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Evaluation of ginkgo as a biomonitor of airborne polycyclic aromatic hydrocarbons

Michio Murakami [a], Maho Abe [b], Yoriko Kakumoto [b], Hiromi Kawano [b], Hiroko Fukasawa [b], Mahua Saha [b], Hideshige Takada [b,*]

[a] "Wisdom of Water" (Suntory), Corporate Sponsored Research Program, Organization for Interdisciplinary Research Projects, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan

[b] Laboratory of Organic Geochemistry (LOG), Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan

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ABSTRACT

The utility of ginkgo leaves as biomonitors of airborne polycyclic aromatic hydrocarbons (PAHs) was evaluated. We investigated PAH concentrations among tree species, the effect of variations in leaf position in a tree, tissue distributions, correlations between ginkgo leaves and air, and seasonal variations. Among the five species examined (*Ginkgo biloba* L., *Zelkova serrata* Makino, *Liriodendron tulipifera* L., *Prunus yedoensis* Matsum, and *Magnolia kobus* DC.), ginkgo accumulated the greatest amount of PAHs from roadside air. Most PAHs (~80%) were accumulated in the wax fraction, and most of the remainder (17%) penetrated the inner tissues of the leaves. PAH concentrations in ginkgo leaves decreased with increasing height and distance from the road, reflecting the derivation of PAHs from vehicle emissions. Seasonal time-series sampling showed that PAH concentrations in ginkgo leaves increased with time, attributable to the effects of temperature and accumulation through long-term exposure. Concentrations in ginkgo leaves collected from various roads showed a strong and significant correlation with those in air collected by a high-volume air sampler ($r^2 = 0.68$, $P < 0.01$). Ginkgo leaf data clearly showed a dramatic decrease in the ratio of low-molecular-weight (LMW) PAHs to high-molecular-weight PAHs from 2001 or 2002 to 2006, indicating that on-road diesel emission regulations effectively reduced LMW PAH concentrations in air.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the product of thermal decomposition, and are formed during incomplete combustion of organic materials and geochemical formation of fossil fuels (Blumer, 1976). The distribution of PAHs is diffuse in air and on the earth's surface (Murakami et al., 2005; Boonyatumanond et al., 2007). The importance of the study of PAHs lies in the fact that they are highly lipophilic and some are carcinogenic or mutagenic (Perera et al., 1992; IARC, 2011). Collins et al. (1998), for example, developed potency equivalency factors for PAHs, and estimated that they posed a cancer risk of 1.8×10^{-5} in the UK. Wickramasinghe et al. (2011) found PAH concentrations around 696 ng m^{-3} in air at heavily trafficked urban locations in Sri Lanka, posing an excess lifetime lung cancer risk of 4.58×10^{-3}. Since PAH contamination is much heavier in urban areas than in rural areas (Saha et al., 2009; Wickramasinghe et al., 2011), the increased risk to health posed by PAHs, due to rapid urbanization, is a matter of concern.

Since traffic is the dominant source of PAHs in the urban atmosphere (Dickhut et al., 2000; Tang et al., 2005; Boonyatumanond et al., 2007), countermeasures aimed at traffic-derived PAHs should reduce concentrations and risk. Okuda et al. (2011) monitored PAHs using an active air sampler during the 2008 Beijing Olympics, and found that traffic-control measures reduced PAHs with molecular weight ranging from 252 to 300. Since PAH concentrations in air fluctuate daily and seasonally (Fon et al., 2007) for many reasons, frequent monitoring is required to assess their pollution status. However, resource limitations restrict intensive data monitoring.

As an alternative, biomonitoring using vegetation is a prospective approach, with the following advantages: (1) it is easy, economical, and non-technical to sample vegetation; and (2) vegetation can reflect accumulation through long-term exposure. Simonich and Hites (1994a) found that vegetation significantly accumulated PAHs. The accumulation mechanisms of PAHs in

* Corresponding author. Tel.: +81 423 67 5825; fax: +81 423 60 8264.
E-mail address: shige@cc.tuat.ac.jp (H. Takada).

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vegetation, and their controlling factors, have been studied as follows. It was demonstrated that vegetation takes up semivolatile organic compounds such as PAHs mostly from air, not soil, and the air quality can be projected (Ryan et al., 1988; McLachlan, 1999; St-Amand et al., 2009). In addition, the partitioning of PAHs between air and vegetation (Simonich and Hites, 1994b; Tao and Hornbuckle, 2001), and its temporal change (Howsam et al., 2001; Alfani et al., 2005; Lehndorff and Schwark, 2009a); the varying distribution in tissue (Kaupp et al., 2000; Wild et al., 2006; De Nicola et al., 2008); the uptake pathways of PAHs (e.g., outer cuticle and stomatal pathways) (Franzaring, 1997; Tao and Hornbuckle, 2001); and photolysis on the leaf surface (Niu et al., 2003; Wang et al., 2005); have all been studied. Furthermore, differences in PAH accumulation among different tree species have been investigated (Howsam et al., 2000; Wang et al., 2008). Biomonitoring of PAHs, using plant leaves, has been conducted in order to understand spatial distribution (Lehndorff and Schwark, 2004; Wang et al., 2008; Lehndorff and Schwark, 2009b; Ratola et al., 2010; De Nicola et al., 2011), the impact of specific anthropogenic activities (Sharma and Tripathi, 2009; Sojinu et al., 2010), and seasonal variations (Prajapati and Tripathi, 2008). Though some studies have demonstrated the impact of traffic on airborne PAHs in urban areas (Lehndorff and Schwark, 2004; De Nicola et al., 2011), very few studies have utilized roadside trees to monitor PAHs in the air near heavily trafficked streets (Wang et al., 2008). The present study focused on roadside trees as biomonitors of PAHs in roadside air. Because roadside air is profoundly affected by traffic-derived PAHs, air monitoring is important in assessing human exposure to the respective carcinogenic compounds. We selected ginkgo (*Ginkgo biloba* L.) as a target species, because ginkgo is a common roadside tree in east Asia, and is grown around the world between 20° and 60° N and between 20° and 50° S (Sogame, 1984). The first objective of the present study was to assess the utility of ginkgo as a biomonitor of PAHs in roadside air, and to optimize the monitoring protocol. In pursuit of this objective we focused on the following elements: (1) PAH accumulation in ginkgo leaves, in comparison to other common species of roadside trees, (2) PAH distribution among the gingko tissues, (3) variation in PAH accumulation as a function of leaf position in the ginkgo tree, (4) the relationship between PAHs in ginkgo tissue and in the ambient air, (5) seasonal patterns of PAH accumulation in gingko leaves. All these are important factors in optimizing PAH air monitoring using tree leaves. However, no previous studies have examined all these aspects for a certain species of tree.

The second objective of the present study was to evaluate the effects of the on-road diesel emission regulations introduced by the Tokyo Metropolitan Government in October 2003, through long-term (five-year) monitoring using ginkgo trees. Diesel vehicles that do not meet the new particulate matter (PM) standard can be replaced or retrofitted with a particulate control device (Tokyo Metropolitan Government, 2006; Rutherford and Ortolano, 2008). Although the effects of the regulations on black carbon, PM, and oxides of nitrogen were reported (Kondo et al., 2006; Rutherford and Ortolano, 2008), the effects on PAHs are not well understood. Thus, we collected annual time-series samples of ginkgo leaves for five years to compare PAH concentrations before and after the regulations. This is the first application of long-term biomonitoring of PAHs using tree leaves.

2. Materials and methods

2.1. Sampling

Six types of sampling procedure were conducted as follows.

2.1.1. Comparison among tree species

To compare PAH concentrations among tree species, we sampled leaves from five species of deciduous tree—ginkgo (*Ginkgo biloba* L.), Zelkova (*Zelkova serrata* Makino), tulip tree (*Liriodendron tulipifera* L.), cherry (*Prunus yedoensis* Matsum.), and Kobushi Magnolia (*Magnolia kobus* DC.)—located either on the walkway or the roadway at Station (St.) 1 (Fuchu on Tokyo Route 133; Table 1) in August 2000.

2.1.2. Tissue distribution

We examined the tissue distribution (i.e., water-washed, wax, and interior fractions) of PAHs in ginkgo leaves collected from the roadway at St. 1 in October 2000.

2.1.3. Effect of leaf position in a ginkgo tree

To examine the effect of the leaf position on PAH concentrations, we collected ginkgo leaves at 2, 3, 4, and 8 m above the walkway, and at 2, 4, and 6 m above the roadway, at St. 2 (Fuchu on Tokyo Route 133; Table 1) in August 2002. The road has six lanes and the

Table 1
Sampling information.

Sampling stations	Location	Street	Traffic density in 1999 (vehicles/12-h)	Traffic density in 2005 (vehicles/12-h)	Heavy vehicle density in 1999 (vehicles/12-h)	Heavy vehicle density in 2005 (vehicles/12-h)
St. 1	Fuchu	Tokyo Route 133	14,042	12,337	2598	2048
St. 2	Fuchu	Tokyo Route 14	26,588	24,224	3483	2931
St. 3	Fuchu (Tokyo University of Agriculture and Technology)	–	0	0	0	0
St. 4	Hachioji	–	0	0	0	0
St. 5	Daidabashi	Route 20 and Expressway 4	43,519 + 61,178 (104,697)	38,684 + 58,012 (96,696)	3569 + 10,094 (13,663)	4797 + 10,036 (14,833)
St. 6	Hatsudai	Route 20 and Expressway 4	43,519 + 61,178 (104,697)	38,684 + 58,012 (96,696)	3569 + 10,094 (13,663)	4797 + 10,036 (14,833)
St. 7	Showa-joshi	Route 246 and Expressway 3	44,548 + 54,620 (84,483)	40,441 + 52,184 (92,625)	6727 + 15,075 (21,802)	6268 + 13,777 (20,045)
St. 8	Kamiuma	Route 246 and Expressway 3	29,863 + 54,620 (84,483)	26,304 + 52,184 (78,488)	4927 + 15,075 (20,002)	4314 + 13,777 (18,091)
St. 9	Sengakuji	Route 15	44,489	42,898	7118	6306
St. 10	Umeshima	Route 4	36,527	34,008	6977	6428
St. 11	Itabashi-honcho	Route 17 and Expressway 5	46,863 + 65,791 (112,654)	46,093 + 56,095 (102,188)	7826 + 14,540 (22,366)	8988 + 14,473 (23,461)
St. 12	Senju-shinbashi	Route 4	48,170	44,116	8237	8691
St. 13	Kameari	Loop 7	31,917	33,539	9639	9056
St. 14	Kakinokizaka	Loop 7	42,205	40,642	9581	8901
St. 15	Takao	Route 20	5588	5657	782	639