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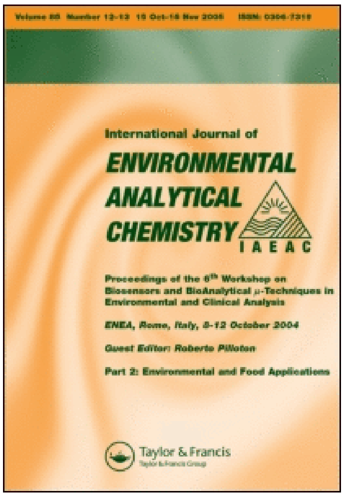

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Paul J. Clarkson[a]; David Larrazabal-Moya[a]; Ian Staton[a]; Cameron W. McLeod[a]; David B. Ward[b]; Vida N. Sharifi[b]; Jim Swithenbank[b]
[a] Centre for Analytical Sciences, Department of Chemistry, University of Sheffield, Sheffield [b] Department of Chemical and Process Engineering, Sheffield University Waste Incineration Centre, Sheffield

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THE USE OF TREE BARK AS A PASSIVE SAMPLER FOR POLYCHLORINATED DIBENZO-*p*-DIOXINS AND FURANS

PAUL J. CLARKSON[a], DAVID LARRAZABAL-MOYA[a],
IAN STATON[a], CAMERON W. McLEOD[a,*], DAVID B. WARD[b],
VIDA N. SHARIFI[b] and JIM SWITHENBANK[b]

[a]*Centre for Analytical Sciences, Department of Chemistry, University of Sheffield, Dainton Building, Brook Hill, Sheffield, S3 7UF;* [b]*Sheffield University Waste Incineration Centre, Department of Chemical and Process Engineering, Sir Robert Hadfield Building, Newcastle Street, Sheffield*

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The potential of using tree bark as a passive sampling medium for detection of Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F) in an urban environment has been investigated. Bark samples (~ 30 g) were extracted with toluene using accelerated solvent extraction. Extracts were then cleaned up via a multi-bed silica column and a Florisil column followed by GC-MS/MS analysis. It is shown that PCDD/F are present in tree bark collected from sites close to a municipal waste incinerator, a crematorium, a hospital and a chemical incinerator. Furthermore, characteristic patterns for dioxin congeners were observed for the suspected emission sources.

Keywords: Tree bark; Dioxins; PCDD/F; Source apportionation; GC-MS; GC-MS/MS

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F) are one class of persistent organic pollutants that have been shown to accumulate in environmental and biological systems [1]. PCDD/F are the by-products of the combustion of organic material in the presence of chlorine or chlorinated compounds, known sources being municipal waste incinerators and high temperature processing operations associated with, for example, the steel and cement industries. There are 210 PCDD/F congeners, of which 17 are considered toxic. It has been reported that different emission sources produce different proportions of the toxic congeners [2]. This creates the possibility for source apportionation based on the observed congener profiles.

From an environmental monitoring standpoint main sample types examined include soils [3,4], water [5], sewage sludge [6], air particulates [7] and vegetation [8]. In the case

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*Corresponding author. Fax: +44-114-2223650. E-mail: c.w.mcleod@sheffield.ac.uk

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of soil analysis [3], for instance, concentrations for total PCDD and PCDF upto 300 ng/kg and 1430 ng/kg have been reported in the UK for rural and urban soils, respectively. All of the aforementioned studies [3–8] are based on high resolution GC-MS instrumentation and because of the considerable investment and high operating costs analytical laboratories, in the main, are not able to provide a low cost screening capability for PCDD/F. An alternative to high resolution GC-MS is tandem GC-MS based on triple quadruple or ion trap technology and, as reported recently by Küchler and Brzezinski [9], the technique can be competitive with high resolution GC-MS. These workers determined 2,3,7,8-TCDD in pulp and paper effluent (concentration $3.8\,\mu g\,L^{-1}$) with a method limit of detection of about $1.0\,\mu g\,L^{-1}$.

Tree bark is an effective substrate for collection of airborne-derived environmental contaminants such as heavy metals [10,11], pesticides [12] and PAHs [13,14]. Bellis *et al.*, have also shown that source apportionation of uranium using isotopic analysis [15], and the mapping of environmental lead pollution using tree bark is possible [16].

Recently Wagrowski and Hites have used tree bark as a substrate for the measurement of PCDD/F in conjunction with soil analysis [17]. Due to their low vapour pressures, PCDD/F are known to be associated with fine airborne particulate matter, either through gas-particle partitioning or through exclusive particle phase bonding [18]. Through wet and dry deposition processes, and through the filtering effects of the tree canopy, PCDD/F will be retained and accumulated by bark over a relatively long time period [19].

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. Present work based on initial method development by Larrazzabal-Moya [20], utilises accelerated solvent extraction/column clean-up and GC-MS/MS and targets a number of combustion facilities in both urban and rural settings in and around the city of Sheffield (UK).

EXPERIMENTAL

Reagents and Materials

Toluene, hexane and dichloromethane (Fisher Scientific, UK) were glass distilled and stored in glass before use. Silica and Florisil (BDH, Poole, Dorset, UK) were activated at 105°C and then stored in a desiccator before use.

Sampling

Tree bark was sampled from various locations as shown in Table I. 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 were removed by scraping the surface and collecting the material. As the organic compounds of interest were deposited on the surface of the tree bark, only the external outer bark, no deeper than 2 mm, was required. Also by taking a sample that contains too much fibrous material from the tree it is possible to cause serious damage to the tree. Between 30 g and 100 g 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, where PCDD/F are likely to accumulate.

TABLE I Sample sites and types

Sample sites	*Potential source*	*Tree type*
Bernard Rd, Sheffield	MSWI	Oak, rough bark
Effingham St. Sheffield	MSWI/Heavy Industry	Poplar, rough bark
Weston Park, Sheffield	Hospital Incinerator	Horse Chestnut, rough bark
City Road Cemetery, Sheffield	Crematorium	Sycamore, smooth bark
Park Square, Sheffield	MSWI/Heavy traffic	Sycamore, Smooth bark
Bolsover, N. Derbyshire	Chemical Waste Incinerator	Oak, rough bark

Sample Preparation

Samples were frozen in liquid nitrogen, in order to make them brittle, prior to crushing in a teemer mill. The powdered tree bark was stored at room temperature in aluminium foil. The powdered tree bark (30 g) was extracted using a Dionex ASE 200 accelerated solvent extractor with toluene. The extraction conditions used were as follows: temperature 150°C, pressure 1500 psi, static time 8 min with 3 static cycles. Independent work has reported that analyte recoveries of 70–95% are realised [21].

The extracts were cleaned up on a combined acid silica/basic silica gel column and a florisil column as described by EPA Method 1613 [22]. The dichloromethane from the final fraction was removed using a rotary evaporator and the sample was reconstituted using 150 μL of nonane (Sigma-Aldrich, UK) containing 50 $\mu g\,L^{-1}$ of 1,5-dichloroanthraquinone as an internal standard.

GC-MS/MS

Extracts of samples and standard solutions were analysed using a Varian 3800 gas chromatograph with Varian Saturn 2000 ion trap mass spectrometer in EI/MS/MS mode. The analytical column was a DBX 5 (30m × 0.25 mm ID × 0.25 μm film) using a temperature programme given in Table II. The optimised parameters for the MS/MS analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans are also given in Table II.

A certified reference material (Incinerator fly ash, BCR 490) was analysed in order to monitor performance, as well as to provide a specific congener pattern (incinerator fly ash).

RESULTS AND DISCUSSION

Basic Analytical Performance

A fly-ash CRM was analysed in order to define and set up the scan segments for each of the different classes of dioxin homologue. This sample was also used for optimising the chromatographic conditions. Figure 1 shows effective separation of 13 tetra-chlorinated dioxins and it is clear that the methodology is well suited for sensitive detection of individual dioxin congeners. Detection response was similar to that reported by Küchler and Brzezinski [9], a signal to noise ratio of 11 being obtained for a 0.32 $\mu g\,L^{-1}$ standard of 2,3,7,8-TCDD. The use of large volume injection with solvent removal also increased the sensitivity of the technique.

TABLE II Gas chromatograph conditions

Parameter	*Conditions*					
GC Parameters						
Flow Rate:	1.2 mL/min He					
Injector:	160°C–(2 mins) then 320°C at 200°C/min (5 min) Split Valve-Open–Initial					
Closed-1.5 min						
Open-3.2 min						
Column Oven:	35 µL injection 160 for 3.50 min 160–235°C @ 24°C/min, Hold 10 min 235–275°C @ 5°C/min, No Hold 275–300°C @ 10°C/min, Hold 5 min					
General MS Parameters						
Parent Ion Isolation Window	2 *m*/*z*					
CID time	20 µs					
Broadband amplitude	30 V					
Multipler Offset	150 V					
Filament current	95 µA					
Ion trap temperature	220°C					
Transfer line temperature	300°C					
MS/MS Parameters						
No. of Chlorine atoms (*m*/*z*)	CID Storage Level (*m*/*z*)	PCDD CID Amplitude (V)	Acquistion Mass Range (*m*/z)	CID Storage Level (*m*/*z*)	PCDF CID Amplitude (V)	Acquisition Mass Range (*m*/*z*)
4	161	1.99	245–324	145	3.11	230–308
5	195	1.82	275–358	179	3.38	265–342
6	229	2.02	315–394	213	3.60	300–376
7	263	2.22	350–430	247	3.24	335–412
8	297	2.42	385–464	283	3.60	370–446

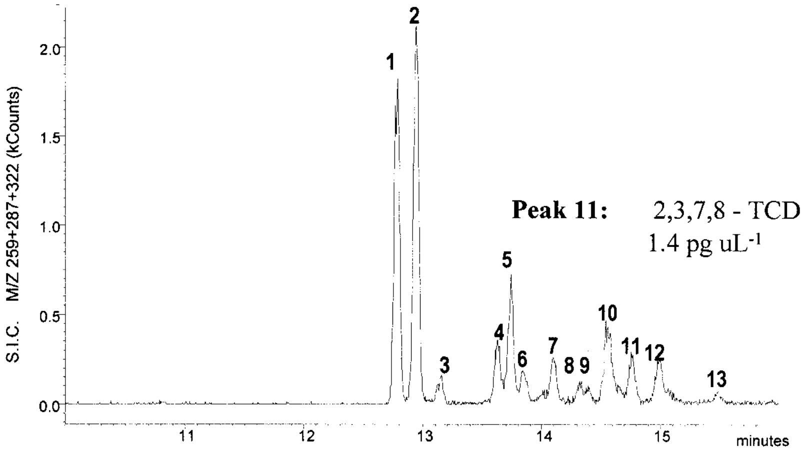

FIGURE 1 Chromatogram showing separation of TCDD in flyash sample.

The identification of the PCDD/F was based on retention times and the CID fragmentation spectra of the molecule. The spectra of the daughter ions showed the loss of both a chlorine atom (*m*/*z* 35) and of a COCl moiety (*m*/*z* 63) from the parent ion. In order to obtain the correct identification of the compound, it is essential that both the parent and daughter ions are present in the mass spectrum.

Tree Bark Analyses

Sampling sites were selected for their proximity to potential sources of PCDD/F, in and around, South Yorkshire and North Derbyshire. As shown in Figs. 2 and 3 it is clear that PCDD/Fs are present in samples of tree bark taken from various locations. The sources of PCDD/F in the samples can be tentatively identified based on the congener patterns obtained.

Bark sampled from near a solid waste incinerator showed distinctive patterns of HpCDD and OCDD congeners. This pattern is evident from both Figs. 2a and 2b, which reflect emissions from a municipal solid waste incinerator and a hospital waste incinerator, respectively. The results for the tree bark sample from near a crematorium showed significantly lower levels of HpCDD (Fig. 2c). Bark samples taken from near the site of a decommissioned chemical incinerator exhibited a characteristic congener pattern that is high in TCDD and PeCDD, yet low in HxCDD, HpCDD and OCDD (Fig. 2d). It should be noted that this plant was decommissioned in 1994, yet, the extracted bark samples are still yielding characteristic dioxin patterns. These results are consistent with the findings of Fisher *et al.* [2] and show the potential for utilising tree bark for source apportionation investigations.

It is of further interest to note the levels of PCDF detected were substantially less than the levels of PCDD. This can be clearly seen in all four chromatograms (Figs. 3a–d). As shown in Figs. 3a and 3b the solid waste incinerator produces higher levels of HxCDF, than any other homologues. In contrast the chemical waste incinerator generates higher levels of TCDF and PeCDF (Fig. 3d). The bark samples from the crematorium showed no detectable PCDF levels (Fig. 3c).

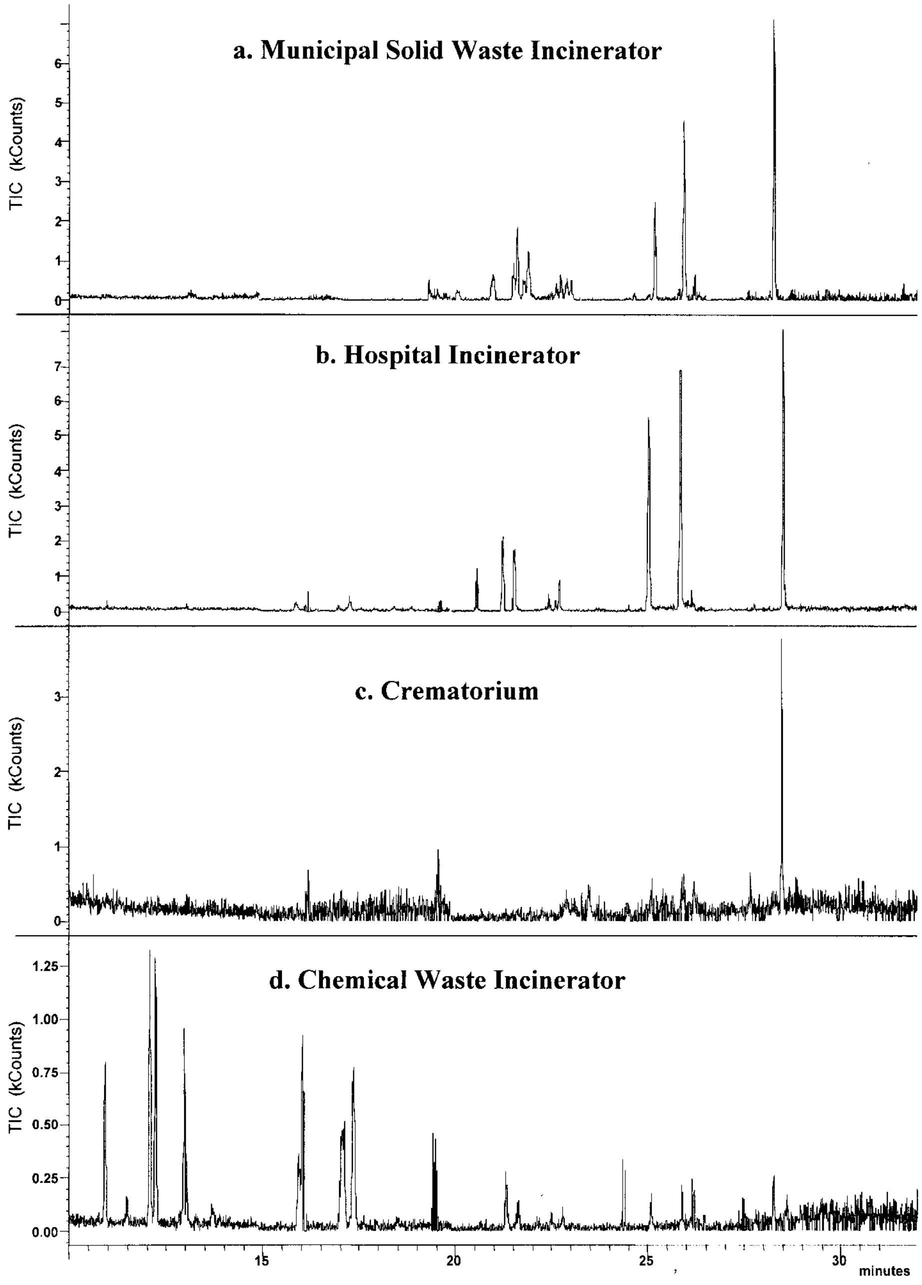

FIGURE 2 Chromatograms showing PCDD congener patterns for tree bark samples from various industrial locations.

The results from the chemical waste incinerator show that the persistence of PCDD/F 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 PCDD/F are deposited on the surface of the

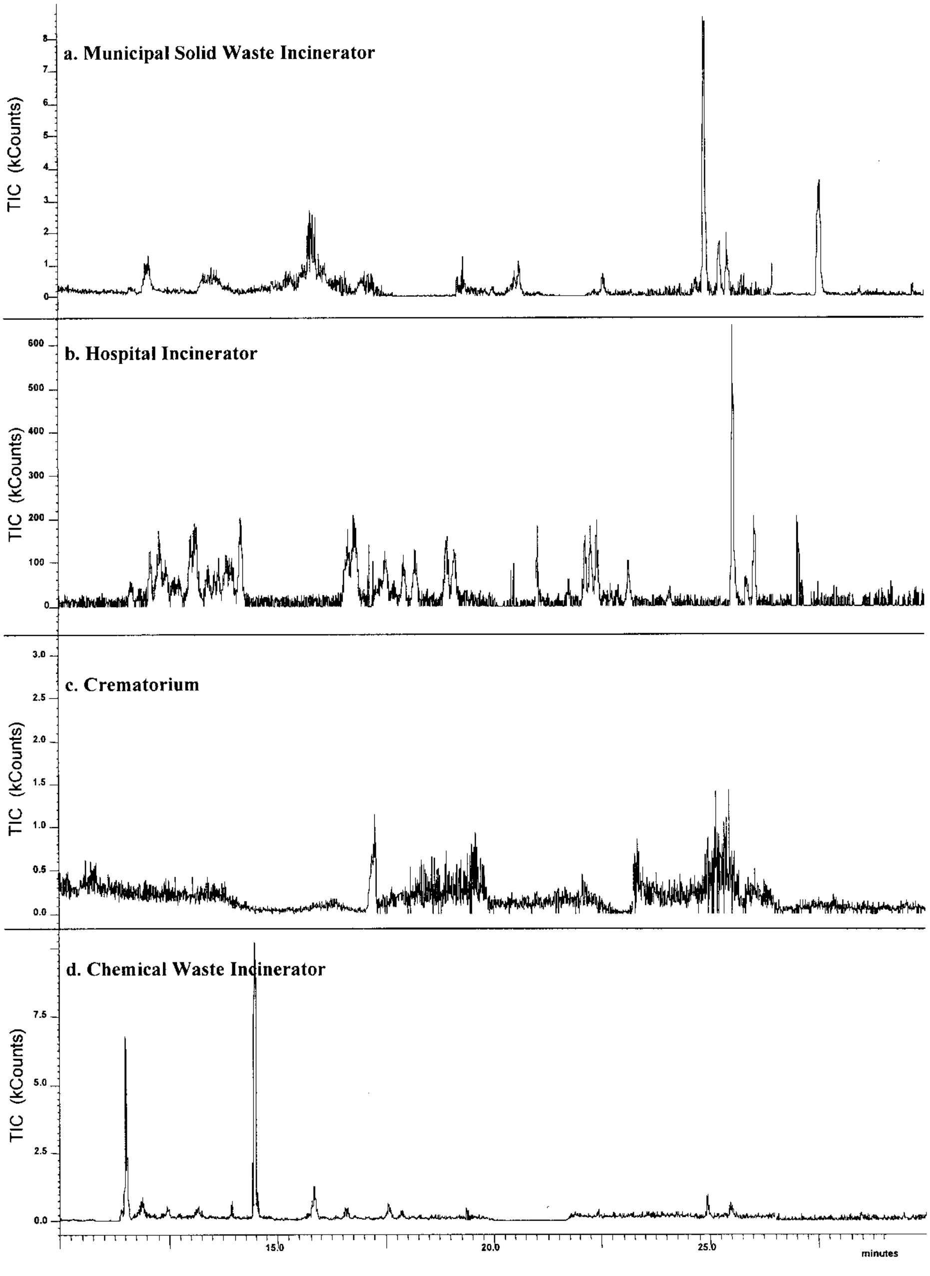

FIGURE 3 Chromatographs showing PCDF congener patterns for tree bark samples from various industrial locations.

bark is unclear, however, it has been reported that deposition fluxes to the canopy for both PCDD and PCDF are homologue specific and are also dependant on tree species [18]. Also Horstmann and McLachlan have shown that deposition rates are significantly higher for the lower homologues (Cl_4–Cl_6) of both PCDD and PCDF in deciduous forests than in coniferous forests or on grass [18].

CONCLUSIONS

Tree bark has been shown to act as a passive sampling media for PCDD/F, 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 PCDD/F 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 quantitative analysis 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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