ISOMER-SPECIFIC ACCUMULATION OF AIRBORNE PERFLUORINATED COMPOUNDS IN CAMPHOR (*CINNAMOMUM CAMPHORA*) TREE BARK AND ACTIVE AND PASSIVE AIR SAMPLERS

Liu JL[1]*, Li SN[2], Dong L[1], Zhou L[1], Huang YR[1]

[1]National Research Center for Environmental Analysis and Measurement, Beijing, China
[2]Beijing University of Agriculture, Beijing, China

Introduction

Perfluorinated compounds (PFCs) are an important group of organic pollutants, widely used as fire-fighting foams, plating plants, textile industries, and packing materials[1]. PFCs have been detected worldwide in rivers[2], oceans[3], sediments[4], wildlife[5], and human[6]. Due to the high energy of carbon-fluorine covalent bonds, PFCs are thermally and chemically stable, and are also resistant to biodegradation. Hence, they are extremely persistent in the environment[1]. PFCs are believed to cause liver toxicity, developmental toxicity, immunotoxicity, and endocrine disrupting effects[7,8]. Perfluoroalkyl carboxylates (PFCAs), mainly perfluorooctanoic acid (PFOA), and perfluoroalkyl sulfonates (PFSAs), mainly perfluorooctane sulfonate (PFOS), are PFCs receiving the most attention. They are the final degradation products of the neutral perfluoroalkyl and polyfluoroalkyl substances, such as fluorotelomer alcohols (FTOHs) and perfluorooctane sulfonamides (FOSAs)[1].

PFCs are mainly produced by two manufacturing processes, including electrochemical fluorination and telomerization. The electrochemical fluorination products are typically a mixture of linear and branched isomers, while the telomerization products are linear[9]. Isomer profiling of perfluorinated substances can be used as a tool for source tracking of production. PFC isomers differ on physical and chemical properties, bioaccumulation and biodegradation, and toxicity[9]. The risks of PFCs to human and wildlife are likely to be affected by their isomer profiles in environment.

An approach to passive air sampling is to use tree bark[10]. They are present almost everywhere, they do not require electricity, and they can be sampled nondestructively. Tree bark makes an excellent passive atmospheric sampler, which can be used to study the air pollution of volatile organic substances[10]. This study aims to investigate PFCs and the isomers in tree bark from an industrialized region of China and compare the isomer profiling with active and passive samples to study the environmental behavior of PFCs and isomers in tree bark, air, and airborne particles.

Materials and methods

Sampling sites are located in Jiangsu Province, the most developed region of China with dense population and industries, e.g. new material industry, IT industry, and pharmaceutical factories. Camphor tree (*cinnamomum camphora*) is a common tree type in this region. All camphor tree bark samples (n=33) were collected in August 2012 in southern Jiangsu. Sampling sites were distributed in the cities of Suzhou, Wuxi, Nantong, Changshu, Zhangjiagang, Kunshan, Jiangyin, and Jingjiang as shown in Fig. 1. According to the different city functional areas, there are four kinds of sampling locations, including background, industry, urban, and rural regions. Each bark sample was chiseled for about 10 cm^2 at a height of 1.5 m above ground level. Air samples in one site of Suzhou, Wuxi, Nantong, Changshu, and Kunshan respectively were collected by active and passive samplers at the same sampling period. Air samples were collected over a 24-h period with sample volumes of approximately 300 m^3 using a modified PS-1 type sampler, comprised of a glass fiber filter for particle phase collection followed by a polyurethane foam (PUF) for trapping gas-phase compounds. Air samples were also collected by Harner passive sampler composed of two PUF disks with sampling period of one month.

Bark samples were freeze-dried and milled. 1-g bark, filter paper, and PUF were shaked in 20-mL methanol for 30min and then ultrasonically extracted for 20min. The extraction process repeated for two times. The extract was then concentrated to 3 mL, and purified by ENVI-Carb cartridges (Supelco). The cartridges were pre-rinsed by 3 mL methanol, and PFCs were eluted by 3 mL methanol. The elutes were evaporated and redissolved in 0.5 mL methanol. PFCs were analyzed by LC/MS/MS (Agilent) in MRM mode. PFC isomers were separated by retention time and ion pairs.

Figure 1. Sampling sites in Jiangsu Province of China

Results and discussion

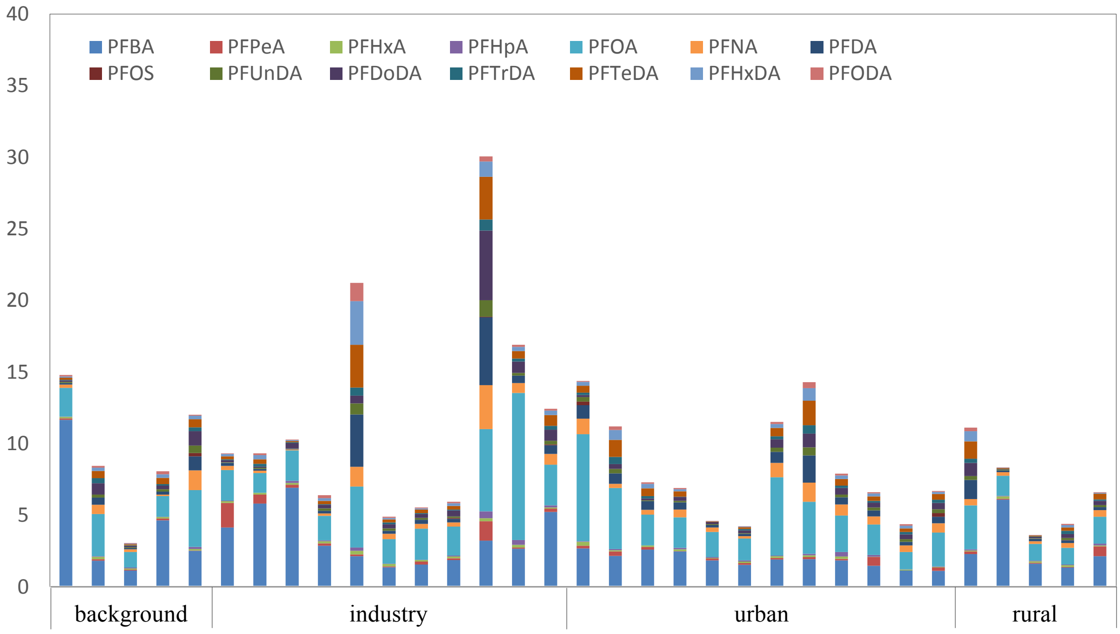

Figure 2. Concentrations of PFC species in different regions of sampling site

The total PFC content of tree bark ranged from 3.1 to 30.1 ng/g dw as shown in Fig. 2. Totally 14 PFCs were detected, including PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFOS, PFUnDA, PFDoDA, PFTrDA, PFTeDA, PFHxDA, and PFODA. Most PFCs are perfluoroalkyl carboxylates, and only one perfluoroalkyl sulfonate, PFOS, was found in bark with detection frequency of 15.2% and concentration of 0.1-0.3 ng/g dw, which are the lowest among all PFCs. Airborne perfluoroalkyl carboxylates and sulfonates are derived from their volatile precursors, such as fluorotelomer alcohols (FTOHs) and perfluorooctane sulfonamides (FOSAs) respectively. Less perfluoroalkyl sulfonates were detected probably due to less use of FOSAs in this region. Another possible reason is that FTOHs are more volatile than FOSAs. More of them might be released into air, adsorbed by tree bark, and degraded into perfluoroalkyl carboxylates. The dominant PFC species are PFBA and PFOA, with content ranges of 1.1-11.7 and 1.1-10.3 ng/g dw respectively. No branched PFBA was found, and 1m-PFOA (m: methyl group) was detected with low ratio of 1-10% in total PFOA content. It seems tree bark tends to adsorb linear PFCs. There is no significant difference in PFC concentration for the four kinds of regions, e.g. background, industry, urban, and rural regions. However, two sites with the highest PFC concentration were found in the industrial regions with total PFCs of 30.1 and 21.2 ng/g dw. The two sites have new material or textile industries in the neighborhood, which may produce or use PFC-related products. The results show PFCs are ubiquitous in the air of investigated region, while industry source may have significant effect on the airborne PFC pollution.

The PFC content range for active sampler is 58.0-166.5 ng/sampler (14.3-117.6 ng/filter for particles and 7.7-61.7 ng/PUF for gas phase), and the content range for passive sampler is 8.2-23.8 ng/sampler. Unlike tree bark, perfluoroalkyl sulfonates, mainly PFBS and PFOS, were found in air samplers, confirming that bark selectively adsorbs perfluoroalkyl carboxylates. PFBS dominates in PUF of active sampler, and PFOA dominates in filter of active sampler and passive sampler, suggesting that PFCs perform differently in tree bark and these kinds of air samplers.

Isomer profiling of PFCs in bark, active sampler, and passive sampler is different as shown in Fig. 3. Branched PFBA and PFOA were found in these samples. For PFBA, branched PFBA (1m-PFBA) dominated compared with linear PFBA in filter of active sampler, while linear PFBA dominated in PUF of active sampler and passive sampler. No branched PFBA was found in tree bark. Branched PFBA prefers to be into the particles, while linear PFBA tends to be in the gas phase, for their different chemical and physical properties. OH^- group of branched PFBA precursor is more reactive than the precursors of linear PFBA, which may involve in the chemical reaction between PFCs and active sites of particles. For PFOA, linear PFOA dominated in all samplers, probably for the property difference between branched and linear PFOA is less compared with PFBA. The result suggests branched and linear PFCs perform differently in airborne particles and gas phase due to their varied characters, which may further affect PFC exposure and risks to human and wildlife.

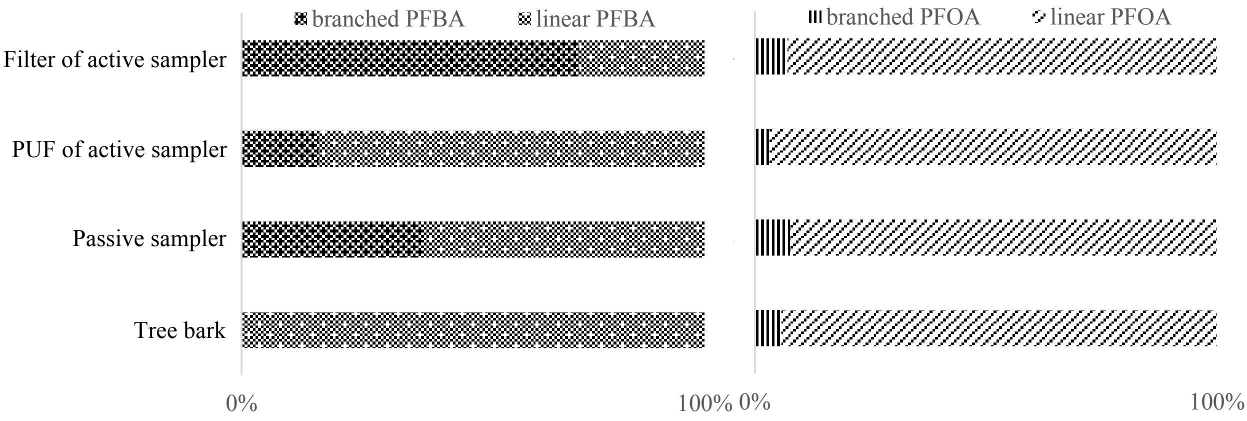

Figure 3. Branched and linear PFCs in different air samplers

References

1. 3M Co. (1999) U.S. Environmental Protection Agency Public Docket AR226-0550: fluorochemical use, distribution and release overview. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxic Substances, Washington DC.
2. Yu, N., Shi, W., Zhang, B., Su, G., Feng, J., Zhang, X., Wei, S., Yu, H. (2013) *Environmental Science & Technology*, 47, 710-717.
3. Yamashita, N., Kannan, K., Taniyasu, S., Horii, Y., Petrick, G., Gamo, T. (2005) *Marine Pollution Bulletin*, 51, 658-668.
4. Higgins, C. P., Field, J. A., Criddle, C. S., Luthy, R. G. (2005) *Environmental Science & Technology*, 39, 3946-3956.
5. Houde, M., Martin, J. W., Letcher, R. J., Solomon, K. R., Muir, D. C. (2006) *Environmental Science & Technology*, 40, 3463-3473.
6. De Silva, A. O., and Mabury, S. A. (2006) *Environmental Science & Technology*, 40, 2903-2909.
7. Lau, C., Butenhoff, J. L., Rogers, J. M. (2004) *Toxicology and Applied Pharmacology*, 198, 231-241.
8. Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J. (2007) *Toxicological Sciences*, 99, 366-394.
9. Benskin, J. P., De Silva, A. O., Martin, J. W. (2010) *Reviews of Environmental Contamination & Toxicology*, 208, 111-160.
10. Peverly, A. A., Salamova, A., Hites, R. A. (2015) *Environmental Science & Technology*, DOI: 10.1021/es505394y.