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SCREENING KNOWN ARCTIC CONTAMINANTS FOR THE NEXT GENERATION OF PERSISTENT ORGANIC POLLUTANTS

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Introduction

Studies focused on monitoring the occurrence of chemicals in the Arctic and identifying new Arctic contaminants have identified a growing list of compounds of emerging concern. Chemicals present in the Arctic at levels high enough to be identified and quantified satisfy at least one of the following conditions: i) they possess physicochemical properties that favor their transport and accumulation in the Arctic, ii) they are produced in very high volumes and thus their mass distribution processes are of global scale, iii) they are produced locally (e.g., natural compounds), iv) they are used and emitted in the Arctic, either directly (e.g., pharmaceuticals or personal care products consumed by the local human population) or indirectly by consumption of materials that are repositories of chemicals. A report that reviews the occurrence of chemicals in the Arctic along with their physicochemical properties is expected to be published at the end of 2016 by the Arctic Monitoring and Assessment Programme (AMAP) 1. Developing sound management strategies for the chemicals identified in the AMAP report can be substantially assisted by ranking and prioritizing them based on their likelihood to be classified as persistent organic pollutants (POPs). POPs are chemicals that meet each of the following exposure-based criteria: i) they are persistent, ii) they have high long-range transport potential and iii) they are bioaccumulative. We employed EPI Suite 2 and the OECD Tool 3, respectively, to estimate physicochemical properties and assess persistence and long-range transport potential for the contaminants of emerging concern that have been identified in the AMAP report. The OECD modeling tool was employed to quantify chemical persistence and long-range transport potential and EPI Suite was used to estimate the logarithm of bioaccumulation factor (log BAF) of the AMAP report chemicals. We developed a ranking method based on benchmarking against a reference set of chemicals with known and well-established hazard potential profiles to assess the relative POP-likeness of the Arctic contaminants identified in the AMAP report.

Materials and methods

I. Contaminants of emerging concern

The upcoming AMAP report describes the detection of a total of 556 individual chemicals in the Arctic. These include per- and polyfluoroalkyl substances, halogenated and organophosphate flame retardants, plasticizers, phthalates, chlorinated paraffins, siloxanes, pharmaceuticals and personal care products, polychlorinated napthalenes, current use pesticides, organotins, polycyclic aromatic hydrocarbons and halogenated natural products. The chemical space of these compounds spans over 40 orders of magnitude of K_{AW} and 20 orders of magnitude of K_{OW} (Figure 1). We assembled a database of EPI Suite estimated physicochemical properties including molecular weight, vapor pressure and subcooled liquid vapor pressure, the logarithms of octanol-air, octanol-water and air-water partition ratios (log K_{OA}, log K_{OW} and log K_{AW}, respectively), the logarithm of the bioaccumulation factor (log BAF) calculated considering estimated biotransformation rate constants (k_M) and the half-lives of these chemicals in air, water and soil.

II. Reference set

We propose a scoring and prioritization scheme for chemicals based on benchmarking of hazard properties against chemicals with relatively well-known properties and environmental fate profiles. For this purpose, we compiled a reference set of chemicals against which the persistence, long-range transport potential and potential for bioaccumulation of the AMAP emerging contaminants could be compared. The reference set provides a basis to synthesize and contextualize screening-level hazard information and as a tool to intuitively rank and prioritize chemicals for disparate hazard metrics on a comparative scale. Our reference set of chemicals consists of 160 compounds which include known POPs, PAHs, pesticides, hydrocarbons and various halogenated compounds. The chemical space of the reference set

(Figure 2) spans over 10 orders of magnitude of KAW and KOW. Similarly to the AMAP contaminants case, we assembled a database of EPI Suite estimated physicochemical properties for the reference set.

III. Benchmarking and ranking
We employed the OECD tool to estimate overall persistence in the temporal remote state (Pov) and two metrics for atmospheric long-range transport potential, characteristic travel distance (CTD) and transfer efficiency (TE), for the reference set compounds. CTD describes the distance from a point source to the atmosphere at which a chemical's concentration falls to 37% of its initial value, while TE is a metric of the amount of chemical that is transported in the atmosphere and deposited to soil or water in a remote target region. We developed two POP-likeness profiles, one based on the multiplicative combination of Pov, BAF and CTD (Profile 1) and one for Pov, BAF and TE (Profile 2). We ranked the chemicals of the reference set by the aforementioned multiplicative combinations to create two 'rulers' ranging from 0 (minimum POP-likeness) to 100 (maximum POP-likeness), one for each profile. To rank the AMAP contaminants against each 'ruler', we merged the two databases and followed the same procedure per profile. The AMAP contaminants were appointed to a total of 160 bins each of which is indicated and bounded by the reference set chemicals. Finally, we assigned values ranging from 0 to 100 to the all the chemicals in the AMAP database, according to their relative ranking against the ruler, again with values of 0 indicating minimum POP-likeness and 100 maximum POP-likeness.

Results and discussion

As regards the reference set, the scores for the two profiles and, correspondingly, the two rulers, are depicted in Figure 3. The wide scatter indicates that the reference set includes chemicals for which the two different POP-likeness profiles describe two different modes of atmospheric transport and deposition. The lack of a correlation, along with the chemical space of the reference set, is evidence that the variability of the chemicals in this set is high enough for the set to be regarded as representative of a wide range of environmental fate profiles for chemicals. Figure 4 illustrates the ranking of the AMAP chemicals after the benchmarking process. In this case, there is a stronger correlation between the two different profiles, especially in the upper right-hand and the lower left-hand side of the graph where chemicals with maximum and, respectively, minimum POP-likeness are found. Such an agreement on the near-edge candidates' ranking implies that the least POP-like chemicals are most probably identified in the Arctic for reasons primarily related to their production/consumption patterns, while the most POP-like compounds should be further examined to determine whether their presence in the Arctic is a result of their physicochemical properties.

Both rulers identify as POP-like chemicals that include Mirex, some polychlorinated naphthalenes (octachloronaphthalene and all the pentachloronaphthalene congeners) and some polychlorodiphenyl ethers (mostly the tetrachlorodiphenyl ether congeners). Similarly, both rulers identify as non-POP-like a wide range of pharmaceuticals and personal care products as well as some phthalates. On the other hand, the two rulers rank differently some perfluorinated compounds (mainly alcohols and carboxylic acids) as well as many pharmaceuticals with log $K_{OA} > 8$ and log $K_{AW} < -2$. The source of these discrepancies is the low ranking of TE values that most of these chemicals have compared to their ranking of CTD values.

According to the Profile 1 ruler, 150 chemicals that are known Arctic contaminants described in the AMAP report are more POP-like than a dioxin (1,2,3,4,6,7,8-Heptachlorodibenzodioxin) and 44 chemicals are less POP-like than Malathion (a widely used insecticide). Similarly, based on the Profile 2 ruler, 140 of the AMAP contaminants are more POP-like than 1,2,3,4-tetrachlorobenzene, and 34 are less POP-like than propanal. Comparisons such as these illustrate the utility of our proposal to conduct screening hazard assessments by benchmarking against a set of chemicals with well-defined physico-chemical properties and environmental fate profiles.

Acknowledgements

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References

1. AMAP Assessment 2014: Contaminants of Emerging Concern in the Arctic (forthcoming AMAP report).
2. US EPA, Estimation Programs Interface Suite for Microsoft Windows v 4.11, United States Environmental Protection Agency, Washington, DC, USA, 2012.
3. Wegmann et al., Environmental Modelling & Software, 24, 2009

Figures

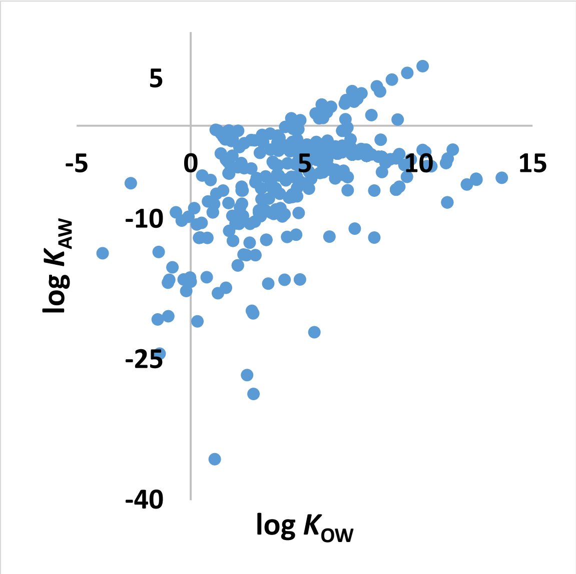

Figure 1 Chemical space of the 556 compounds found in the AMAP report.

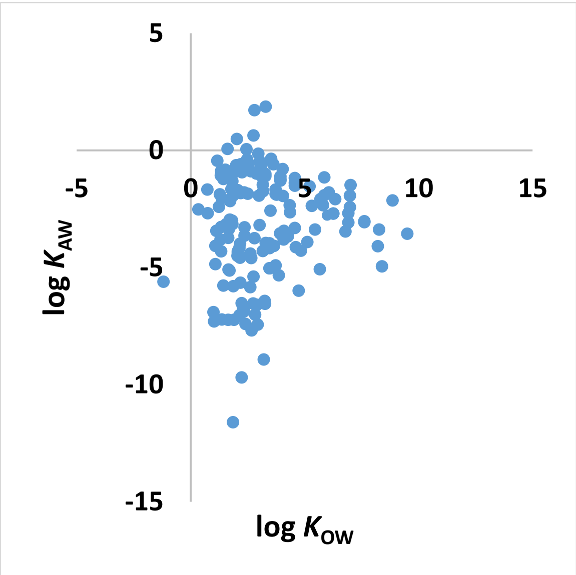

Figure 2 Chemical space of the 160 compounds of the reference set.

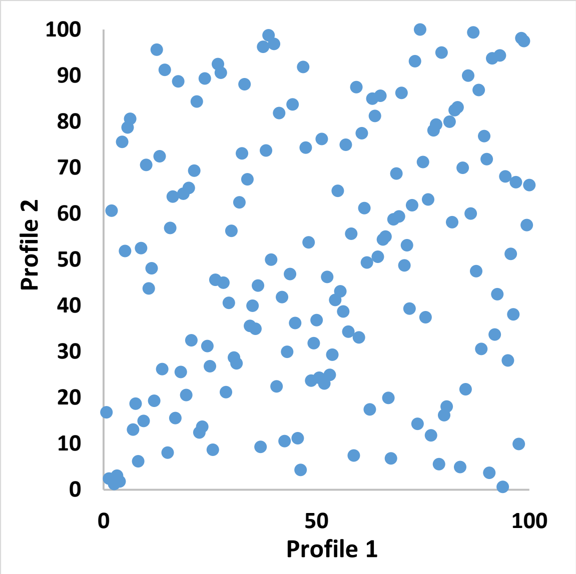

Figure 3 Comparative ranking of the 160 compounds of the reference set based on the different POP-likeness profiles

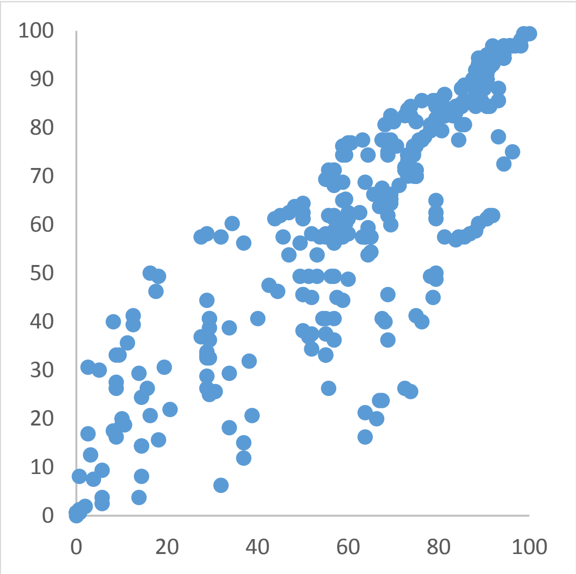

Figure 4 Comparative ranking of the two POP-likeness profiles for the 556 AMAP contaminants by their final score as a percentile relative to the reference set