The Role of Snow in the Environmental Fate of PBDEs

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Introduction. Falling snow and a seasonal snow cover have the potential to greatly affect the air-surface exchange of semi-volatile organic chemicals (SVOCs), such as the poly-brominated diphenylethers (PBDEs). Here we use a combination of (1) scavenging efficiency calculations, (2) simulations with a multimedia environmental fate model, which includes a seasonally changing snow compartment, and (3) field measurements of air concentrations during the snow melt season in Southern Ontario, to explore the role that snow may play in the environmental fate of brominated diphenyl ethers, in particular 2,2',4,4'-tetrabrominated diphenyl ether (BDE-47).

Scavenging of BDE-47 by Rain and Snow. Lei and Wania[1] recently presented calculations regarding the influence of temperature on the potential for precipitation to scavenge SVOCs from the atmosphere. If vapor pressure (P_L), air-water partitioning coefficient (K_{AW}), water surface-air and snow surface-air sorption coefficient (K_{IA}, K_{SA}) are known for a SVOC as a function of temperature, then it is possible to estimate the dominant deposition pathways, the vapor scavenging efficiency, and the total scavenging efficiency in the environmentally relevant temperature range[1]. For BDE-47 these partitioning parameters were derived as follows: P_L from Wong et al.[2], K_{AW} from Wania and Dugani[3], and K_{IA} and K_{SA} using predictive relationships presented by Roth et al.[4,5].

At temperatures above freezing, the log particle-air partition coefficient for BDE-47 (log $K_{particle/air}$) falls between 11 and 12.5, whereas the log rain droplet-air distribution coefficient (log $K_{rain/air}$) is around 3.5 to 5. This implies that BDE-47 is deposited by dry gaseous deposition, wet and dry particle deposition, and wet gaseous deposition with very similar efficiency[1]. At temperatures below freezing, log $K_{particle/air}$ ranges from 12.5 to 14, and the log snow flake-air distribution coefficient log $K_{snow/air}$ from 6 to 8. This means that gas scavenging by sorption to the snow surface and particle deposition processes likely dominate the atmospheric deposition of BDE-47 at sub-zero temperatures[1]. Using these partitioning properties and assumptions and parameters reported by Lei and Wania[1], total scavenging ratios (W_{tot}) and the percentage of scavenging which occurs in the vapor phase were calculated for the temperature range between -25 to +25 °C (Fig. 1). The scavenging efficiency, W_{tot}, for BDE-47 is high, greatly increases with decreasing temperature, and is considerably higher for snow than for rain. BDE-47 sorbs strongly to the water and snow surface, and scavenging efficiencies and the mechanism of

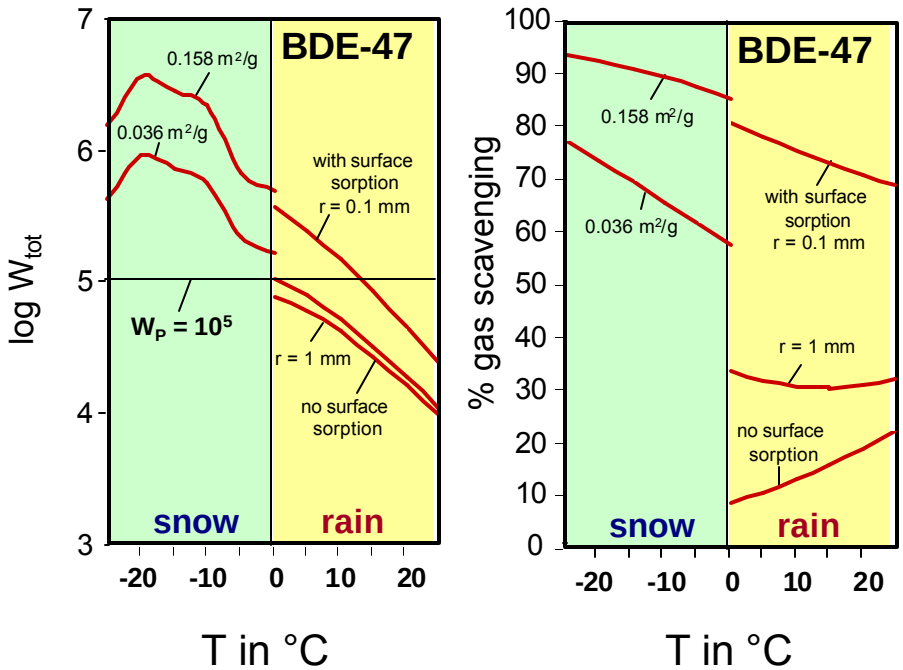

Fig. 1 Total precipitation scavenging efficiencies, W_{tot}, and percentage of precipitation scavenging occurring in the vapor phase calculated for BDE-47 in the temperature range -25 to +25 °C, using the method described by Lei and Wania[1].

scavenging are thus highly dependent on the specific snow surface area and the size of the rain droplets.

Fate of PBDEs in a Seasonal Snow Pack. Daly and Wania[6] recently modified the dynamic level IV fugacity-based multimedia fate and transport model CoZMo-POP by including a dynamic water balance and seasonal snow pack compartment. As temperatures drop below 0°C, the model treats precipitation as snow and a homogeneous snow pack compartment develops during the winter. As temperatures rise above freezing during the early spring, the snow pack compartment shrinks and eventually disappears[6]. This model was used to evaluate the mass transfer of PBDEs into and out of a typical seasonal snow pack. Pathways being considered include vapor and particle scavenging during a snowfall event, subsequent dry gaseous and particle deposition to the existing snow pack, and rain falling onto the melting snow pack during the snowmelt period.

The model suggests that more than half of the total amount of both BDE-47 and decaBDE (BDE-209) emitted into the atmosphere over a one-year period will be deposited to the snow pack. Vapor scavenging is the dominant route of entry to the snow pack for BDE-47. For BDE-209, an extremely involatile chemical, wet and dry particle deposition processes contribute greatly to its mass transfer from the atmosphere to the developing snow pack. In agreement with the scavenging calculations above, the calculated relative importance of the various pathways into the snow pack is strongly dependent on the numerical values for the snow surface area and the particle scavenging ratio for snow. Thus, the relative importance of the deposition mechanisms may vary for different snow fall events and types. Chemicals are removed from the snow pack by

degradation, volatilization, runoff with the melt water and transfer to soils and fresh water with particles. For BDE-47 and 209, only the last of these processes is relevant, indicating that the fate of these sparingly soluble and highly involatile chemicals in the snow pack is governed by what happens to the particles to which they sorb.

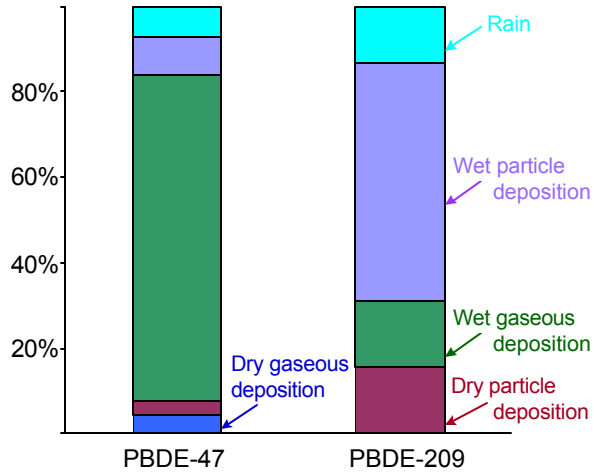

Fig. 2 Relative contribution of different path-ways into a seasonal snow pack.[6]

Measurement of PBDE Air Concentrations During Snow Melt. Seasonal or short-term variability of SVOC air concentrations are likely highest in the winter-spring period, when temperature, vegetation and snow cover are subject to significant change. To study this variability, Gouin et al.[7] collected high-volume air samples during the winter and spring of 2002 in a forested location at the James McLean Oliver Ecological Centre (JMOEC), located 115 km NE of Toronto. 24-hour air samples were collected every 6 days from January 23 to April 11, 2002, daily from April 11 to 28, 2002, a period of rapidly warming temperatures, and again every 6 days from May 4 to June 6, 2002. The temporal trend of the air concentrations of BDE-47 showed a period of elevated concentrations immediately following snow melt, but prior to bud burst (Fig. 3)[7].

Model vs. Measurements. The model by Daly and Wania[6] was used to ascertain if it is possible to reproduce the observed peak in atmospheric concentrations for BDE-47 described by Gouin et al.[7] and thus elucidate its probable causes. Meteorological data collected at JMOEC were used as model input parameters, as were other parameters describing the forest and soil in the area. A steady emission to air corresponding to an inflow of air with a constant concentration was assumed. The measured time profile of air concentrations at JMOEC were compared to simulation results obtained with the model[7] (Fig. 3). Three sets of model simulations were performed to investigate the mechanisms influencing the observed "spring pulse". In the most realistic scenario the model environment contained both snow pack and forest canopy compartments. Additional simulations were performed without the snow pack and without the forest compartment. The model simulation that includes both a snow and forest compartment, predicted a period of elevated concentrations between days 105 and 115, which corresponds to the time after snow melt (day 101) but prior to bud burst (day 117). The measured air concentration maxima also fell into this time period, although there are some discrepancies with respect to the relative size and exact timing of these maxima (Fig. 3).

The simulated BDE-47 peak occurs in the time period after snow melt and before the emergence of new foliage (day 110 to 115), and is a result of deposition rates being lower during this interval than either before snowmelt or after bud burst. Prior to snowmelt,

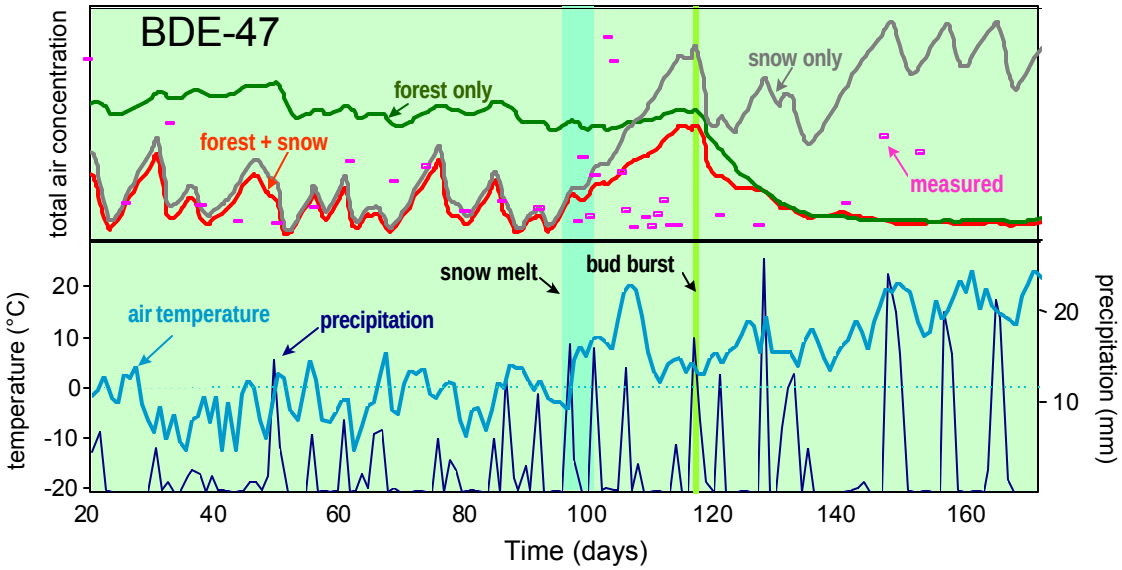

Fig. 3 Comparison of the temporal trends for simulated and measured air concentrations of BDE-47. Results for three separate model simulations are shown. Model with (i) both a snow and forest compartment (red line), (ii) only snow (grey line), and (iii) only forest (green line). Also shown are the ambient air temperatures and precipitation rate, and the dates for the period of snowmelt (days 98 – 101) and the date of bud burst (day 117).

efficient snow scavenging reduces air concentrations (grey line in Fig. 3 is lower prior to snow melt than after). After bud-burst, efficient uptake in new foliage again increases deposition rates (green line in Fig. 3 lower after bud-burst than before). In the warm and relatively dry interval, neither of these two deposition mechanisms is operating and BDE-47 levels temporarily increase (red line in Fig. 3). The timing of the measured BDE-47 concentration peak, however, occurs earlier than in the simulated time profile and coincides with a peak in temperature. Likely reasons for the discrepancy between observed and model results are either due to direct air mass transport from a warmer source region or evaporation of BDE-47 from the terrestrial surface, newly exposed after snow melt, or a combination of both.

References

[1] Lei, Y.D., F. Wania. *Atmos. Environ.* **2004**, in press.
[2] Wong, A., Y. D. Lei, M. Alaee, F. Wania. *J. Chem. Eng. Data* **2001**, *46*, 239-242.
[3] Wania, F., C. B. Dugani. *Environ. Toxicol. Chem.* **2003**, *22*, 1252-1261.
[4] Roth, C.M., K.-U. Goss, R.P. Schwarzenbach. *J. Colloid Interf. Sci.* **2002**, *252*, 21-30.
[5] Roth, C.M., K.-U. Goss, R.P. Schwarzenbach. *Environ. Sci. Technol.* **2004**, *38*, in press.
[6] Daly, G.L., Wania, F., *Environ. Sci. Technol.* **2004**, *38*, in press.
[7] Gouin, T., T. Harner, G.L. Daly, F. Wania, D. Mackay, K.C. Jones. *Atmos. Environ.*, submitted.
[8] Gouin, T., G.O. Thomas, I. Cousins, J. Barber, D. Mackay, K.C. Jones. *Environ. Sci. Technol.* **2002**, *36*, 1426-1434