Advances in integrated assessment of Arctic environmental pollution

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Work Package 4 – Integrating in-situ, satellite and model components for improved environmental assessment

Task 4.4. – Impact assessment and future exposure scenarios of pollutants in the Arctic

Deliverable 4.4.2

Version 001

Advances in integrated assessment of Arctic environmental pollution

Introduction

Predicting human exposure to an environmental contaminant based on its emissions is one of the great challenges of environmental chemistry. As a contribution to iCUPE, we successfully modelled concentrations of PCB 153 in breast milk at a global scale by combining the multimedia fate and transport model BETR Global 3.0 and the human exposure model ACC-HUMAN.[1] BETR Global 3.0 used emission estimates as inputs, and described how chemicals distributed in different parts of the global environment,[2] and ACC-HUMAN modelled chemical transfer along exposure vectors from environmental media to humans.[3]

However, BETR Global 3.0 assumes equilibrium partitioning of chemicals between the gas and particle phases, which is known to overestimate the fraction of low volatility chemicals (e.g. BDE 209) in the particle phase.[4-8] This would, in turn, bias modelled concentrations of such low volatile chemicals in air in remote regions such as Arctic and Antarctic towards low values, and ultimately result in underestimating chemical concentrations in human body. Within iCUPE, we developed a steady-state mass balance method to predict gas-particle concentration ratios of low-volatility chemicals. The method has been validated in a regional model (see Deliverable 4.4.1 - Report on Enhanced Modelling Capabilities for POPs), and also implemented in BETR Global 3.0 to produce a new version of the model, BETR Global 4.0 (see iCUPE Milestone 4.4.1 - Enhanced PMCAMx and BETR Global ready).

The human exposure model ACC-HUMAN assumes equilibrium partitioning between the gas and particle phases, like BETR Global 3.0 and most environmental chemical fate models. Because BETR Global 4.0 separates particles from gas phases outputs from the new model could not be readily used to drive the ACC-HUMAN exposure model, and implementing the steady-state gas-particle partitioning model in ACC-HUMAN was beyond the scope of our work.

However, our earlier work on PCB-153 demonstrated that human exposure to POPs in the Arctic is driven by accumulation through the marine food chain, which is in turn proportional to concentrations of POPs in air and marine water. In addition, there is a high uncertainty on the Arctic diet scenario, and are very little monitoring Arctic human milk data for comparison. Therefore, in this report, we compare concentrations of BDE 209 in air and marine water from the Arctic obtained from old version (BETR Global 3.0) and new version (BETR Global 4.0) of BETR Global, as a proxy measure to assess the effect of the improved gas-particle partitioning sub-model. Modelled concentrations of BDE 209 are compared with measurements to assess the performance of the new version of BETR Global.

Methods

Physicochemical properties

Physicochemical properties of BDE 209 are shown in Table 1.

Emissions

The spatially and temporally distributed emissions of BDE 209 were provided by Dr. Li Li (University of Nevada, Reno), based on the paper by Abbasi et al. 2019. The emission data provided by Dr. Li had a 15°×15° spatial resolution and 3 months temporal resolution from 1970 to 2050.[9] The paper of Abbasi et al. 2019 contains high and low scenarios of emissions. In this report we used the average of these two scenarios to drive the BETR Global 3.0 and 4.0 models. In addition, we assumed that 100% of the emissions are to the gas-phase in BETR Global 4.0. Assuming emissions to the gas phase leads to the largest differences when comparing BETR Global 3.0 with BETR Global 4.0, and also led to the best agreement between measurements and monitoring data for BDE 209 in our model development work (see Deliverable 4.4.1 - Report on Enhanced Modelling Capabilities for POPs).

Measurements

We collected measurement data from the Arctic from the literature for gas-particle concentration ratios, concentrations of BDE 209 in the air and concentrations of BDE 209 in marine water to evaluate the performance of the two versions of the model. Measurement data and references are shown in Tables 2-4.

Results and Discussion

Gas-particle concentration ratios

Gas-particle concentration ratios ($\log K_P^*$) are clearly overestimated by both the equilibrium model in BETR Global 3.0 and the steady-state model in BETR Global 4.0 (Figure 1). However the steady-state model provides results that are closer to measurements than the equilibrium model. The BETR Global 4.0 modelled logK_P^* are 3.5 orders of magnitude smaller than equilibrium logK_P^* in Alert and 1.5 orders of magnitude in Toolik Lake, which are significantly closer to measurement data.

Since logK_P^* near sources is strongly affected by the phase of emissions (ie, whether emission occurs in the particle or gas phase), comparing two regions in the Arctic, Alert which is far away from sources and Toolik Lake which is nearer to sources is helpful for interpretation. LogK_P^* calculated by BETR Global 4.0 decreases over time at Alert but remains constant in Toolik Lake (Figure 1). In the end of the simulation period, logK_P^* in both regions approaches the same value, of approximately 2.5.

The different behaviours of BETR Global 4.0 modelled logK_P^* in Alert and Toolik Lake are caused by the effect of phases of emissions. Based on our study in Deliverable 4.4.1, when 100% emissions are particle-bound, BETR Global 4.0 modelled logK_P^* are the same as equilibrium logK_P^*, and logK_P^* decreases when the fraction of gas phase emissions increases. In Toolik Lake, logK_P^* remains constant over time because local sources are dominant and are assumed to be 100% to the gas phase. However, at Alert where there is no local source, BETR Global modelled logK_P^* is close to the equilibrium logK_P^* in the beginning of the simulation period and then decreases over time. This is because at the beginning of the simulation period the source of BDE 209 to Alert is fine particles transported from the other cells. A potential explanation for the change over time is that as the simulation time increases, local emissions of BDE-209 to the gas phase increase near Alert due to increasing importance of secondary volatilization sources, which in turn causes logK_P^* to decrease. Such an explanation was also proposed by the authors of the study where the gas-particle partition ratio data are reported[15].

BETR Global 4.0 modelled logK_P^* are in better agreement with measurements than BETR Global 3.0, but are still 3 orders of magnitude larger than the measured values. Bias in some parameters used in the model may explain some of the over-prediction (please see details of model uncertainty and sensitivity n Deliverable 4.4.1). However, possible measurement bias can also contribute to the discrepancy. It is well known that accurate and simultaneous measurements of gas- and particle concentrations of low volatile chemicals is notoriously challenging over the relevant atmospheric time scales.[10-13] This is particularly true given the semi-volatile nature of the species in question together with their affinity with the polyurethane typically used in the sampling setups.[10]

Concentrations of BDE 209 in the Arctic air and marine

BETR Global 4.0 modelled concentrations of BDE 209 in the fine particle phase are 2-3 orders of magnitude larger than they are in gas phase and coarse particle phase throughout the simulation (Figure 2a). The total average concentrations of BDE 209 in the Arctic air simulated by BETR Global 4.0 is one order of magnitude larger than in BETR Global 3.0, which demonstrates that the new steady-state model predicts more efficient transport of BDE 209. The higher concentrations in the Arctic air obtained from BETR Global 4.0 in turn lead to higher concentrations in Arctic marine water in BETR Global 4.0 compared to BETR Global 3.0.

Both BETR Global 3.0 and BETR Global 4.0 tend to over-estimate the measured concentrations of BDE 209 in Arctic air (Figure 2a), while results from the two versions of the model lie on either side of measured concentrations in Arctic marine water (Figure 2b). Given the small amount of measurement data and the high variability it exhibits over short time scales, it is difficult to draw firm conclusions about the relative model performance from these comparisons.

Since the exposures through the inhalation and the Arctic marine food chain are proportional to concentrations in the Arctic air and marine water, respectively, concentrations in human milk obtained from BETR Global 4.0 should be 2-3 orders larger than they are in BETR Global 3.0. However, there are very little monitoring data for Arctic human milk data for comparison, so more experimental work are needed to determine if model performance at predicting internal body concentrations of BDE 209 has been improved in BETR Global 4.0.

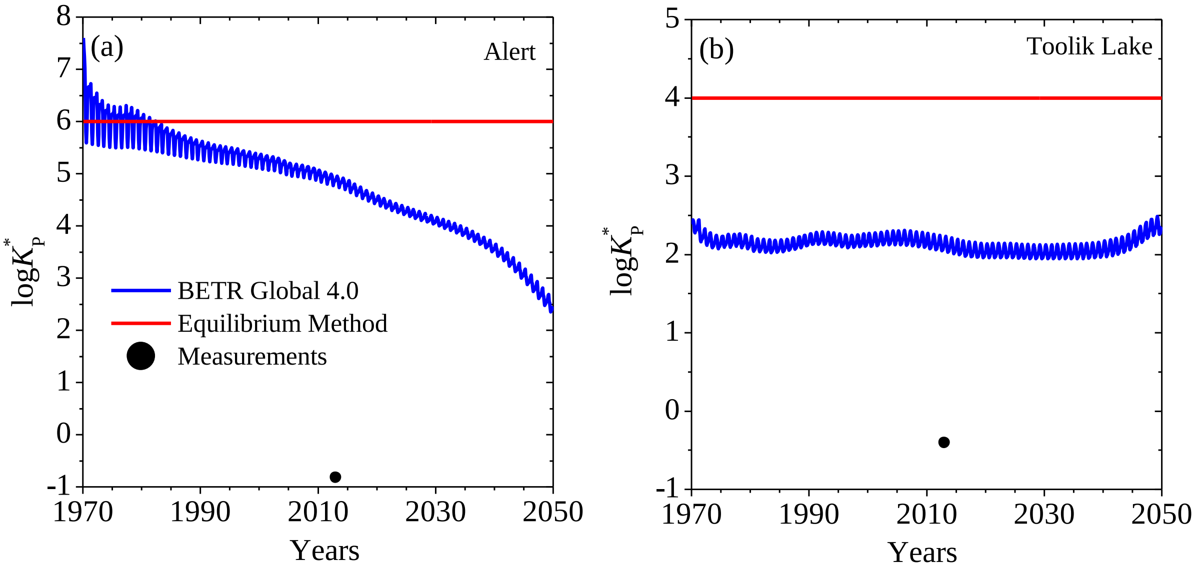

Figure 1. $\log K_P^*$ of BDE 209 in (a) Alert and (b) Toolik Lake.

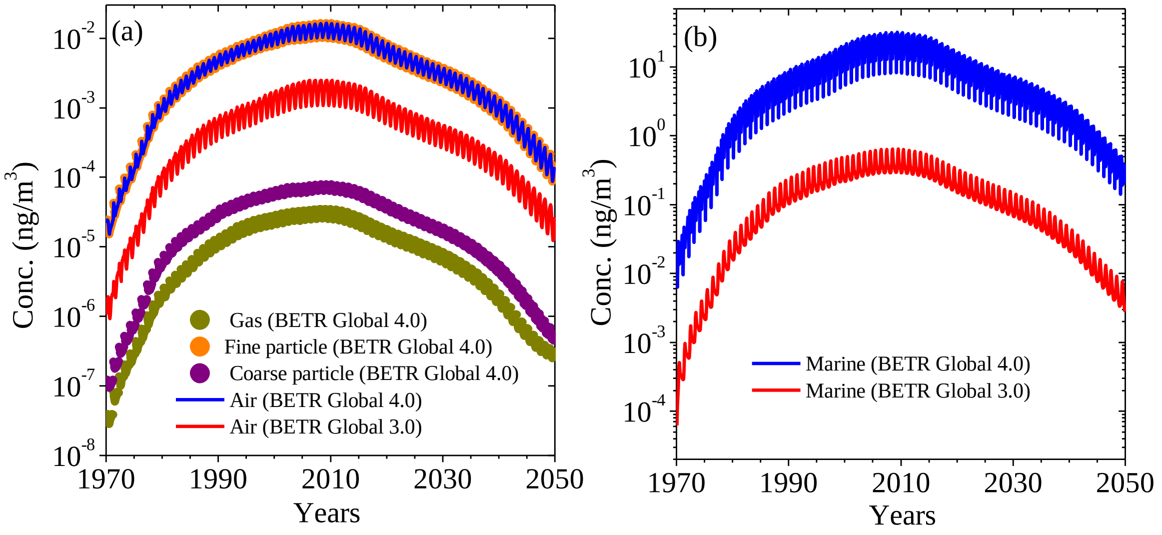

Figure 2. Average concentrations of BDE 209 in the Arctic (a) air and (b) marine.

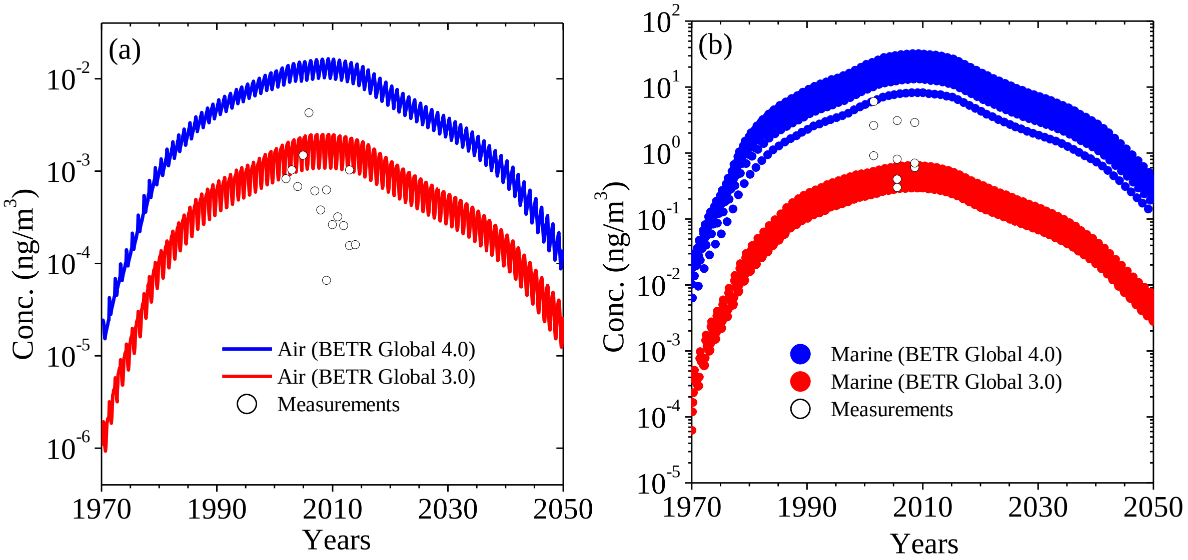

Figure 3. Comparison of modelled results with measurement data.

Table 1. Physicochemical properties of BDE209

Molecular mass (*g/mol*)	959.2
Partitioning coefficient between air and water	-4.81
Partitioning coefficient between octanol and water	9.97
Partitioning coefficient between octanol and air	16.8
Degradation half-life in gas phase (*h*)	7632
Degradation half-life in fine particle phase (*h*)	0
Degradation half-life in coarse particle phase(*h*)	0
Degradation half-life in vegetable (*h*)	37992
Degradation half-life in freshwater (*h*)	37992
Degradation half-life in ocean (*h*)	37992
Degradation half-life in soil (*h*)	75960
Degradation half-life in sediment (*h*)	228000
Internal energy of phase change octanol-air (*J/mol*)	-145000
Internal energy of phase change octanol-water (*J/mol*)	-80000
Activation energy in air (*J/mol*)	10000
Activation energy in fine particle (*J/mol*)	110000
Activation energy in coarse particle (*J/mol*)	110000
Activation energy in vegetable (*J/mol*)	20000

Activation energy in freshwater (*J*/*mol*)	20000
Activation energy in ocean (*J*/*mol*)	20000
Activation energy in soil (*J*/*mol*)	20000
Activation energy in sediment (*J*/*mol*)	20000

Table 2. Measurement data for gas-particle concentration ratios.

Location	Years	logK_P*
Alert	2013	-0.82[14]
Toolik Lake	2013	-0.4[15]

Table 3. Measurement data for concentrations of BDE 209 in the air.[9]

Location	Years	air concentrations (ng/m^3)
Toolik Lake	2013	1.03E-03
Greenland east	2009	6.50E-05
Arctic Canada	2002	8.20E-04
Arctic Canada	2003	1.03E-03
Arctic Canada	2004	6.73E-04
Arctic Canada	2005	1.47E-03
Arctic Canada	2006	4.24E-03
Arctic Canada	2007	6.03E-04
Arctic Canada	2008	3.78E-04
Arctic Canada	2009	6.21E-04
Arctic Canada	2010	2.60E-04
Arctic Canada	2011	3.18E-04
Arctic Canada	2012	2.56E-04
Arctic Canada	2013	1.54E-04
Arctic Canada	2014	1.58E-04

Table 4. Measurement data for concentrations of BDE 209 in marine water.[16]

Location	Years	marine concentrations (ng/m^3)
Chukchi sea	2005	0.8
East Siberian Sea	2008	0.6
Laptev Sea	2008	2.9
Kara Sea	2008	0.7
Barents Sea	2001	2.6
Norwegian Sea	2001	6

Beaufort Sea	2005	3.1
SNCAA	2005	0.4
Central Arctic Ocean Basin	2001	0.9
East of Greenland	2005	0.3

References

1. McLachlan, M. S.; Undeman, E.; Zhao, F. Y.; MacLeod, M., Predicting global scale exposure of humans to PCB 153 from historical emissions. *Environmental Science-Processes & Impacts* **2018,** *20* (5), 747-756.Z

2. MacLeod, M.; von Waldow, H.; Tay, P.; Armitage, J. M.; Wohrnschimmel, H.; Riley, W. J.; McKone, T. E.; Hungerbuhler, K., BETR global - A geographically-explicit global-scale multimedia contaminant fate model. *Environ. Pollut.* **2011,** *159*, 1442-1445.

3. Czub, G.; McLachlan, M. S., A food chain model to predict the levels of lipophilic organic contaminants in humans. *Environmental Toxicology and Chemistry* **2004,** *23* (10), 2356-2366.

4. Mackay, D.; Celsie, A. K. D.; Parnis, J. M., Kinetic Delay in Partitioning and Parallel Particle Pathways: Underappreciated Aspects of Environmental Transport. *Environmental Science & Technology* **2019,** *53* (1), 234-241.

5. Shiraiwa, M.; Seinfeld, J. H., Equilibration timescale of atmospheric secondary organic aerosol partitioning. *Geophysical Research Letters* **2012,** *39*.

6. Riipinen, I.; Pierce, J. R.; Donahue, N. M.; Pandis, S. N., Equilibration time scales of organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics. *Atmospheric Environment* **2010,** *44* (5), 597-607.

7. Cetin, B.; Odabasi, M., Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. *Chemosphere* **2008,** *71*, 1067-1078.

8. Saleh, R.; Donahue, N. M.; Robinson, A. L., Time Scales for Gas-Particle Partitioning Equilibration of Secondary Organic Aerosol Formed from Alpha-Pinene Ozonolysis. *Environmental Science & Technology* **2013,** *47* (11), 5588-5594.

9. Abbasi, G.; Li, L.; Breivik, K., Global Historical Stocks and Emissions of PBDEs. *Environmental Science & Technology* **2019,** *53* (11), 6330-6340.

10. Mohr, C.; Thornton, J. A.; Heitto, A.; Lopez-Hilfiker, F. D.; Lutz, A.; Riipinen, I.; Hong, J.; Donahue, N. M.; Hallquist, M.; Petaja, T.; Kulmala, M.; Yli-Juuti, T., Molecular identification of organic vapors driving atmospheric nanoparticle growth. *Nature Communications* **2019,** *10*.

11. Hytonen, K.; Yli-Pirila, P.; Tissari, J.; Grohn, A.; Riipinen, I.; Lehtinen, K. E. J.; Jokiniemi, J., Gas-Particle Distribution of PAHs in Wood Combustion Emission Determined with Annular Denuders, Filter, and Polyurethane Foam Adsorbent. *Aerosol Science and Technology* **2009,** *43* (5), 442-454.

12. Bilde, M.; Barsanti, K.; Booth, M.; Cappa, C. D.; Donahue, N. M.; Emanuelsson, E. U.; McFiggans, G.; Krieger, U. K.; Marcolli, C.; Tropping, D.; Ziemann, P.; Barley, M.; Clegg, S.; Dennis-Smither, B.; Hallquist, M.; Hallquist, A. M.; Khlystov, A.; Kulmala, M.; Mogensen, D.; Percival, C. J.; Pope, F.; Reid, J. P.; da Silva, M.; Rosenoern, T.; Salo, K.; Soonsin, V. P.; Yli-Juuti, T.; Prisle, N. L.; Pagels, J.; Rarey, J.; Zardini, A. A.; Riipinen, I., Saturation Vapor Pressures and Transition Enthalpies of Low-Volatility Organic Molecules of Atmospheric Relevance: From Dicarboxylic Acids to Complex Mixtures. *Chemical Reviews* **2015,** *115* (10), 4115-4156.

13. Krieger, U. K.; Siegrist, F.; Marcolli, C.; Emanuelsson, E. U.; Gobel, F. M.; Bilde, M.; Marsh, A.; Reid, J. P.; Huisman, A. J.; Riipinen, I.; Hyttinen, N.; Myllys, N.; Kurten, T.; Bannan, T.; Percival, C. J.; Topping, D., A reference data set for validating vapor pressure measurement techniques: homologous series of polyethylene glycols. *Atmospheric Measurement Techniques* **2018,** *11* (1), 49-63.

14. Muir, D.; Kurt Karakus, P.; Stow, J., NCP 2013: Canadian Arctic Contaminants Assessment Report On Persistent Organic Pollutants – 2013. *Northern Contaminants Program, Aboriginal Affairs and Northern Development Canada, Ottawa, ON, xxiii C 487 pp. C Annex* **2013**.

15. Davie-Martin, C. L.; Hageman, K. J.; Chin, Y. P.; Nistor, B. J.; Hung, H., Concentrations, gas-particle distributions, and source indicator analysis of brominated flame retardants in air at Toolik Lake, Arctic Alaska. *Environ. Sci.-Process Impacts* **2016,** *18*, 1274-1284.

16. Salvado, J. A.; Sobek, A.; Carrizo, D.; Gustafsson, O., Observation-Based Assessment of PBDE Loads in Arctic Ocean Waters. *Environmental Science & Technology* **2016,** *50* (5), 2236-2245.