Semivolatile organic chemicals (SOCs) in leaves collected in Brisbane, Australia

Jochen F. Müller[1,3], Michael S. McLachlan[2], Darryl W. Hawker[3], Des W. Connell[3]

[1]Nat. Research Center for Environm. Toxicol., Kessels Rd, Coopers Pl. 4108, Qld Australia
[2]Ecological Chemistry and Geochemistry, University of Bayreuth, D-95440 Bayreuth, Germany.
Current address: Baltic Sea Research Institute Warnemünde, D-18119 Warnemünde, Germany.
[3]Faculty of Environmental Sciences, Griffith University, Nathan 4111 Qld. Australia

Introduction

Uptake of persistent atmospheric SOCs in vegetation is the first step in food chain accumulation that may result in the contamination of animals and humans. Many plants have relatively large surface areas covered with waxes that facilitate the accumulation of hydrophobic chemicals[1]. The use of plants as 'passive samplers' for atmospheric pollution by organic compounds has been suggested by many authors[2-4]. Plants have been used as biomonitors to evaluate the extent and sources of pollution[5,6] as well as to demonstrate historical trends in the occurrence of atmospheric SOCs[7,8]. However, the concentrations of SOCs in leaves are not only affected by the atmospheric concentrations but also by various factors related to the plant composition[9,10] and surface characteristics of the plant[11,12]. This study presents results from field experiments in which leaves from an evergreen tree species and grass samples collected in Brisbane, Australia were analysed for polycyclic aromatic hydrocarbons, tetra- to octachlorinated dibenzodioxins and dibenzofurans and selected tri- to octachlorinated biphenyls.

Materials and Methods

Melaleuca leucadendron, an evergreen Australian native tree with relatively thin, lanceolate, lipid rich (up to 10 % of fresh weight) leaves, was selected as the primary vegetation species since it is widely distributed throughout the study area and often planted on strips along road sides. Leaves were collected at a number of sites in Brisbane either from plants growing there or from potted plants. The majority of samples were collected from plants exposed at Griffith University (Site 1) which is located in the center of a forest reserve. Additionally, a few leaf samples were collected from roadside trees located 10 m from an intersection of a major arterial road with a traffic volume of about 42,000 vehicles day^{-1} (Site 2). Grass samples were collected about 10 m from a medium size road with a traffic density of about 13,000 vehicles day^{-1} (Site 3). A detailed description of these sites is given in Müller et al.[13]. The leaves from the plants exposed at Griffith University were collected between December 1994 and July 1995. In order to measure diurnal variations, leaves were also collected in six hour intervals over a 24 hour period in the winter of 1995.

The samples were freeze dried and ground. Most samples were sent to the University of Bayreuth where they were analysed using a method described in detail elsewhere[14]. In brief, about 20 g of sample was soxhlet extracted using toluene which was spiked with internal standards containing known amounts of 14 deuterated three to seven ring PAHs, 12 $^{13}C_{12}$ labelled 2,3,7,8-Cl substituted dibenzodioxins and dibenzofurans, seven $^{13}C_{12}$ labelled tri- to octachlorinated biphenyls and $^{13}C_6$ labelled hexachlorobenzene. Sample extracts were split: 10 % was used to determine PAHs while

the remainder was analysed for PCDD/Fs, PCBs and HCB. The PAH fractions were filtered through anhydrous Na_2SO_4, concentrated and then purified using gel permeation chromatography on Biobeads SX 8 (Bio Rad) with toluene as the solvent. The organochlorine fraction was first cleaned up on an acid/base activated silica column. Separation of the PCDD/Fs from PCBs and HCB was performed on an aluminum column (Alox B-super). The fraction containing the PCDD/Fs was concentrated almost to dryness and a $^{37}Cl_4$-2,3,7,8-tetrachlorodibenzodioxin recovery standard was added. The samples were analysed for a range of individual PAHs, PCDD/Fs, PCBs and HCB on a Hewlett Packard 5890/II GC (splitless) coupled to a VG Autospec Ultima mass spectrometer. The quantification was performed based on the known amount of the relevant internal standard added for a particular compound or PCDD/F homologue group. The mass spectrometer was operated at a resolution of 5500 – 9000 for the PAHs, PCBs and HCB and 9000 – 10000 for the PCDD/Fs. For quality control the GC retention times of the analyte in a sample had to conform with the retention times of standards and were not allowed to differ from those of the internal standards by more than 2 seconds. Furthermore, the chlorine and carbon isotope ratios were not allowed to differ by more than 10 % from the theoretical values. As a rule, the mass fragment with the highest intensity was used for quantification.

The limit of quantification for an individual compound in a given sample was defined by a signal to noise ratio greater than 3 times the average baseline variation in the retention window and a substance quantity in the sample greater than 3 times the quantity in the respective matrix and solvent blank. The recoveries for the PAHs, PCBs, and HCB were estimated using an external calibration method while PCDD/F recoveries were determined with the $^{37}Cl_4$-2,3,7,8-TCDD recovery standard. With the exception of HCB in a few samples, the recoveries were greater than 50 %. The reproducibility of the complete procedure, including sampling, was tested by collecting duplicate samples from a variety of sites. The normalised difference in the concentrations in parallel samples averaged 17 %.

Results and Discussion

The sum of the concentration of the 3-6 ring PAHs (Σ 3-6 ring PAHs) quantified in mature *Melaleuca* leaves exposed at Site 1 for 5 weeks to 7 months ranged from ~180 - 240 ng g^{-1} dw. The results for the grass sample from Site 3 were similar (180 ng g^{-1} dw). However, the concentrations of Σ 3-6 ring PAHs in mature leaves from *Melaleuca* plants growing at Site 2 were substantially higher, ranging from 2,100 to 2,600 ng g^{-1} dw. These levels reflect the much higher atmospheric concentrations at this site which are attributed to the road traffic[13]. Overall, the PAH levels were within the range reported in studies conducted in urban areas in other industrialised nations[15-17]; the *Melaleuca* leaves from Site 1 lay at the lower end, while the *Melaleuca* leaves from Site 2 (roadside) lay at the upper end.

PAH profiles and ratios

While the Σ 3-6 ring PAH levels were found to be very similar in *Melaleuca* leaves collected from Griffith University and grass leaves collected from the urban site, the PAH profiles, and hence the concentrations of individual compounds differed significantly (see Fig. 1). For example, in *Melaleuca* leaves exposed at Site 1 the Phe concentrations were more than a factor of 4 higher, the Flu and Pyr concentrations were approximately the same, and the B(g,h,i)P concentrations were about a factor of 10 lower in the *Melaleuca* leaf samples than in the grass leaf sample. Thus, in comparison to the PAH compound profiles in *Melaleuca* samples, the PAH profile in grass leaves

showed a relative shift towards PAHs with a higher molar mass. Since the atmospheric concentrations and profiles of PAHs are similar at both sites, these differences are likely to be related to characteristics of the plant species. The volumetric fraction of the lipophilic compartment in *Melaleuca* is at least a factor of 5 larger than in grass leaves. Thus, for a given atmospheric concentration the equilibrium leaf concentration in *Melaleuca* can be expected to be larger. Because only the Phe concentrations were significantly higher in the *Melaleuca* leaves, the data suggest that Phe may have approached equilibrium in both the *Melaleuca* and the grass leaves, while the other compounds likely did not. The fact that the concentrations of the 5- and 6-ring PAHs were much higher in grass than in *Melaleuca* may indicate that grass captured and retained particle-bound SOCs more effectively.

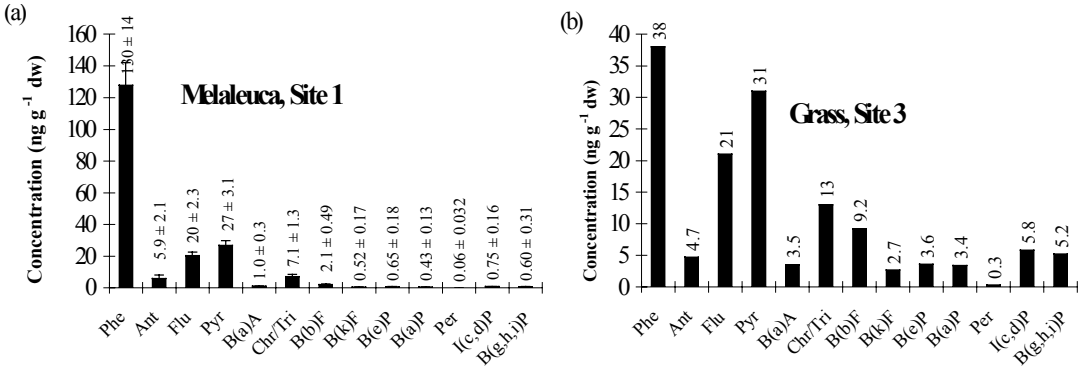

Figure 1: Concentration of PAHs in (a) Melaleuca samples from Site 1 and (b) grass samples from Site 3

Levels of PCDD/F in leaf samples

The sum of the concentrations of the PCDD/Fs (Σ PCDD/F) in mature *Melaleuca* leaves collected at Site 1 ranged from 16 - 29 pg g^{-1} dw. These levels are lower than in spruce needles from sites in rural and urban Germany[19], and similar to those determined in pine needles collected in a forest park in Montana, USA[6]. The Σ PCDD/F concentration determined in grass was about twice as high as in *Melaleuca* leaves from Site 1. 2,3,7,8-TCDD was not quantifiable in any of the leaf samples. However, other 2,3,7,8 substituted PCDD/Fs were determined and 2,3,7,8-TCDD toxicity equivalencies (I-TE) were calculated: 0.14 - 0.34 pg I-TE g^{-1} dw in *Melaleuca* leaves from Site 1 and 0.35 pg I-TE g^{-1} dw in the grass leaves.

Homologue profiles of PCDD/Fs have been used to investigate both sources and uptake pathways of PCDD/Fs found in vegetation[6,15]. The homologue profiles determined in mature *Melaleuca* leaf samples from Site 1 are dominated by OCDD, TCDF and TCDD (see Fig. 2a). While OCDD and TCDF have often been found to dominate PCDD/F homologue profiles of leaf samples, the relative importance of the TCDD is unusual.

In the grass sample, the ΣTCDF concentrations were comparable to the levels in the *Melaeuca* leaves (see Fig. 2b) (the ΣTCDD concentrations were below the limit of quantification), while the OCDD concentrations were a factor of ~4 higher. The trend to higher concentrations with increasing degree of chlorination is evident for the other homologues as well. This is the same

behaviour that was observed for the PAHs. It can also be explained by a higher capacity of grass leaves to retain particle-bound material on a per gram dry weight basis.

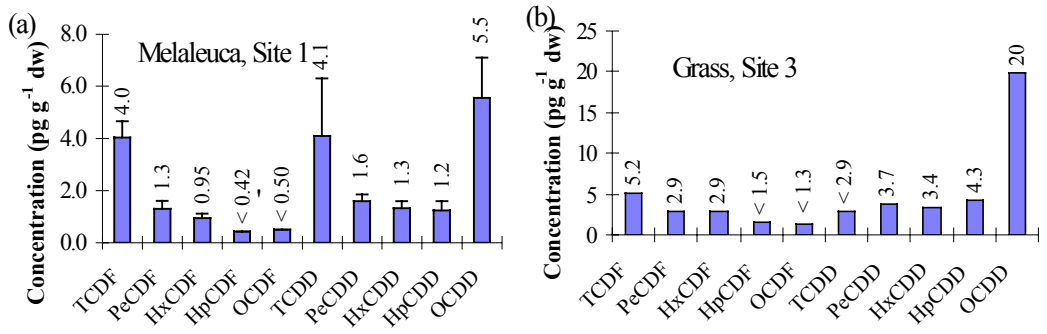

Figure 2: Concentration of PCDD/Fs in (a) *Melaleuca* samples from Site 1 and (b) grass samples from Site 3

References

1. Riederer M *Plant Contamination - Modeling and Simulation of Organic Chemical Processes* Chapter 6 Ed. S. Trapp and J. Mc Farlain Lewis Publisher **1995** ISBN 0566700787.
2. Grimmer G and Hildebrandt A *Deutsche Lebensmittel Rundschau* **1965**, 61, 237.
3. Eriksson G, Jensen S, Kylin H and Strachan W *Nature* **1989**, 341, 42.
4. Kylin H, Grimvall E and Oestman C *Environ. Sci. Technol.* **1994**, 28, 1320.
5. Meredith ML and Hites R A *Environ. Sci. Technol.* **1987**, 21**,** 709.
6. Safe S, Brown KW, Donnelly KC, Anderson CS, Markiewicz KV, McLachlan MS, Reischl A and Hutzinger O *Environ. Sci. Technol.* **1992**, 26, 394.
7. Jones KC, Sanders G, Wild SR, Burnett V and Johnston AE *Nature* **1992**, 356, 137.
8. Kjeller L-O, Jones KC, Johnston A E and Rappe C 1996 *Environ. Sci. Technol.* **1996**, 30, 1398.
9. Simonich S and Hites R *Environ. Sci. Technol.* **1994**, 28**,** 939.
10. Komp P and McLachlan M S *Environ. Sci. Technol.* **1997**, 31, 2944.
11. McCrady J *Chemosphere* **1994**, 28, 207.
12. Bakker MI, Tolls J, Sijm D and Kolloffel C *217 ACS Nat. Meet., Anaheim CA, USA, March* **1999**.
13. Müller JF, Hawker DW and Connell DW *Chemosphere* **1998**, 37, 1369 .
14. Müller JF Occurrence and distribution of semivolatile organic chemicals in the atmosphere and leaves, PhD Thesis, Griffith University, Brisbane, **1997**.
15. Wagrowski D and Hites R *Environ. Sci. Technol.* **1997**, 31, 279.
16. Tremolada P, Burnett V, Calamari D and Jones KC; *Environ, Sci. Technol.* **1996**, 30, 3570.
17. Nakajima D, Yoshida Y, Suzuki J and Suzuki S *Chemosphere* **1995**, 30**,** 409.
18. Hülster A Transfer von Dioxinen & Furanen aus Böden in Pflanzen. Ulrich Grauer Verlag **1994** ISBN 3861860619.
19. Reischl A, Reissinger M, Thoma H and Hutzinger O *Chemosphere* **1989**, 18, 561.