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Melting scenario affects the dynamics of polycyclic aromatic hydrocarbons released from snowpack

Shasha Liu\textsuperscript{1,2}, Zucheng Wang\textsuperscript{1,2} and Xiaoyun Xu\textsuperscript{1,2}

\textsuperscript{1} Key Laboratory of Geographical Processes and Ecological Security in Changbai Mountains, Ministry of Education, Northeast Normal University, Changchun, Jilin, People’s Republic of China

\textsuperscript{2} Jilin Provincial Key Laboratory for Wetland Ecological Processes and Environmental Change in the Changbai Mountains, People’s Republic of China

E-mail: wangzc100@nenu.edu.cn

Abstract

Melting snowpack can release semi-volatile organic contaminants (SVOCs) to both terrestrial and aquatic ecosystems, resulting in high ecological risk. The dynamics of polycyclic aromatic hydrocarbon (PAH) released from snowpack under controlled laboratory (intense melting) and field (melt/freeze melting) snowmelt experiments was investigated in this study. In the laboratory: dissolved organic carbon (DOC) controlled the first flush of dissolved PAHs released from snowpack, except for napthelene, which is also affected by its solubility. The particles released early from snowpack usually contained high PAH concentrations (more than 100 μg g$^{-1}$) and those released at the end contained low PAH concentrations (<20 μg g$^{-1}$). The total PAH release pattern was determined by composition of all PAHs, including type 2 enrichment with a final peak and type 4 enrichment with double-peak. In field melting: all dissolved PAHs were released constantly, except napthelene, which also showed a first flush but to a lesser extent. DOC controlled the release pattern of all detected dissolved PAHs from snowpack. High PAH concentrations were observed in particles released from snowpack at both the beginning and the end of the melting event. Concentrations of both total PAHs and PAH compositions in meltwater showed an increasing trend with melting time (from 1.3 to 4.0 μg l$^{-1}$ and from 1.7 to 5.3 μg l$^{-1}$ in meltwater from each of the two snowpacks), which coincided with Type 3 enrichment. Overall, our results suggest intense melting of snowpack results in the shift of some hydrophobic PAH compositions from Type 2 to Type 4 enrichment, depending on their partition coefficients. In contrast, melting with melt/freeze cycles may cause the shift of PAHs from Type 2 to Type 3 enrichment. Our study indicates changes of the melting scenarios due to global warming could affect dynamics of SVOCs released from snowpack, which is useful for risk management for water and soil quality.

1. Introduction

Semi-volatile organic contaminants (SVOCs) are chemical pollutants of high environmental and human health concern because of their toxicity and bioaccumulation (Sharma \textit{et al} 2015). They include polychlorinated biphenyls, dichlorodiphenyldichloroethane and the polycyclic aromatic hydrocarbons (PAHs). They are typically emitted to the atmosphere from anthropogenic sources and transported over long distances either in the gaseous phase or adsorbed to particles in the atmosphere (Ma \textit{et al} 2011, Oliveira \textit{et al} 2016). Subsequently, they are deposited on the land surface through dry and wet precipitation and preferentially absorbed to soil/sediment particles because of their hydrophobicity (Ravindra \textit{et al} 2008). Furthermore, they may be degraded by certain bacteria or photolyzed by sunlight during transportation or accumulated in both terrestrial and aquatic ecosystems through the food chain, posing a high ecological risk (Meyer and Wania 2008, Wang \textit{et al} 2016, Wawra \textit{et al} 2018).

In northern areas, snow can influence the fate of SVOCs in the environment in a multitude of ways (Wania \textit{et al} 1999, Macdonald \textit{et al} 2002, Meyer \textit{et al} 2006),
especially through seasonal snowpack. For example, atmospheric SVOCs scavenged from atmosphere by snowfall could be preserved in seasonal snowpack for long time (Franz and Eisenreich 1998, Meyer and Wania 2008), reducing the volatilization and degradation of SVOCs because of the low temperature. The accumulated SVOCs in seasonal snowpack are then released into environment over a short time during the snowmelting period (Meyer et al 2006), causing a flush of contaminants. Previous studies have reported high concentrations of SVOCs in urban snowpack (Wei et al 2017), and observed concentration peaks of contaminants in various environmental mediums coinciding with the snow-melt-related pulses in temperate regions resulting in much higher ecotoxicological effects to organisms than expected because of an insufficient scientific response to revealing release pattern of organic contaminant from snowpack during snowmelt. In particular, a combination of field work and controlled laboratory studies on eluviation of organic contaminant from snowpack during snowmelting is imperative (Meyer and Wania 2008). The investigated contaminant data in snowpack therefore have not been effectively interpreted because of an insufficient understanding regarding the interaction between organic chemicals and melting snow (Meyer et al 2006).

PAHs are a class of carcinogenic, mutagenic and teratogenic SVOC, which contains more than two benzenes. The 16 PAHs studied in this study were listed by United States Environmental Protection Agency (EPA) as priority pollutants. Although PAHs can originate from both petrogenic and pyrogenic sources, most PAHs in the urban environment originate from pyrogenic sources associated with energy consumption and energy generation by human activities, such as incomplete combustion of coal and fossil fuels, vehicle emissions, and tailpipe emissions from factories (Yunker et al 2002, Hu et al 2011). Therefore, PAHs will be continuously emitted into the air and widely distributed in the atmosphere for a long time. Several studies have found high concentrations of atmospheric PAHs in both the gaseous and particle phases in North China, especially in winter when domestic heating consumes a large amount of coal (Liu et al 2007, Liu et al 2008). Consistently, high concentrations of PAHs have also been observed in seasonal snowpack in Northeast China because of effective scavenging by snowfall (Wei et al 2017). Further studies have suggested the increase of PAH concentrations in urban watershed during snowmelt. Considering highly sensitive to the PAHs...
effect of fish embryos and larvae (Hodson 2017), PAHs released from snowpack indicates high ecological risk during the melting season to urban water environment.

Although previous studies have found dissolved organic carbon (DOC) affect PAH transportation in water, recent studies suggest that chemical partitioning of PAHs, snow pack and melt characteristics play more important roles in PAH release from snowpack (Meyer et al 2006, 2009a, 2009b). As PAHs are preferentially associated with organic matter in particles, the release of PAHs from snowpack can be expected to coincide with Type 2 enrichment during snowmelt. However, global warming changes the melting scenarios from frequent melt/freeze cycles to intense melting, which may affect the PAH release pattern from snowpack. This study therefore takes PAHs as an example to investigate the release pattern of SVOCs from snowpack under laboratory (intense melting) and field (melt/freeze melting) conditions. The aim of this study was to investigate the release patterns of PAHs from snowpack according to different melting scenarios. This study is not only helpful to understand PAH release pattern during in different condition but also useful to predict PAH risk of water environment and take actions during snowmelt.

2. Materials and methods

2.1. Chemicals and reagent

All organic solvents (HPLC grade) used in sample processing were purchased from Macklin. Water was purified by a Milli-Q system. The mixture of 16 PAHs standard was dissolved in dichloromethane (DCM), and the initial concentration was 2000 mg l$^{-1}$. Decafluorobiphenyl is at purity >99%, which was diluted with hexane to the concentration level at 10 mg l$^{-1}$. Silica gel and anhydrous sodium sulfate were AR grade.

2.2. Sampler design and sample collection

The snow-can was modified from the design of Herbert et al (2004), and made from stainless steel with a cap to prevent additional PAH deposition to snowpack during snowmelting (figure 1). Its volume exceeded more than 40 l, making it suitable for sampling low-density snow (e.g. <0.25 kg l$^{-1}$), because larger snow volumes can ensure enough collection times of meltwater during snowmelt to establish curves of PAH release pattern. In this study, about 50 l snow samples were added to each snow-can to obtain about 20 l meltwater totally. And more than 12 times meltwater collection was conducted from each snow-can during snowmelt. Two-way Swagelok taps were fitted to the base of the snow-can, allowing drainage of meltwater. The snow-can was rinsed with DCM before use.

Snow samples were collected from the same area of campus of Northeast Normal University (125°19′51″E, 43°51′45″N) prior to snowmelting in March 2018 and filled into the snow-can using a solvent-cleaned stainless-steel shovel. The snow-cans were then put in to the open ground in campus and laboratory (10 °C, consistent room temperature) to allow the snowmelt, respectively. Duplicate snow-cans were conducted in both the field and the laboratory (W1 and W2 for the field, and N1 and N2 for the laboratory). The meltwater was collected every few hours, and the volume was determined and recorded. Saturated mercuric chloride was added to inhibit PAH degradation in meltwater. The snow samples were completely melted for about 90 h in the laboratory, whereas in the field they were subjected to several melt/freeze cycles for over 200 h until melting. If the meltwater was less than 500 ml in one collection, it was combined with the next collection. The meltwater was then filtered by pre-incinerated (450 °C for 4 h) and pre-weighed glass fiber filters (pore size = 0.7 μm). The 500 ml of meltwater from each collection or combined collection was used for PAH analysis. Filters were dried and weighed after filtering, and preserved in a desiccator before PAH analysis.

Figure 1. Diagram of the snow-can.
2.3. PAH extraction and analysis
The following 16 PAHs listed as priority pollutants by both United States Environmental Protection Agency (EPA) and the European Community were analyzed: naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (An), fluoranthene (Flua), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k,j]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3]pyrene (IndP), dibenzo[a,h]anthracene (DahA) and benzo[g,h,i]perylene (BghiP). The first six PAHs with 2–3 ring benzene were defined as low molecular weight (LMW) PAHs, while the other PAHs were named as high molecular weight (HMW) PAHs. Decafluorobiphenyl was used as the surrogate standard for recovery calculations. The filtered meltwater was mixed with 50 μl of 10 mg l⁻¹ surrogate solution, and extracted by 50 ml DCM for three times (150 ml DCM were used totally for each filtered meltwater samples). The extracts were combined and purified by passing through a column of 10 g anhydrous sodium sulfate, and replaced by hexane and condensed into 1 ml using a rotary evaporator, and stored in a freezer at −18 °C before PAH analysis.

PAH extraction from particles on filters followed a protocol from our previous study (Wei et al. 2017). In brief, dried filter pieces with surrogate standard solution (50 μl of 10 mg l⁻¹) were extracted with accelerated solvent extraction (ASE-350) using a mixture of acetone and DCM (1:1 v/v). The extraction cells were heated to 100 °C until a pressure of 10 MPa was reached. The static time was 5 min, the flush volume was 60%, and the purge time was 90 s. The final volume of the extract was further concentrated to 2 ml by a rotary evaporator. The analytes were then purified using a column packed with activated silica gel and topped with 1 cm of anhydrous sodium sulfate. The beginning eluent with 15 ml of hexane was discarded. The following eluent with 70 ml of dichloromethane/hexane (3:7 v/v) was collected. Finally, this solution was reduced and exchanged with hexane to about 1 ml by a rotary evaporator, and stored in a freezer at −18 °C for later gas chromatography–mass spectrometry (GC/MS) analysis.

PAHs were analyzed using GC/MS (ThermoFisher Trace1310, SQS, USA). The GC/MS was equipped with a HP-5MS capillary column (30 m × 0.25 mm i.d., film thickness 0.25 μm), with helium as the carrier gas at a flow rate of 1 ml min⁻¹. We used a selective ion-monitoring mode to detect PAHs. Ions detected ranged from 126 to 279 atomic mass units, with a dwell time per ion of 200 ms. The oven temperature was maintained at 40 °C for 1 min, then increased to 270 °C at a rate of 10 °C min⁻¹, after which it was maintained at 270 °C for 20 min. The temperatures of the injector and detector were 260 °C and 230 °C, respectively. The injection volume was 1 μl, samples were injected in the splitless mode. All 16 PAHs were eluted from the GC column between 8 and 40 min.

2.4. DOC analysis
DOC was defined as the total organic carbon which passed through 0.7 μm filter (Whatman GF/F). DOC in filtered meltwater was determined by catalytic combustion (oxidation) method using a total organic carbon analyzer (OI Analytical MODEL 1030). Before analysis, filtered meltwater was acidified and sparged with purified air to removed inorganic carbon. DOC concentrations then were calculated using a calibration curve which ranged from 0 to 10 mg l⁻¹.

2.5. Quality assurance/quality control
The melting experiments were conducted in duplicate in both the laboratory and the field. Although the concentration values of each duplicate were different because of the different total PAH content, the PAH release trend from each duplicate snowpack was similar. The background contamination was determined in another blank experiment which conduct the same procedure as for the samples without samples. No PAHs were detected in our blank except for Nap. Thus, the blank values of Nap were subtracted for all samples. The surrogate recoveries of PAH composition were 80%–124% and 63%–114% for meltwater and particles, respectively. The limit of quantitation for PAH compositions ranged from 0.01 to 0.03 mg l⁻¹. The standard external method was used to calculate the concentrations of the 16 PAHs. The three-points smoothing method was used to draw figures of the PAH release pattern from snowpack in SigmaPlot 14.0.

3. Results and discussion
3.1. PAH release from snowpack under laboratory conditions
3.1.1. Dissolved PAH concentrations in meltwater released from snowpack
The dissolved PAH concentrations in the collected meltwater released from the N1 and N2 snowpack ranged from 0.3 to 1.1 and from 0.4 to 1.1 μg l⁻¹, respectively. The release pattern of total detected dissolved PAHs showed the highest concentrations at the early stage of melting and elevated concentrations at the end of melting (figure 2(a)). The released curve of total dissolved PAHs were mainly attributed to the release pattern of Nap which had relatively high water solubility (figure 2(b)). Nap can be absorbed by both the snow grain surface and particles in snowpack. On one hand, the portion that accumulated at the snow grain surface is easily dissolved in the downward percolating meltwater front (Meyer et al 2009a), resulting in the highest concentration at the early stage of snowmelt (Jonannessen and Henriksen 1978, Colbeck 1981). On the other hand, most particles and
the Nap accumulated on them are trapped by snowpack until the end of snowmelting because of the snow filter effect (Meyer et al. 2011). Consistent with this, higher concentrations of particles were also observed in the later meltwater than in the early meltwater in this study. In this case, particulate Nap can then be dissolved in meltwater because of its relative high solubility, causing elevated concentrations at the end of the snowmelt.

Other more hydrophobic PAHs were also mainly released at the beginning of melting; however, only a slight increase in concentrations was observed at the end of the melting event (figure 2(c)). Although the release pattern of these hydrophobic PAHs and Nap

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**Figure 2.** Released patterns of dissolved total PAHs (a), naphthalene (b) and PAHs except naphthalene (c) from snowpack melting in the laboratory.
was similar, the impact factors controlling their release may be different. Our results showed the significant correlation between these dissolved PAHs and DOC (figure 3(a), $r = 0.7$, $p < 0.01$). This was consistent with previous studies which also reported a good correlation between dissolved PAHs and DOC in water. Thus, association with DOC rather than dissolution in meltwater may determine dissolved PAH release from melting snow (Gschwend and Wu 1985, Chiou et al 2000). In contrast, neither DOC nor meltwater volume was correlated with Nap concentration, indicating both dissolution and partition mechanism contributed to dissolved Nap in the meltwater.

3.1.2. Particulate PAH concentrations in meltwater released from snowpack

PAHs can be redistributed among each phase (such as particulate, gaseous and aqueous phase) during melting, and would further reach equilibrium in meltwater after their release from the snowpack. Because of their hydrophobicity, PAHs are mainly in the particulate phase in meltwater. Most previous studies therefore focus on total particulate PAH concentrations in meltwater and few studies have investigated PAH concentrations in released particles from snowpack. PAHs in snowpack can be partitioned between ice interface and particles, and the relative capacity of ice interface and particles in snowpack determines where most of the organic chemicals will be found (Meyer and Wania 2008). PAHs are preferentially absorbed to the interface in fresh snow, whereas they shift to the particles as snow ages (Meyer and Wania 2008), resulting in high PAH concentrations in particles. Our results showed the particles released at the early stage of melting event contained more PAHs than those released at the end of the snowmelt (figure 4(a)). For example, the PAH concentration in early released particles from snowpack N1 was more than 100 $\mu$g g$^{-1}$, whereas it was less than 20 $\mu$g g$^{-1}$ at the end of melting event. Usually, small particles with a large surface area can absorb more PAHs, while large aggregates contain low PAH concentrations because of their small specific surface area. Under laboratory conditions, micro-soot particles may form aggregates to a lesser extent and fewer dirt cones are generated in snowpack because of consistently melting at
temperatures above 0 °C (Nakamura and Okada 1976, Drab et al 2002, Meyer et al 2009b). As a result, fine micro-soot particles with high PAH concentrations are moved by meltwater vertically toward the ground rather than perpendicular to the sloped surface of dirt cones (Meyer et al 2009b). In contrast, the large coagulates with low PAH concentrations, which are accumulated in the surface layer of the snowpack or on top of surface dirt cones, are washed out until the end of the melt (Schöndorf and Herrmann 1987).

The particle concentrations released from both N1 and N2 increased considerably with melting time, which is consistent with previous studies (figure 4(b)). For example, particle concentrations in meltwater of each collection increased from 0.01 to 0.16 g l⁻¹ from N1 snowpack. This can be attributed to efficient filter effect of snowpack in trapping the particles, which is rendered by snow densification during melting (Meyer et al 2009b). Because of the low density of particles at the start of the melting event, the particulate PAH concentrations in meltwater were lower at the beginning (figure 4(c)), although the concentrations of PAHs in particles were high. In general, the concentrations of particulate PAH increased with melting time with a reduction at the middle stage (figure 4(c)). Dissolved PAHs were released at the beginning of melting event because a large fraction of Nap and DOC associated PAHs are washed out from the snow grain surfaces by the early meltwater. In contrast, PAHs adsorbed to particles tended to be released toward the end of the melt period as particle-associated chemicals are efficiently retained within the snowpack until the end of melting.

3.1.3. Total PAH concentrations in meltwater released from snowpack

As PAHs are hydrophobic compounds, total PAH concentrations in meltwater are dominated by particulate PAHs, which accounted for more than 50% of total PAHs. Thus, the release pattern of PAHs from snowpack during a melting event should be consistent with that of Type 2 contaminants, which are characterized by a strong attachment to organic matter (Meyer and Wania 2008). Therefore, the PAHs are prevented from eluting from snowpack at the beginning of the melting event, and are removed in one strong pulse at the end of the melting event. Although enrichment of particle-bound substances such as PAHs at the end of the melting event declined because of the increased temperature in the laboratory (Meyer et al 2009b), our results showed high concentrations at the end of the melting event (figure 4(d)). However, our results also showed a higher concentration of total PAHs at the beginning stage of melting snowpack.

Figure 4. PAH concentrations in particles released from snowpack (a) and the particle concentrations (b), particulate PAH concentrations (c) and total PAH concentrations (d) in meltwater released from snowpack in the laboratory.
development (figure 4(d)). This is consistent with the release pattern of Type 4 contaminants, which show double peaks at the beginning and at the end of the melting event. This is likely to be related to the mixture of different PAHs. Some PAHs, such as Flu (figure S1(a) is available online at stacks.iop.org/ERL/15/064025/mmedia), are fairly equally distributed between the dissolved phase and the particulate phase (30%–70% presence in either of the two phases) and thus show Type 4 enrichment (Meyer et al 2011). The peak of Flu at the beginning was attributed to the early release of the dissolved fraction during the melt. In contrast, other PAHs that are largely associated with particles, such as BaP, showed one clear peak at the end of the melt (figure S1(b)), which is consistent with Type 2 enrichment. Therefore, the total PAH release pattern was affected by both Type 2 and Type 4 enrichment, resulting in double peaks. However, other PAHs belonging to Type 2 enrichment, with partition coefficient (Koc) values between Flu and BaP, also showed double peaks during melting (Type 4 enrichment), such as BaA (figure S1(c)), which is attributed to the melting scenario at high temperature (Meyer et al 2009b).

Although PAHs are particle-bound contaminants, there is an initial flush of dissolved PAHs, which may be attributed to both dissolution of PAHs in meltwater and the association of PAHs with DOC released from snowpack. In general, the pattern of PAHs released from snowpack under laboratory conditions is dependent on the varies between different PAHs, including Type 2 and Type 4 enrichment. Intense melt of the snowpack at relative high temperature therefore can result in the shift in some hydrophobic contaminants from Type 2 to Type 4 enrichment, depending on their Koc values.

3.2. PAH release from snowpack under field conditions

3.2.1. Dissolved PAH concentrations in meltwater released from snowpack

Concentrations of total dissolved PAHs in meltwater ranged from 0.1 to 0.6 μg l⁻¹ and from 0.5 to 0.9 μg l⁻¹ in each collection from W1 and W2, respectively. Similar to the laboratory conditions, a first flush of PAHs was observed and driven by an elevated concentration of Nap (figures 5(a), (b)). The Nap concentration was approximately 200 ng l⁻¹ in the first snowmeltwater, then rapidly decreased to about 70 ng l⁻¹ in the second snowmeltwater and remained stable until the end of the snowmelt. In the field, melt/freeze cycles cause compaction and snow metamorphism, resulting in snowpack densified and the increase of meltwater at the expense of snow surface and pore space. Therefore, PAHs absorbed to the snow grain surface would either start to dissolve in meltwater or sorb to particles, depending on the Koc value. For example, BghiP is likely to gradually transition from snow grain surface to the particle phase during melting, whereas Phe can more easily be dissolved (Meyer et al 2009a). As Nap has a low Koc value, it can be expected to dissolve in meltwater. The Nap concentrations were correlated with DOC in meltwater (figure 3(b), r = 0.5, p < 0.05), indicating that its combination with DOC controlled the first flush of dissolved Nap in meltwater released from snowpack, which is different from that under laboratory conditions. Consistently, no elevated Nap concentrations were found at the end of the melting event, again suggesting that dissolution plays a minimal role in Nap enrichment in meltwater under field conditions because of the low solubility of Nap at low temperatures.

For other PAHs, only Flu and Phe were detected in field conditions because of the low Koc values and solubilities of PAHs in water at low temperature. Flu and Phe concentrations were significantly correlated with DOC (figure 3(b), r = 0.6, p < 0.01), which is similar to the results under laboratory conditions, indicating Koc rather than PAH solubility controls hydrophobic PAHs in meltwater released from snow under both field and laboratory conditions. However, Flu and Phe are released at a relatively constant concentration and no first flush of Flu and Phe was found during the whole snowmelt period under field conditions (figures 5(a), (b)), which is different from that under laboratory conditions. This indicates that snowmelt at low temperatures may release organic carbon, which is not preferentially absorbed by PAHs (hydrophobic contaminants).

3.2.2. PAH concentrations in particles released from snowpack

Total PAH concentrations in particles from meltwater range from 11.3 to 131.5 μg g⁻¹, and are dominated by HMW PAHs except in the first collection of meltwater. The peak concentrations of total PAHs and group PAHs (LMW PAHs and HMW PAHs) in particles were observed at the beginning of each snowmelt period (shown in figures 6(a) and S2(a), (b), respectively), which is consistent with the finding for laboratory conditions. A freezing-out of small particles from the ice lattice during snow metamorphism could occur prior to snowmelt or during melt/freeze cycles (Meyer and Wania 2008). These particles therefore have high PAH concentrations because of the hydrophobicity of PAHs as discussed before. Furthermore, they can percolate downward with meltwater until the point at which the snow filter effect prevents the elution of particles (Meyer and Wania 2008), resulting in high PAH concentrations in particles at the beginning of the melting event. In addition, the first collection of meltwater under field conditions took more than 20 h because of the low temperature at the initial of melting, indicating that there was enough time for PAH to partition between ice interface or meltwater and small particles. The small particles therefore were further
enriched with PAHs because PAHs preferentially partition to the particulate phase from the aqueous phase (Chiou et al 2000). Unlike dissolved PAHs in meltwater, all PAHs bonding to particles showed high concentrations at the beginning of melting, which is attributed to the hydrophobicity of PAHs.

Elevated concentrations of both total PAHs and group PAHs (LMW and HMW PAHs) in particles were also observed from the last meltwater (shown in figures 6(a), S2(a), (b), respectively), which is different from that under laboratory conditions. On the one hand, melt/freeze cycles under field conditions cause a shift of PAHs from the ice interface to particles as melting time increases. On the other hand, melt/freeze cycles also cause a delay in the release of these PAH-concentrated particles. Groups of particles are pushed together to form aggregates under the increased dehydration during freezing. For instance, micro-soot particles, which have been suggested to be associated with PAHs (Naes et al 1998), can form aggregates with a lower density than that of water while freezing. During melting, the coagulated micro-soot particles and the PAHs absorbed to them may accumulate in the surface layer of the snowpack (Colbeck 1981). In addition, freeze/melt cycles also generate dirt cones, which could prevent elution of large particles (Meyer et al 2009a). Thus, these PAH concentrated particle coagulates are efficiently prevented from being washed out from the bulk snow until the end of the melt period (Schöndorf and Herrmann 1987).

Consistently with the particle release pattern under laboratory conditions, the particle concentrations released from both W1 and W2 increased considerably with melting time (figure 6(b)), which was attributed to the filter effect of snow during snowmelt as discussed before. Unlike particulate PAH concentration in meltwater released under laboratory conditions, particulate PAHs released from snowmelting in the field showed slightly elevated concentrations in the first sample, and an increased release pattern with the highest concentrations occurring towards the end of the melt (figure 6(c)). The slightly high particulate concentration in the early melting stage could be

**Figure 5.** Release patterns of dissolved total PAHs, naphthalene, fluorene and phenanthrene from snowpack W1 (a) and W2 (b) melting in the field.
attributed to the particles released prior to the snow filter preventing further elution of particles. The occurrence of the highest particulate PAH concentrations at the end of the melting event is attributed to the snow filter effect.

3.2.3. Total PAH concentrations in meltwater released from snowpack
Taking dissolved and particulate PAHs together, PAH concentrations in snowmeltwater ranged from 1.3 to 4.0 μg·L⁻¹ and from 1.7 to 5.3 μg·L⁻¹ in meltwater from W1 and W2, respectively. The release pattern of PAHs in meltwater is also controlled by the particulate PAH release pattern because of the hydrophobicity of PAHs and the limited dissolved PAHs detected in meltwater at low temperatures. Under field conditions, both increasing total PAH and group PAH (LMW PAHs and HMW PAHs) concentrations was observed with melt time, with a slight elevated concentration at the beginning (shown in figures 6(d) and S3(a), (b), respectively), which is different from that under laboratory conditions. Although PAHs are considered particle-bound organic contaminants, the release pattern of PAHs from snowpack under field conditions was not coincident with that of Type 2 contaminants. It was also not consistent with the release pattern under laboratory conditions which showed the release pattern varied among PAHs. In contrast, the pattern was similar to the Type 3 release pattern, which is associated with contaminants that are somewhat water soluble and have a high affinity for snow grain surfaces (Meyer et al 2011). Under field conditions, most energy is used by melting snow because of the low temperature, thus, there is insufficient energy for PAH partitioning from the snow surface to particles. This indicates that the PAHs are mainly absorbed by snow grain surface rather than by particles in the snowpack in the field. With progressing melt and increasing PAH concentrations at the snow grain surface, chemical equilibrium between the bulk snow phases can only be maintained when an increasing amount of PAHs transfer into the aqueous phase, leading to the ascending elution sequence (Meyer et al 2011). The slightly elevated concentration at the beginning of the melt may be attributed to the shallowness of the sampled snowpack in which vertical flow channels at the onset of melting can easily break through to the ground, creating shortcuts of meltwater flow in which even larger particle coagulates are washed out (Simmsleit et al 1986).

Overall, the first flush of dissolved PAHs in meltwater from snowpack was driven by Nap, and all dissolved PAH compositions were correlated with DOC released from the snowpack. Most PAHs accumulated
in snow surface rather than in particles in the field because of the insufficient energy from heating, resulting in Type 3 enrichment during the melting event.

4. Conclusion

PAH concentrations in both meltwater and particles released from snowpack under different melting scenarios were measured, showing different release patterns. Total PAHs released from snowpack showed double peaks during the intense melting event (Type 4 enrichment), which was attributed to a mixture of different PAH compositions. In contrast, the PAHs released from snowpack under melt/freeze melting coincided with Type 3 enrichment, which showed an increasing concentration in meltwater until the end of the season, when the maxima occurred. Our results suggest PAH release pattern from snowpack during snowmelt is not consistent with Type 2 enrichment which is obtained by models, whenever in current melt/freeze melting scenarios or in future intense melting scenarios. In current climate conditions, first flush of PAHs in water may not exist. More attention should be paid at the end of snowmelt season because PAH concentrations in water is highest at the end. However, global warming may result in intense melting of snowpack, maybe leading to first flush of PAHs in water during snowmelt season. Therefore, attentions should be paid at both early stage and late stage of snow melting in furture.

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