TREE BARK AS A PASSIVE SAMPLER FOR POLYCHLORINATED DIBENZO-P-DIOXINS AND FURANS

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Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F), commonly known as dioxins, are one class of persistent organic pollutants that are known to accumulate in environmental and biological systems.[1] It has been observed that different sources of PCDD/F produce different proportions of the toxic congeners.[2] This creates the possibility for the characterisation of the source of the PCDD/F from the observed congener profiles.

To date a wide range of matrices including include water, soils, sewage sludge, air particulates and vegetation have been analysed for PCDD/F in order to achieve a better understanding of the mechanisms of formation and their effects on ecosystems.[3-7]

Tree bark is an effective substrate for collection of airborne-derived environmental contaminants such a heavy metals, PCBs and PAHs. Given that PCDD/F are likely to be associated with fine airborne particulate matter which, through wet and dry deposition processes, will be retained and accumulated by bark over a relatively long time period, tree bark represents a potentially important new sampling strategy for high sensitivity PCDD/F measurement.

In combination with ion trap GC-MS the possibility therefore exists to develop a low cost high throughput screening capability for detection of airborne-derived PCDD/F. By comparing background levels from soil with data from seasonal sampling of vegetation such as leaves and grasses it is possible to obtain temporal data for the release of PCDD/F into the environment. However, to study the long-term accumulation of organic pollutants in the environment it is necessary to use a species that is not subject to seasonal change.

As trees are ubiquitous throughout both the urban and rural environment, it was decided to investigate the use of tree bark as a matrix for the trapping of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans. This work utilises accelerated solvent extraction/column clean-up and GC-MS-MS and targets sampling sites in and around a major UK city.

Experimental

Between 30g and 100g of bark were removed from the surface of each tree, 1-2 m above the ground, paying particular attention to the rain run off areas on the trunk and stored in screw top vials at room temperature until sample preparation. The nature of bark determined the sampling procedure: Peeling bark was manually collected by removing the bark bits from the trunk. Other types of bark was removed by scraping the surface and collecting the material. As the organic compounds of interest are deposited on the surface of the tree bark, only the external outer bark, no deeper than 2 mm, was required. Samples were frozen in liquid nitrogen prior to crushing in a teemer mill. The powdered tree bark was stored at room temperature in aluminium foil.

Extractions were performed using accelerated solvent extraction with toluene (Fisher Scientific, Loughbrough, UK) as the extraction solvent. The extraction conditions used were as follows: Temperature 150°C, pressure 1500psi, static time 8 minutes with 3 static cycles.

The extracts were cleaned up on a combined acid silica/basic silica gel column and a aluminium oxide column as described by Horstmann[8]. The dichloromethane from the final fraction is removed using a rotary evaporator and the sample is reconstituted using 150μL of nonane (Fisher Scientific, Loughbrough, UK) containing 50pg mL^{-1} of 1,5-dichloroanthraquinone as an internal standard.

Varian 3800 gas chromatograph with Varian Saturn 2000 ion trap mass spectrometer in EI/MS/MS mode was used. The GC column was a 30m x 0.25mm ID x 0.25μm film DBX 5. Using helium as a carrier gas, the GC oven temperature was programmed from 155°C (3.5 mins) to 235°C at 25°C min^{-1}, followed by 10 minutes at 235°C, then to 275°C at 5°C min^{-1}, then to 320°C at 10°C min^{-1}; the final temperature being held for 3 minutes. The validity of the method is shown in figure 1 below, with the separation of 13 TCDD congeners.

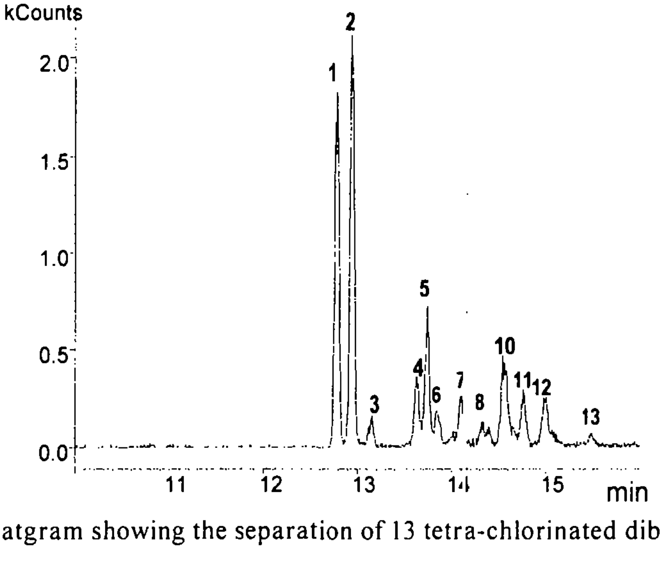

Figure 1: Chromatgram showing the separation of 13 tetra-chlorinated dibenzo-p-dioxins

Conclusions

Tree bark has been shown to act as a passive sampling media for dioxins, which in combination with GC-MS-MS provide a new measurement strategy for long term assessment of environmental contamination. By combining the data obtained from the analysis of dioxins in tree bark with that from seasonally dependent herbage such as grasses it would be possible to better characterise the occurrence, spatial distribution and sources of dioxins in the environment. There is scope for further development and refinement of methodology and future papers will deal with fully quantitative analysis using EPA 1613 and direct comparison with high resolution GC/MS. It is proposed to perform a detailed survey of the urban and rural environment (tree bark, soils, herbage) in the near future.

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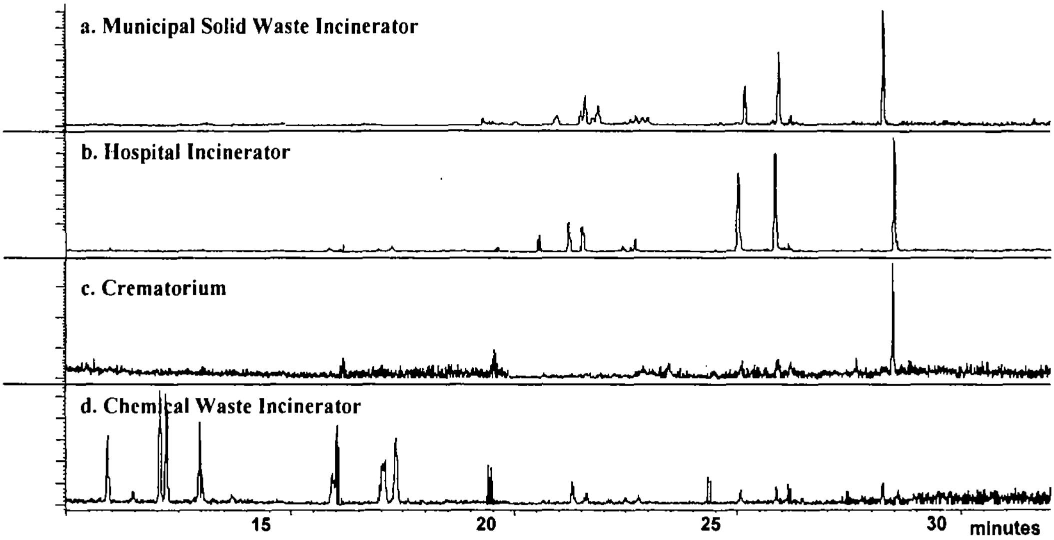
The MS/MS parameters for the analysis of PCDD/F were optimised to give maximum sensitivity and selectivity. Quantitation was achieved by calculating the peak area for both parent and daughter ions of the congeners under investigation. For the purposes of this investigation, a single internal standard compound was used, and all congeners were quantified relative to this.

Results and Discussion

It was observed that tree bark samples taken from near to different emission sources showed different patterns of congeners. Figure 2, below, shows typical chromatograms for PCDD obtained from tree bark samples. The sources of dioxin in the samples can be tentatively identified based on the congener patterns obtained.

Figure 2: Chromatograms showing PCDD congener patterns for tree bark samples from various industrial locations



Bark sampled from near a solid waste incinerator showed distinctive patterns of HpCDD and OCDD congeners. Whereas bark samples from near a decommissioned chemical waste incinerator, show distinctive TCDD and PeCDD patterns. Distinct differences were observed in the PCDF data.

The results from both the hospital and chemical incinerators show that the persistence of dioxin in the environment is a long-term problem, with the tree bark still showing appreciable levels of dioxin several years after the removal of the emission source. At present the processes by which the majority of the dioxins are deposited on the surface of the bark is unclear, yet the obvious health implications associated with inhalation of fine airborne particulate matter needs to be assessed.

Using a simple quantitative approach it is possible to determine that PCDD were present in the range of 10-190 ng kg^{-1} and PCDF in the range 10-100 ng kg^{-1}.