Synthetic musk fragrances and heavy metals in snow samples of Beijing urban area, China

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ABSTRACT

Seven typical synthetic musk fragrances (musk xylene (MX), musk ketone (MK), Galaxolide (HHCB), Tonalide (AHTN), Celestolide (ADBI), Traseolide (ATII) and Phantolide (AHMI)) and seventeen heavy metals (Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Ti and Pb) were measured in 42 snow samples from Beijing urban area of China. Galaxolide (HHCB) and Tonalide (AHTN) showed the highest concentrations (6.5–75.1 and 2.2–16.4 ng/l, respectively) and highest detection frequency (nearly 100%) among the musks. MX, MK and ATII were only found in several samples. HHCB concentrations were not significantly relative with DOC, while AHTN concentrations were found positively correlated with DOC ($p < 0.05$). Moreover, Mn, Zn, Sb, Ba, Cu and As could be detected in most of snow samples, ranged in N.D.–71.3 $\mu\text{g/L}$. No significant correlation was observed in metal concentrations and DOC ($p > 0.05$). Significant correlations exist between the concentrations of HHCB and AHTN in snow samples ($p < 0.001$) of Beijing, China.

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1. Introduction

Snow is important for the troposphere and the ecosystem because of the influence on energy balances and hydrological fluxes. As an important long-range transport media, snow has also been proved to be an effective scavenger to the removal of pollutants from atmosphere both in temperate and polar regions (Lei and Wania, 2004). There are numerous reports about occurrence of natural and synthetic compounds in snow samples, such as polycyclic aromatic hydrocarbons (PAHs) (Masclat et al., 2000; Zhang et al., 2008); polychlorinated biphenyls (PCBs) (Lafrenère et al., 2006; Wania et al., 1998), organochlorine pesticides (OCPs) (Lafrenère et al., 2006; Huang et al., 2010), methyl tert-butyl ether (MTBE) (Kolb and Püttmann, 2006), 4-nonylphenol(4-NP) (Fries and Püttmann, 2004) and so on.

Synthetic musk fragrances (SMs) have been widely used in a variety of personal care products and household cleaners as

well as in technical products and consume goods (Richardson, 2009). Nitro and polycyclic musks are used more frequently than other kinds of musks. Now, polycyclic musks nearly occupy the main musk market of the world (Käfferlein and Angerer, 2001). In recent years, more and more studies have reported the potential estrogenic and anti-estrogenic effects of the polycyclic musks (Yamauchi et al., 2008). At the same time, they have been found in many types of environmental matrices and biota samples, such as wastewater, sewage sludge, fish, breast milk, and indoor dust and so on (Reiner et al., 2007; Guo et al., 2010; Lignell et al., 2008; Wan et al., 2007; Peck and Hornbuckle, 2006). SMs are lipophilic, persistent and bioaccumulative in the aquatic environment and biota samples, which are similar with those of PAHs and PCBs and so on (Wania et al., 1998). Therefore, musks may be also detected in the snow samples. However, there is little information about the occurrence of synthetic musk fragrances in snow samples.

Many heavy metals would be emitted into atmosphere with the increase of population density and anthropogenic activities (Zheng et al., 2010). Toxic metals have been

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observed in atmosphere, such as Pb, Cd, Zn, Cr and As and so on (Schneidmesser et al., 2010). As scavenger of atmosphere, snow plays an important role. However, there is little information about the distributions and concentrations of heavy metals in snow samples in Beijing of China.

In the present study, 42 snow samples from urban area of Beijing were collected. Seven typical SMs, seventeen heavy metals, pH values and dissolved organic compounds (DOC) of the snow samples were analyzed. The objective of the present study is mainly to investigate the occurrence of SMs and heavy metals in snow samples. This is the first report about synthetic musk fragrance concentrations in snow samples.

2. Experimental

2.1. Materials and methods

Seven musk standards (AHTN, HHCB, ADBI, AHMI, ATII, MK and MX), surrogate standard d_3 -AHTN and internal standard (HCB) $^{13}\text{C}_6$ were obtained from Dr. Ehrestorfer (Augsburg, Germany). C-18 discs were from Supelco ($\emptyset$ 47 mm, Bellefonte, USA).

2.2. Sampling

42 snow samples were collected directly from snow layers at the urban area of Beijing on November 11 2009. To avoid contamination, sampling sites are far away from any road traffic. Sampling sites were shown in Fig. 1. After melting, all samples were transferred into precleaned amber glass bottles and kept at 4 °C until analysis. Before extraction, the melted snow samples were filtered through nylon film (0.45 μm). Sample extraction and analysis method were in Appendix A.

2.3. Quality control and quality assurance

In the present study, d_3 -AHTN and HCB $^{13}\text{C}_6$ were used as surrogate standard and internal standard, respectively. Recoveries of the d_3 -AHTN were in the range of 89.7%–104.9%. HCB $^{13}\text{C}_6$ was used to quantify musk concentrations. The

reported concentrations of samples had been corrected using recovery of d_3 -AHTN, which would be spiked into samples before pretreatment.

For calibration purposes, six different concentrations of musk standard solutions were analyzed by GC-MS. A standard calibration was performed. Correlation coefficient R^2 are >0.99 . Matrix spike recovery studies were carried out. The limits of detection (LODs) of musks based on a signal-to-noise ratio of 5 were in the range of 1.2–4.0 ng/l. To avoid the possible contamination, all glassware was soaked in $\text{K}_2\text{Cr}_2\text{O}_7$ – H_2SO_4 lotion for at least 12 h, and all equipment was rinsed with acetone in advance. A procedural blank was processed with each batch of 6 samples. Furthermore, a field blank was included during sampling. The all musk concentrations were below detection limits in all the blank samples.

2.4. Statistical analysis

Differences in musk concentrations and metals in snow samples from south and north were calculated using the Mann–Whitney U test. A p -value below 0.05 was considered significant. All the statistical analyses were performed by the software of SPSS 13.0.

3. Results and discussions

3.1. Musk concentrations in snow samples

Two polycyclic musks, HHCB and AHTN, were observed in all the snowmelt samples. The concentrations of AHTN and HHCB were in the range of 2.2–205.9 ng/l (mean: 11.0 ng/l), and 6.5–754.1 ng/l (mean: 33.3 ng/l), respectively. MX and MK were detected in 4 and 5 snow samples, ranged in 4.4–16.1 and 6.7–43.2 ng/l, respectively. ATII was only found in one snowmelt sample (8.4 ng/l). Other musks were all below the detection limits. It should be noted that musk concentrations from sampling spot A were much higher than those from other sampling spots (HHCB: 754.1 ng/l; AHTN: 205.9 ng/l). However, for other sampling spots they were in the range of 6.5–75.1 (mean: 15.7) ng/l and 2.2–16.4

Fig. 1. Sampling sites of snow samples in Beijing urban area of China.

(mean: 6.3) ng/L, respectively. Because there is no other study reporting the occurrence of synthetic musks, comparisons were only conducted between concentrations of musks and other organic compounds in snow samples, such as 4-NP, PAH and PCB and so on. The results showed that musk concentrations were slightly higher than OCP concentrations detected in Mt. Qomolangma (20–1650 pg/L) (Wang et al., 2007) and slightly lower than levels of 4-NP reported in Germany (ND–0.802 µg/L) (Fries and Püttmann, 2004). Compared with PAH, levels of SMs were also lower than those of PAH reported both in Greenland (Masclet et al., 2000) and USA (Franz and Eisenreich, 1998), up to 100–10000 pg/g and 18 µg/L, respectively. Additionally, SMs levels in the present study were comparable with levels of PCB in USA (7.9 ng/L) (Franz and Eisenreich, 1998) and MTBE (16–127 ng/l) (Kolb and Püttmann, 2006) in Germany. To obtain direct knowledge about SMs pollution, comparison was also conducted between snows and effluents from wastewater treatment plants. The results showed that musk concentrations were also slightly lower than those in effluents from wastewater treatment plants of Beijing (Zhou et al., 2009; Hu et al., 2011). Moreover, Mann–Whitney *U* test was conducted. The results showed no significant geography-related statistical difference was observed in the concentration of HHCB and AHTN ($p > 0.05$).

Significant positive relationship was found between HHCB and AHTN concentrations ($p < 0.001$). The feature is similar with those found in human blood (Hu et al., 2010), influents, effluents and sewage sludge of wastewater treatment plants of Beijing reported by our group. As to the ratios of HHCB/AHTN, they were detected in the range of 0.68–14.99 (median: 2.68) in the present study. The value was also similar with those found in human blood samples (about 2.3) collected from 11 cities of China (Hu et al., 2010). It was reported that ratios of HHCB/AHTN would show decreasing trends during transport, because HHCB is quickly removed by atmospheric degradation relative to AHTN. Their ratios could be low to 0.1–0.4 (Xie et al., 2007). Apparently, our results were much higher than the values. The phenomena could be explained by the fact that much of musks would be emitted into atmosphere every day and input of HHCB and AHTN could decrease influence on ratios from degradation of the two compounds.

3.2. Heavy metals in snow samples

In the present study, seventeen metals were measured, including Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Ti and Pb, shown in Table 1 (Appendix B). The results showed that detection frequencies of metals (Mn, Zn, Sb, Ba, Cu and As) were higher than those of other metals in the snow samples. Especially Mn, Zn, Sb and Ba, they could be detected in all the samples. Cu and As could be found in nearly 67% and 83% of snow samples, respectively. Cd was found in 4 snow samples, and Ni and Cr could be only detected in 7 and 5 samples in the present study. Be, Co, Ag and Ti was not detected in all the 42 snow samples. Other metals including Al, V, Se, Mo, Pb and Se could be observed in about 8–18 snow samples. In the present study, the concentrations of Mn, Zn, Sb, Ba, Cu and As were in the range of 1.16–54.62 µg/L, 3.91–71.33 µg/L, 0.55–2.86 µg/L, 2.80–65.93 µg/L, N.D.–9.63 µg/L and N.D.–3.36 µg/L, respectively.

It was concluded that the concentrations of Zn were higher than those of Cu. The phenomena were similar with those reported by Wang et al. (2001). They reported that the Zn concentrations were higher than those of Cu in atmospheric particle matter (APM) not only in winter time with heavy coal combustion but also in summer time without heavy coal combustion. In the present study, the concentrations of Al were in the range of 0.1–3.5 µg/L, which were lower than Al^{3+} concentrations detected in snow samples (106–783 µg/L) as well as in rainwater (3.51–196.56 µg/L) from Beijing, reported by Xu and Han (2009) in 2006. Mann–Whitney *U* test showed that the concentrations of Mn, As, Sb and Ba were higher in the southern samples than those in northern snow samples ($p < 0.05$). Nevertheless, there was no relationship between geography and concentrations of Cu and Zn ($p > 0.05$).

In the present day, DOC values were detected in the range of 0.15–8.1 (mean: 1.19 mg C/L). The values were much lower than those detected in Japan in 1993 (mean: 14.1 mg C/L) (Sempère and Kawamura, 1994) and in USA in 1992 (mean: 4.5–18.4 mg C/L) (Franz and Eisenreich, 1998). pH in snow sample of Beijing urban area was in the range of 5.26–6.50. It was reported that pH values were 4.63 and 5.53 in snow samples of Beijing detected in 2006 (Xu and Han, 2009). Apparently, our results were higher than those years ago.

3.3. Relationships between DOC and concentrations of musks, heavy metals

In the present study, the relationships between DOC and musk concentrations (HHCB and AHTN), metals were investigated. The results showed that positive correlations existed between AHTN and DOC concentrations ($p < 0.01$). However, there was no correlation between HHCB and DOC concentrations ($p > 0.05$). There was also no significant statistical relationship observed between DOC and metals. Different from our results, Chen et al. (2010) have reported that positive correlations existed between TOC and metals, including Cd, Cu, Zn and Pb, in soil samples from Beijing area.

4. Conclusions

We measured the levels of seventeen typical SMs in snow samples collected in urban area of Beijing, China. High detection frequencies of SMs in snow samples may provide an indication that wet deposition would be an important removal pathway of synthetic musks from the atmosphere. Among the musks, HHCB and AHTN were the most abundant compounds. The levels of HHCB and AHTN in the present study were comparable with the snow concentrations of PCB in USA and MTBE in Germany, but slightly lower than 4-NP concentrations in Germany and PAH concentrations from Greenland and USA. Musk concentrations in the present study were also lower than those of effluents in wastewater treatment plants in Beijing. Mn, Cu, Zn, As, Sb and Ba could be detected in most of the snow samples. The Al concentrations were lower than those detected in snow and rainwater of Beijing in 2006. Additionally, pH values were higher, while DOC values were lower, compared with those detected in 2006.

Supplementary materials related to this article can be found online at doi:10.1016/j.atmosres.2011.09.002.

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