to surface media in a remote region (TE – transfer efficiency[13]). However, neither of these metrics explicitly addresses the potential for accumulation in surface media in a remote region.[14] Rather, the main outputs of the model are two charts plotting CTD and TE, respectively, against P_{OV}, *i.e.*, the assessment is based on the assumption that the combination of a LRTP metric and P_{OV} identifies chemicals potentially hazardous to remote regions.

The first version of The Tool became available in 2005, whereas the current version (2.2) was published in 2009.[10] This software has been applied in the regulatory assessment of a large number of POP candidates under the SC (Annex E, risk profiles). Recent examples include UV-328,[15] Dechlorane Plus,[16] and medium chain chlorinated paraffins.[17] It has also been used in scientific studies screening chemicals for LRTP.[18,19] We have recently identified a number of limitations of the LRTP metrics in The Tool which could lead to false positive and negative categorisations in LRTP assessment: (1) Neither CTD nor TE allow for combined transport in water and air. (2) The TE does not account for transfer to a remote region *via* media other than air, nor does it consider reversible atmospheric deposition and the consequences thereof. (3) Neither CTD nor TE assess accumulation in environmental surface media. As an alternative to CTD and TE, we have proposed a set of alternative metrics, collectively referred to as the Emission Fractions Approach (EFA),[20] which offers opportunities for more coherent LRTP assessments.

The objective of this study was to assess the implications of the choice of LRTP metrics when screening a large set of chemicals. Of specific interest was the extent of agreement between the outcome of LRTP assessments based on the current approach [plots of CTD or TE *versus* P_{OV}] *versus* an alternative EFA metric, which in addition to dispersion and transfer explicitly accounts for accumulation in surface media in a remote region.

2. Methods

We used a version of The Tool (version 2.2) that calculates the EFA metrics[20] in addition to P_{OV}, CTD and TE.[10] We refer to Wegmann *et al.*[10] for a detailed description of The Tool and the existing metrics and offer only a brief description herein. The Tool is a consensus-based model reflecting the state-of-science at the time of its development.[7,8,10,21,22] It is a steady-state (level 3), fugacity-based multimedia model[23] with one air, one water and one soil compartment. It is not spatially resolved, and the parameters have been chosen to reflect the global environment.[10] For example, the surface area of soil and water in the model reflect the area of the globe covered by land and ocean, respectively. The input parameters required to characterize each chemical are degradation half-lives in air, water and soil, as well as the logarithm of the equilibrium partitioning ratios between air and water ($\log K_{AW}$) and octanol and water ($\log K_{OW}$). Each chemical is simulated three times, using three different emission scenarios (100% emissions to air, water and soil, respectively). The maximum values for P_{OV}, CTD and TE across these emission scenarios are highlighted in the tabulated outputs and are used in the CTD/TE *vs.* P_{OV} plots. Hence, the default output for P_{OV}, CTD and TE of a chemical may not necessarily reflect the same emission scenario.[10] For example, the highest CTD is typically obtained for the model scenario with 100% emissions to air, whereas the highest value for P_{OV} for chemicals with a relatively high hydrophobicity (high $\log K_{OW}$) is likely to be calculated in the scenario with 100% emissions to soil.

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Environ. Sci.: Adv., 2023, **2**, 1360–1371 | **1361**

Table 1 Definition of the three metrics of the emission fractions approach. Each metric is a fraction of the total emissions as well as a fraction of the preceding metric

Metric	Definition
ϕ_1	The environmentally dispersed fraction (ϕ_1) quantifies the relative extent to which a chemical can reach remote regions
ϕ_2	The remotely transferred fraction (ϕ_2) expresses to what relative extent a chemical can reach surface media in remote regions
ϕ_3	The remotely accumulated fraction (ϕ_3) assesses the fraction of chemicals emissions accumulating in surface media of remote regions

The three metrics of the EFA approach are described in Breivik et al.[20] and defined in Table 1. Because these three metrics are all normalized by the rate of global emissions, they are all intensive properties, i.e., are independent of the amount of chemical. The environmentally dispersed fraction ϕ_1 expresses the relative potential of a chemical to undergo dispersion (i.e. long-range environmental transport) by air and water combined. The remotely transferred fraction ϕ_2 expresses the relative extent to which a chemical is net transferred to surface compartments of a remote region, accounting for environmental dispersion in air and water (ϕ_1). The remotely accumulated fraction ϕ_3 expresses the relative extent to which a chemical is accumulating in surface compartments of a remote region, accounting for dispersion (ϕ_1) and transfer (ϕ_2) in air and water. Hence, CTD and ϕ_1 are transport-oriented LRTP metrics, TE and ϕ_2 are transfer-oriented LRTP metrics, whereas ϕ_3 is a metric which explicitly targets remote accumulation, similar to the Arctic contamination potential.[14] Neither CTD nor TE mirrors the scope of ϕ_3. The model in The Tool can be used to calculate the three EFA metrics.

While all environmental input parameters for our calculations were taken from Wegmann et al.,[10] we modified the code to account for the intermittency of precipitation.[20] While this will lead to different numerical results for chemicals subject to wet deposition compared to outputs from the existing version of The Tool, it ensures a consistent approach in the analysis presented herein.

For the analysis we chose a data set of 12 615 HPVs curated by Arnot et al.,[24] because it contained the required physical–chemical partitioning properties and degradation half-lives. The point of departure for this data set was a list of 15 800 organic chemicals identified by their CAS numbers that included not only neutral chemicals, but also acids, bases, and salts. Structural information was used to remove dissociating chemicals from the dataset. The properties of the final set of discrete chemical structures span a wide range. Specifically, log K_{AW} varies from −12 to 3 while log K_{OW} ranges from −4 to 9. Degradation half-lives in air, water and soil vary from <2 s to >150 years, 12 hours to >10 years, and 23 hours to 23 years, respectively.

The thresholds for the LRTP metrics and P_{OV}, shown in Table 2 were determined as the lowest values obtained for a set of 14 legacy POPs with any of the three default emission scenarios.[20] Table 2 also gives the number and percentage of chemicals out of the 12 615 exceeding each threshold. We have also identified the chemical which defines each threshold (i.e., the POP which has the lowest value of a metric).

3. Results

3.1. Existing metrics (CTD–P_{OV} and TE–P_{OV} plots)

Fig. 1 displays the CTD–P_{OV} and TE–P_{OV} plots. Chemicals falling into each quadrant in these plots are highlighted with differently colored markers. The combined assessment based on CTD–P_{OV} (Fig. 1a) flags 8997 out of 12 615 chemicals (71.3%) as non-POP like for both LRTP and P_{OV} (green markers). 306 chemicals (2.4%) are assessed as not having LRTP according to CTD (i.e., CTD below the threshold in Table 2) but POP-like P_{OV} (black markers). 2107 chemicals (16.7%) are assessed as having LRTP (CTD) but not POP-like P_{OV}, while 1205 chemicals (9.6%) are flagged with POP-like LRTP behavior and persistence.

The assessment relying on TE–P_{OV} (Fig. 1b) predicts that (i) 7115 chemicals (56.4%) are not POP-like regarding both LRTP and P_{OV}, (ii) 238 chemicals (1.9%) do not exceed the threshold for TE, but exceed the threshold for P_{OV}, (iii) 3989 chemicals (31.6%) are POP-like in terms of TE, but not above the threshold for P_{OV}, and (iv) 1273 chemicals (10.1%) are POP-like according to both TE and P_{OV}.

1131 chemicals (9.0%) are flagged as POP-like by both TE–P_{OV} and CTD–P_{OV}, i.e., fall into the upper right quadrant in both the CTD–P_{OV} plot (Fig. 1a) and TE–P_{OV} plot (Fig. 1b). Another 216 chemicals exceed either the CTD–P_{OV} criteria or the TE–P_{OV} criteria, but not both.

Table 2 Thresholds for POP-like behavior derived on the basis of selected legacy POPs (selected PCBs, cis- and trans-chlordane, γ-HCH, pp-DDT, pp-DDD and HCB), along with the POP which dictates the threshold. The number of chemicals out of a set of 12 615 organic chemicals exceeding each of these thresholds are included

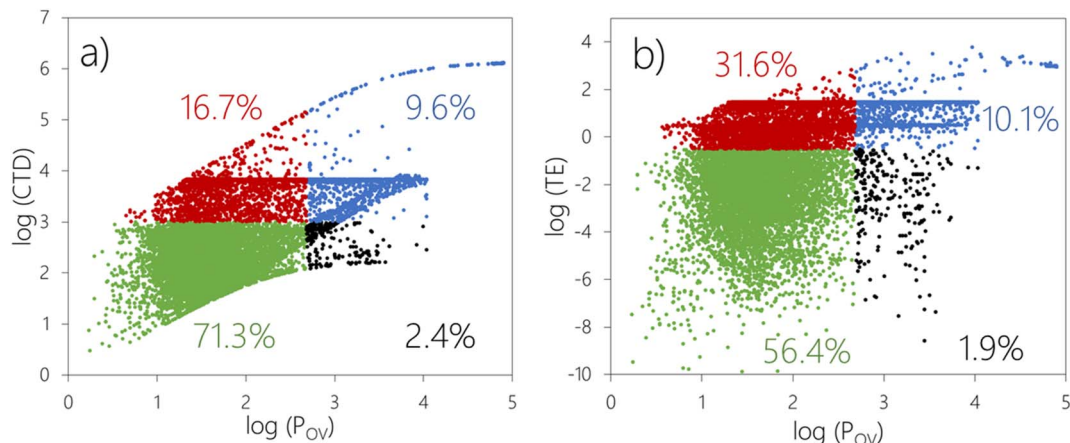| $N = 12\,615$	ϕ_1	ϕ_2	ϕ_3	CTD	TE	P_{OV}
Threshold	7.7×10^{-4}	8.4×10^{-5}	8.2×10^{-6}	1021 km	0.32	480 days
Threshold (log)	−3.1	−4.1	−5.1	3.01	−0.49	2.68
Chemical defining the threshold	cis-Chlordane	trans-Chlordane	PCB-28	cis-Chlordane	trans-Chlordane	HCB
$N \geq$ threshold	3538	5986	2980	3312	5262	1511
$N \geq$ threshold (%)	28.0	47.5	23.6	26.3	41.7	12.0

Fig. 1 Plots of CTD *versus* P_{OV} panel (a) and TE *versus* P_{OV} panel (b) from The Tool for 12 615 organic chemicals. The percentages of chemicals falling into each of the four quadrants are included. Chemicals identified as POP-like are located in the upper right quadrant (blue markers).

3.2. CTD *versus* ϕ_1 and TE *versus* ϕ_2

In Fig. 2a, we have plotted the existing as well as the alternative transport-oriented metrics against each other, *i.e.*, CTD *versus* ϕ_1. Please note that the CTD here is the larger of the CTD in air

or water. The existing and alternative transfer-oriented metrics, *i.e.*, TE *versus* ϕ_2, are analyzed in Fig. 2b–d.

3.2.1. CTD *versus* ϕ_1. CTD_A and ϕ_{1A} (using subscript A for air) convey the same mechanistic information.[20] The same applies to CTD_W and ϕ_{1W} (using subscript W for water).[20] Hence,
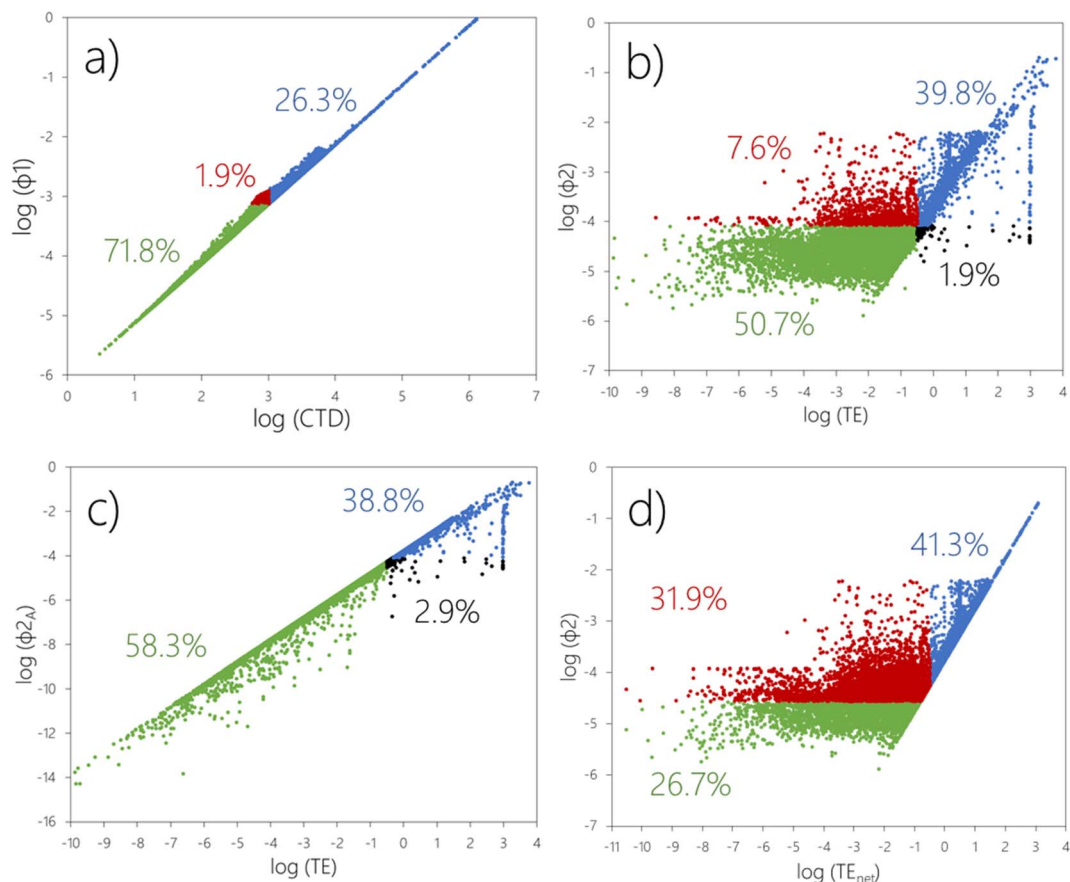
Fig. 2 Comparison of metrics describing dispersion and transfer as calculated with The Tool for 12 615 organic chemicals: (a) log CTD *versus* log ϕ_1, (b) log TE *versus* log ϕ_2, (c) log TE *versus* log ϕ_{2A}, and (d) log TE_{net} *versus* log ϕ_2.

if the two pairs of transport-oriented metrics are plotted against each other, the plots will show a straight line. The main difference between the two CTDs and ϕ_1, is that ϕ_{1A} and ϕ_{1W} are additive, i.e., $\phi_1 = \phi_{1A} + \phi_{1W}$, whereas that is not the case for CTD_W and CTD_A, i.e., CTD is equal to the larger of the two. The thresholds for both CTD and ϕ_1 are defined by cis-chlordane (Table 2), which is a semi-volatile organic chemical capable of undergoing both LRAT and LRWT. The threshold for CTD represents CTD_A because $CTD_A > CTD_W$ for cis-chlordane. The threshold for ϕ_1 in Fig. 2a is therefore defined by the ϕ_{1A} for cis-chlordane for the sake of comparison. This explains why in a plot of ϕ_1 against CTD a model-predicted ϕ_1 value for a given chemical either falls on or above the 1 : 1 line. In Fig. 2a, 242 chemicals (1.9%) fall into the region highlighted with red markers. These chemicals are above the threshold for ϕ_{1A}, but below the threshold for CTD (Table 2). In other words, these are chemicals which only will be classified as having POP-like LRTP if combined transport in air and water is considered. While the fraction of chemicals affected may appear small, it clearly indicates the potential for false negative LRTP classification, even if CTD_A and CTD_W are both taken into consideration. We note that two decades ago, Beyer and Matthies[25] already used model simulations to show that "combined transport in coupled air–ocean systems can accelerate the overall transport into remote regions", and later Stroebe et al.[26] confirmed that combined transport may enhance the transport efficiency for some chemicals.

3.2.2. TE versus ϕ_2. Fig. 2b compares the gross atmospheric transfer to surface media of the remote region (TE) with the net transfer to surface media as a result of both LRAT and LRWT (ϕ_2) with thresholds defined by trans-chlordane for both metrics (Table 2). The two differences between the two metrics are that ϕ_2 accounts for transport in water while TE does not (causing false negatives by TE), and ϕ_2 considers reversibility of deposition while TE does not (causing false positives by TE).[10] The TE may additionally exceed 100% (see Text S1 in the ESI†). The relatively large fraction of chemicals that is categorized as having POP-like LRTP based on ϕ_2 but not TE (red markers in Fig. 2b, $N = 961$ or 7.6%) would indicate that ignoring LRWT affects a considerably larger number of chemicals than ignoring reversible atmospheric deposition (black markers, $N = 237$ or 1.9%). However, for some chemicals, the biases of the TE may counteract each other.

3.2.3. TE versus ϕ_{2A}. When we isolate the impact of using gross deposition to calculate TE by recalculating ϕ_2 while neglecting LRWT (we call this ϕ_{2A}, i.e., ϕ_2 for dispersion via air only), a given chemical either falls on or below the 1 : 1 line in a plot of ϕ_{2A} against TE (Fig. 2c). This is because the only difference between the two metrics is that ϕ_{2A} considers reversibility of atmospheric deposition whereas TE does not. The TE therefore overestimates atmospheric inputs to surface media of the remote region for any chemical that undergoes repeated air–surface exchange,[10,20] causing false positives for 374 chemicals in the screening data set (2.9%) (Fig. 2c, black markers).

3.2.4. TE_{net} versus ϕ_2. When we isolate the impact of transfer in water by comparing ϕ_2 with a TE that accounts for

the reversibility of deposition, which we call TE_{net}, a given chemical either falls on or above the 1 : 1 line in a plot of ϕ_2 against TE_{net} in Fig. 2d. This is because ϕ_2 allows for transport to the remote region with water whereas this pathway is not accounted for in the TE_{net}. In Fig. 2d, there also appears to be an upper boundary for $\log \phi_2$ occurring around -2.3 for chemicals with a $\log TE_{net} < 1.5$. This is because any involatile chemical that is emitted to air and undergoes LRAT has a predicted TE (and TE_{net}) of 0.5% and a predicted ϕ_{2A} (and ϕ_2) of 0.005. ϕ_{2A} is also identical to ϕ_{1A} because airborne involatiles readily deposit in the remote region. Note that similar mechanistic inferences cannot be made based on the existing transport- and transfer-oriented metrics (CTDs and TEs) as these are inconsistent with each other.

In summary, the TE's failure to account for transport in water affects a far larger fraction of screened chemicals (31.9%, red markers in Fig. 2d) than TE's failure to account for reversible deposition (2.9%, black markers in Fig. 2c). However, the failure to account for reversible deposition often compensates for the failure to account for water transport, so overall TE misclassifies "only" 9.5% of screened chemicals (red plus black markers in Fig. 2b).

3.3. LRTP–P_{OV} versus accumulation (ϕ_3)

The aim of Annex E of the SC is to evaluate whether the chemical is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and/or environmental effects, such that global action is warranted.[27] The existing approach to LRTP assessment does not have a metric that seeks to quantify the accumulation of a chemical in a remote region, even though such accumulation is arguably a prerequisite for significant adverse effects to occur. To assess whether an existing LRTP metric and a persistence metric in combination identify chemicals with the potential for accumulation in remote regions, we first compare the chemicals categorized as having POP-like LRTP based on a metric directly quantifying remote accumulation (ϕ_3) versus CTD and TE without consideration of the P_{OV} (Fig. 3a), and next with the chemicals identified as POP-like in the CTD–P_{OV} and TE–P_{OV} plots in Section 3.1 above (Fig. 3b).

From Table 2, we see that there are 3312, 5262 and 2980 chemicals which exceed the thresholds for CTD, TE, and ϕ_3, respectively. Fig. 3a can be used to explore how successful CTD and TE would be at identifying chemicals that are judged by ϕ_3 to have potential for accumulation in a remote environment. Of the 2980 chemicals with a ϕ_3 above the threshold, 731 (25%) and 436 (15%) are not identified by CTD and TE, respectively. If both CTD and TE were used, there would be 819 (27%) false negatives among the 2980 chemicals with POP-like ϕ_3, whereas the number of false negatives would be reduced to 348 chemicals (12%) if either CTD or TE was used. Thus, CTD and TE are moderately useful for screening for accumulation in remote regions.

In Fig. 3b we compare the overlap between categories of chemicals which exceed CTD–P_{OV} and/or TE–P_{OV} and/or ϕ_3. There are 1693 chemicals (13.4% in the screening data set)
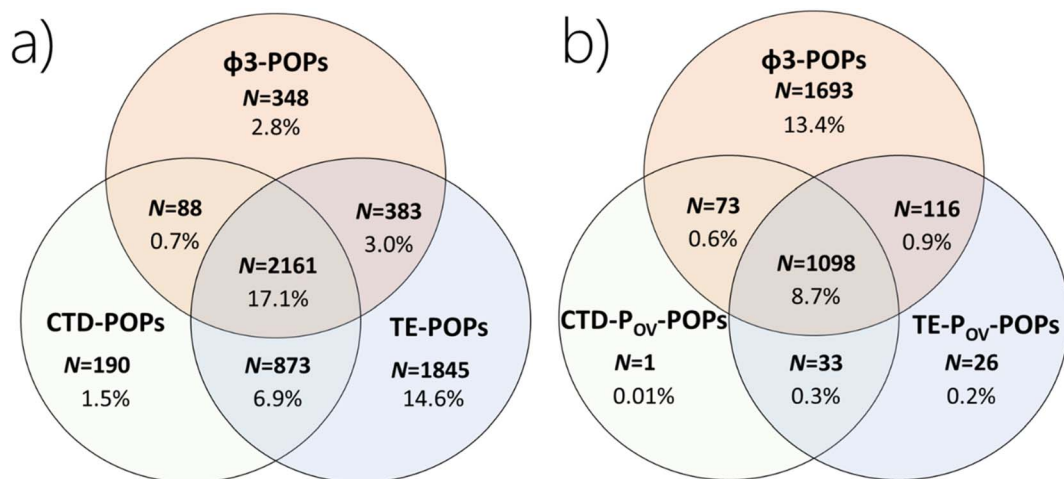
Fig. 3 Comparison of the number of chemicals in the screening data set which (a) exceed the criteria for CTD, TE and ϕ_3, and (b) CTD−P_{OV}, TE−P_{OV} and ϕ_3 (percentages of all 12 615 chemicals studied).

which are not captured as POP-like according to ϕ_3 using either CTD−P_{OV} or TE−P_{OV}. The number of chemicals which are POP-like using the existing approach (CTD−P_{OV} and TE−P_{OV}) is 1131 or 9.0%, whereas the number of chemicals which are either CTD−P_{OV} or TE−P_{OV} but not both is 216 (1.7%). In comparison, the total number of chemicals which exceeds the criterion for POP-like accumulation (ϕ_3) is 2980 or 23.6% (Table

2), *i.e.*, more than 2.6 times the number of chemicals fulfilling both the CTD−P_{OV} and the TE−P_{OV} criteria. Among the 2980 chemicals in the screening data set which exceed the criterion for POP-like accumulation (ϕ_3), there are 1400 chemicals which fulfill the criterion for P_{OV} and 1580 chemicals which do not. In other words, there are many chemicals assessed to have the potential to accumulate in remote regions (based on ϕ_3) without
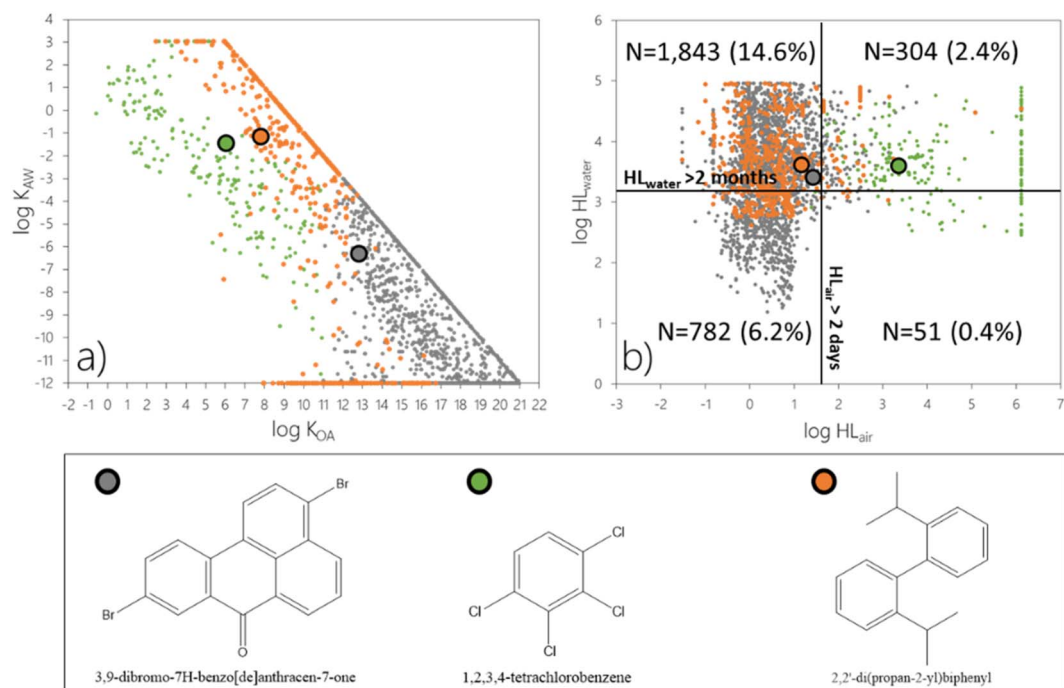
Fig. 4 Diagnostic plots for those chemicals which exceed the threshold for ϕ_3 ($N = 2980$). Panel (a) shows results in a chemical partitioning space, whereas panel (b) shows the results when plotting degradation half-life in air (hours) *versus* degradation half-life in water (hours). The number of chemicals falling into each of the four quadrants in panel (b) are included. The colors of the markers identify chemicals which accumulate in surface media in the remote region (i) because of LRAT and with a log K_{OA} > 11 (grey), exemplified by 3,9-dibromo-7*H*-benzo[de] anthracen-7-one, and (ii) because of LRAT and with a log K_{OA} < 11 (green) with 1,2,3,4-tetrachlorobenzene chosen as an example. The remaining chemicals only exceed the threshold for ϕ_3 when both LRAT and LRWT are accounted for (orange) as exemplified by 2,2′-di(propan-2-yl) biphenyl. The bottom panel shows the molecular structures for three example chemicals.

meeting the P_{OV} criterion. We conclude that using the CTD–P_{OV} and/or TE–P_{OV} combination to identify chemicals that have remote accumulation potential would be prone to many false negative decisions.

3.3.1. Chemicals exceeding the threshold for ϕ_3. What then are the combinations of properties that allow a chemical to accumulate in remote regions? In order to elucidate the role LRAT and LRWT play for chemicals with a ϕ_3 above the threshold, we first calculated how many of those chemicals have a ϕ_{3A} (the remotely accumulated fraction without dispersion in water) above the threshold value for ϕ_3: 19.5% ($N = 2466$) of all chemicals were predicted to accumulate in remote surface media as result of LRAT, leaving 4.1% ($N = 514$) which accumulate in remote surface media only when both LRAT and LRWT are accounted for (data not shown). Fig. 4 displays the partitioning and degradation properties of the chemicals with a ϕ_3 above the threshold using green and grey markers to designate those undergoing LRAT with a $\log K_{OA}$ below or above 11, respectively. Orange markers are used to identify the rest of the chemicals which exceed the threshold for ϕ_3 only if both LRAT and LRWT are considered. While the $\log K_{OW}$ and $\log K_{AW}$ of the chemicals in the screening data set were capped at values of 9 and -12, respectively[24] (as apparent in Fig. 4a), the model result is not sensitive to these partitioning properties, when they exceed these values. Fig. 4 additionally highlights model predictions for one chemical from each of these three categories. Data on physical–chemical properties and environmental degradation half-lives for individual chemicals discussed herein are included in Table S1.†

Most chemicals which exceed the criterion for ϕ_3 as result of LRAT have a $\log K_{OA}$ above 11 ($N = 2242$ or 17.8%) and therefore are predominantly sorbed to atmospheric particles in The Tool. They can undergo LRAT even if their degradation half-life in air is relatively short (Fig. 4b; grey markers) because it is assumed that sorption to particles prevents them from undergoing atmospheric degradation reactions. An example is 3,9-dibromo-7H-benzo[de]anthracen-7-one with a degradation half-life in air of 28 h and an estimated $\log K_{OA}$ of 12.8 (Table S1 and Fig. S1a†). This chemical, if emitted to air, exceeds the threshold for ϕ_3 (Table 2) by more than an order of magnitude (Table S2†). Under this emission scenario, 3,9-dibromo-7H-benzo[de] anthracen-7-one is furthermore prone to be dispersed in the atmosphere (ϕ_1), transferred to water (72.6%) and soil (27.4%) (ϕ_2), and to mainly accumulate in water (ϕ_3) (bars in the lower part of Fig. S1a†). This chemical is also predicted to exceed the threshold for ϕ_3 if it is emitted to water (Fig. S1a†). As 3,9-dibromo-7H-benzo[de]anthracen-7-one is not prone to evaporate from the water compartment if emitted to water, the predicted dispersion, transfer, and accumulation are all almost exclusively associated with the water compartment (Fig. S1a†).

On the other hand, chemicals which exceed the criterion for ϕ_3 as a result of LRAT but predominantly occur in the atmospheric gas phase, *i.e.*, have an estimated $\log K_{OA} < 11$ ($N = 224$ or 1.8%, green markers), need to be relatively persistent in air (HL$_{air}$ > 1 day) (Fig. 4b). 1,2,3,4-Tetrachlorobenzene with a $\log K_{OA}$ of 6.07 and a degradation half-life in air of 98 days serves as an example (Table S1†). This chemical exceeds the thresholds

for ϕ_1, ϕ_2, and ϕ_3 irrespective of the mode of emissions (Fig. S1b†).

Not surprisingly, the 514 chemicals (4.1%) that only exceed the ϕ_3 threshold when both LRAT and LRWT are accounted for are not readily degraded in water, and all have a HL$_{water}$ > 17 days (orange markers in Fig. 4b). They also have partitioning properties that do not allow for significant evaporation from water, either because they have a low $\log K_{AW}$ (approximately below −4) or because they are particle-bound in water (have a $\log K_{OW}$ > 6) (orange markers in Fig. 3a). 2,2′-Di(propan-2-yl) biphenyl qualifies for the latter criterion with a $\log K_{OW}$ of 6.67. This chemical exceeds the criterion for accumulation (ϕ_3) only if emitted to water (Fig. S1c†). While 2,2′-di(propan-2-yl) biphenyl is predicted to be dispersed from the source region in both air and water in equal amounts under this emission scenario, it is transferred to, and accumulates mostly in, water (Fig. S1c†). These results demonstrate that the combination of diagnostic plots (Fig. 4) in concert with the plots shown in Fig. S1† offer a powerful tool to assess the factors which dictate LRTP of chemicals in screening exercises.

3.3.2. Chemicals exceeding the threshold for ϕ_3 but not the thresholds for CTD–P_{OV}/TE–P_{OV}. What properties cause the CTD–P_{OV} and/or TE–P_{OV} combinations (LRTP–P_{OV}) to not recognize the potential of many of the 2980 chemicals displayed in Fig. 4 for high remote accumulation (POP-like according to ϕ_3)? Fig. 5 is a version of Fig. 4, which only displays the 1693 chemicals with a ϕ_3 above the threshold that were not identified by an assessment based on CTD–P_{OV} and/or TE–P_{OV} (Fig. 3b). Fig. 5 indicates that these LRTP–P_{OV} combinations do not recognize the elevated remote accumulation potential of representatives of all three groups of chemicals: more than half of the involatiles with a $\log K_{OA}$ > 11 ($N = 1204$ out of 2242 or 9.5% of the screening data set, grey markers), close to half of the chemicals undergoing LRAT in the gas phase ($N = 99$ out of 224; 0.8%, green markers), and most of the chemicals subject to LRWT ($N = 390$ out of 514; 3.1%, orange markers). In terms of partitioning ratios, these 1693 chemicals span a very wide range. Log K_{OA} varies by more than 17 orders of magnitude (3.5 to 21), $\log K_{AW}$ varies by ∼15 orders of magnitude (−12 to 3), while $\log K_{OW}$ varies by 13 orders of magnitude (−4 to 9) (Fig. 5a). Clearly, partitioning ratios are poor predictors to identify chemicals which are POP-like according to ϕ_3 but not TE–P_{OV} and/or CTD–P_{OV}.

A comparison of the grey markers between Fig. 4b and 5b reveals that it is mostly the involatile chemicals that are highly persistent in surface media (with a $\log(HL_{water}/hour) > 4$) that are recognized by the LRTP–P_{OV} approach as being subject to remote accumulation. This is in contrast to the EFA, which recognizes involatile chemicals as prone to remote accumulation above the threshold for ϕ_3 in spite of relatively short degradation half-lives in surface media. Docosanamide and to some extent 1,2,3,4,7,8-hexabromocyclododecane serve as examples (Fig. 5; S2a and S2f†). While a high potential for remote accumulation of chemicals which have short degradation half-lives in surface media may appear counterintuitive, this is a result of the multiplicative feature of the EFA. Any involatile chemical is predicted to have high ϕ_1 and ϕ_2 if emitted to air.
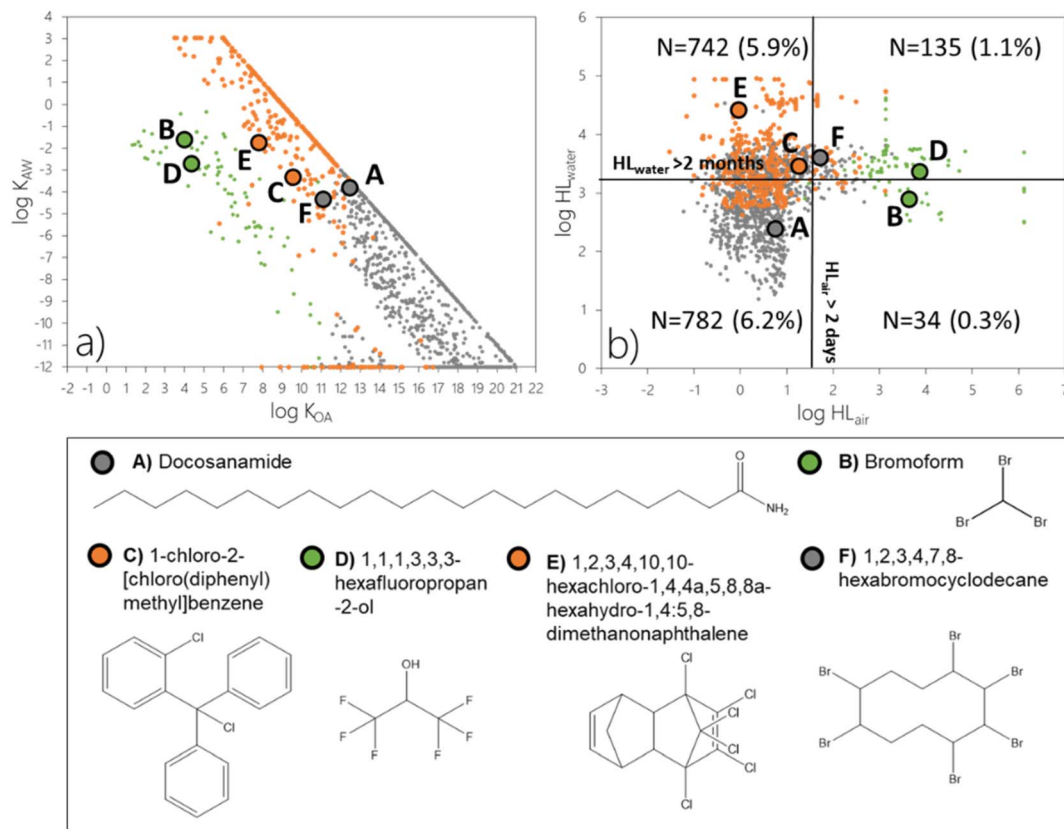

dispersion, transfer and accumulation in surface media of the remote region according to the EFA. Fig. 5 illustrates that the explanation for this is not simple. The failure to account for combined air and water transport is one of the reasons. Another is that some chemicals have the potential for remote accumulation without meeting the P_{OV} persistence criterion.

3.4. Implications for LRTP assessments

The listing of a new POP in the Stockholm Convention involves two steps: The proposal, outlined in Annex D, should provide evidence that the nominated chemical is persistent, bioaccumulative, has the potential for long range transport and elicits adverse effects. A subsequent risk profile, described in Annex E, "further elaborates on, and evaluates, the information referred to in Annex D" with the purpose of establishing in the assessment "whether the chemical is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and/or environmental effects, such that global action is warranted" (paragraph 7a of article 8). This procedure is built on the premise that a chemical needs to fulfill the four criteria in Annex D in order to fulfill the ultimate listing requirement in Annex E, in other words it did not foresee the possibility that a chemical can lead to significant adverse effects in remote regions without being persistent and bioaccumulative. However, clearly the main criterion of Annex E should supersede the criteria of Annex D. The Stockholm Convention is not targeting chemicals that meet formal criteria of P, B, LRTP, and T. These criteria rather are meant to aid in the task of identifying chemicals that meet the definition in paragraph 7a of article 8.

The results above demonstrate that accumulation in remote regions cannot be approximated by the intersection of P_{OV} and TE/CTD and that a metric such as ϕ_3 is better suited to provide insight for assessment within the context of Annex E of the SC. This is because ϕ_3 screens for accumulation in the remote environment, while the CTD–P_{OV} or TE–P_{OV} combination screens for LRTP and persistence relevant for Annex D. The question arises whether the existing approach (LRTP–P_{OV}) and the EFA (ϕ_3) are consistent with each other when the former is applied for Annex D and the latter for Annex E? The answer is no because any assessment based on predictions of LRTP–P_{OV} by the existing version of The Tool alone may eliminate many chemicals with a potential to accumulate in remote regions at the screening stage ($N = 1693$ or 13.4%, Fig. 3b). One may then ask whether the consistency of the EFA approach also ensures consistency across the two Annexes of the SC? In other words, that all chemicals identified as having a potential for remote accumulation in the context of Annex E would have been flagged during the screening stage if CTD/TE are replaced with ϕ_2? The answer is no because a chemical may fall below the threshold for ϕ_2 yet remain above the threshold for ϕ_3 (Fig. S4†). Secondly, it is not necessarily the same emission scenario which leads to the highest ϕ_1, ϕ_2 and ϕ_3. It may then be prudent to assess whether all 2980 chemicals which fulfill the criterion for ϕ_3 will be captured during the screening stage based on degradation half-lives in air (LRATP criteria) and water (persistence criteria)? Our results suggest that

this is not the case as only 304 chemicals among the 2980 chemicals which exceed the threshold for ϕ_3 will be identified in this manner (Fig. 4b, upper right quadrant and Fig. S5†). Even if the existing approach (LRTP–P_{OV}) is applied in addition to these half-life criteria, there will still be 1558 chemicals left out (Fig. 5b, upper left, lower left and lower right quadrants). Note that the number of chemicals falling into the lower left quadrant of Fig. 4b and 5b is identical ($N = 782$). Hence, 12.4% of the chemicals in the screening data set will not be identified as having a potential for accumulation in the remote region in the context of Annex E, even if LRTP–P_{OV}, degradation half-life in air, as well as degradation half-life in water are applied under Annex D. Among the reasons for this are (i) the assumption that involatile chemicals do not degrade in air (grey markers in Fig. 4a), (ii) the possibility of chemicals undergoing LRT when both LRAT and LRWT are accounted for (orange markers in Fig. 4a), and (iii) the possibility of chemicals undergoing LRT without exceeding the half-life criteria (Fig. 4b). This suggests that a screening step relying on simple LRTP–P_{OV} criteria may wrongly screen out most of the chemicals with a potential to accumulate in the remote region according to ϕ_3.

This study demonstrates that there are many chemicals in the screening data set which have the potential to accumulate in a remote region without meeting the screening criteria under Annex D. This highlights that the screening for LRTP under Annex D leads to possible false negatives in the context of Annex E, which suggests that the tiered screening under the SC does not work very well. In other words, the possible LRTP screening using degradation half-lives in air or water, transport- or transfer-metrics may lead to false negatives if it eliminates chemicals that may qualify as POP-like if ϕ_3 is the endpoint of interest. There may be two approaches to overcome the issue of inconsistency of metrics. The simple approach would be to use ϕ_3 in the context of both Annex D and Annex E. The other metrics can then be disregarded. The other approach would be to define thresholds for the other metrics that are consistent with ϕ_3. This could be done by identifying the lowest value of CTD, TE, ϕ_1, ϕ_2, P_{OV}, HL$_{air}$, and HL$_{water}$ among the chemicals that exceed the threshold for ϕ_3. This implies, however, that the numerical thresholds would be dependent on the selection of chemicals used.

Following the original approach in The Tool, thresholds for LRTP and P_{OV} were derived by using the lowest value of a metric obtained for a select subset of 14 POPs (Table 2). We established these thresholds to be able to explore our main question on how the choice of metric affects the outcome for a non-regulatory screening of 12 615 chemicals. The use of these thresholds in this study does not mean that regulatory decision should be based on thresholds derived from this particular subset of POPs, or even that thresholds based on reference or benchmark chemicals should be used at all.

Obviously, the choice of reference POPs can influence the threshold values, and in a regulatory context this choice would have to be well justified. While it may be tempting to suggest that the set of benchmark POPs should comprise all chemicals listed in the Annexes of the Stockholm Convention, this would result in fairly low thresholds because The Tool calculates low

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LRTP metric values for several POPs. For example, if methoxychlor, chlorpyrifos and UV-328 were added to the group of 14 reference POPs (Table S3†), the threshold for CTD would be defined by the value for UV-328 (CTD = 228 km) instead of *cis*-chlordane (CTD = 1021 km; Table 2). The number of chemicals exceeding the threshold for CTD would increase from ~3300 (26.3%) to ~7300 (57.9%). An approach that classifies a huge fraction of assessed chemicals as having LRTP will cease to be useful in discriminating between chemicals in need of global regulatory action and those that can be regulated within national or regional jurisdictions. While thresholds were defined here to enable the screening of thousands of chemicals, the primary interest in other contexts may be the LRTP assessment of a single chemical. Alternative model-based strategies could then become feasible, such as comparative approaches that rank a chemical along with all regulated POPs.

3.5. Cautionary notes on simplified model assumptions

The reader should furthermore keep in mind that The Tool is a relatively simple evaluative model for non-ionizing substances. The chemical fate processes in the multimedia model within The Tool are described relying on a number of simplifying assumptions[10] which affect the outcome of the screening. Examples explicitly mentioned by Wegmann *et al.*[10] are the use of an average aerosol size, an average deposition velocity and a constant rain fall rate. While the latter simplification has been addressed by implementing a description of intermittent precipitation in this study, another simplification which deserves to be highlighted is that involatile substances that are sorbed to particles in the atmosphere (*i.e.*, have a high K_{OA}) are assumed to be completely persistent in air. Chemicals which undergo reactions in the atmospheric particle phase[28] may be incorrectly classified as undergoing LRAT.[20] We have shown that the EFA flags many high-K_{OA} chemicals emitted to air as having a ϕ_3 above the threshold even if they are not particularly persistent in surface media (Fig. 4).

The parameterization of the sinking velocity of chemicals that are sorbed to solids in water ($\log K_{OW} > \sim 6$) furthermore becomes an important consideration when accounting for the combined transport in air and water. The sinking of hydrophobic chemicals sorbed to solids is expected to be subject to considerable environmental variability.[29,30] Further in-depth LRTP assessments may therefore be warranted, using more sophisticated models that account for spatial and temporal variability. A major advantage of the EFA is that the calculation of emissions fractions is not tied to a particular, simple model but can be implemented in higher-tier models which in turn can be evaluated against observations. Secondly, because the EFA is better suited than the existing LRTP metrics to identify which processes dictate LRTP for a particular chemical, it could additionally help guide LRTP assessments using higher-tier models.

4. Conclusions

While The Tool was only developed to screen for two hazard criteria[10] as relevant for Annex D, it has nonetheless been extensively applied in the Risk Profiles of various chemicals under Annex E. It is important to note that the existing approach leads to a risk of false positive/negative decisions not only in the context of Annex D, but also in the context of Annex E.

Here, we demonstrate that the existing and alternative LRTP metrics do not convey the same information and do not lead to similar outcomes in LRTP assessments. We propose that the coherent set of EFA metrics represents a more mechanistically sound approach to LRTP assessment than the existing metrics. Specifically,

• Assessing dispersion potential with CTD instead of ϕ_1 does not account for the possibility of chemicals undergoing combined LRT in air and water.

• Assessing potential for transfer to a remote region with TE instead of ϕ_2 does not account for (i) reversible atmospheric deposition, and (ii) the possibility of chemicals being transferred to the remote environment in water.

• Neither the CTD–P_{OV} combination nor the TE–P_{OV} combination quantify the potential for accumulation in a remote region.

• Any assessment of the potential for accumulation in a remote region with the CTD–P_{OV} combination instead of ϕ_3 will not capture chemicals that accumulate in remote regions (i) without meeting persistence criteria and (ii) due to transport in air and water combined.

• Any assessment of the potential for accumulation in a remote region with the TE–P_{OV} combination instead of ϕ_3 will not account for chemicals that accumulate in remote regions (i) without meeting persistence criteria and (ii) due to transport in water.

By integrating LRT, persistence and partitioning, ϕ_3 may serve as an indicator of accumulation in remote environments in the context of the Stockholm Convention and beyond.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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