Transfers of Airborne PCDD/Fs to Bulk Deposition Collectors and Herbage

Kevin C. Jones and Raquel Duarte-Davidson+, Institute of Environmental and Biological Sciences
Lancaster University, Lancaster, LA1 4YQ, UK

+ Current address: MRC Institute for Environment and Health
94 Regent Road, Leicester, LE1 7DD, UK

Abstract
Air PCDD/F concentrations, bulk deposition fluxes and grass concentrations/offtakes were measured concurrently at 6 sites in Bolsover, Derbyshire, northern England over a year during 1992/3. The data can be used to examine how the airborne PCDD/Fs transferred to bulk deposition collectors and the grass. Generally the mixture of PCDD/F 2,3,7,8-substituted congeners and homologs were the same in the air, in the bulk deposition and in the grass over a given sampling period at a given site. This suggests that PCDD/Fs of different levels of chlorination were transferring with similar efficiencies from the air to the collectors and grass, despite having different gas:particle partitioning behaviour in the air. The similarities in the PCDD/F mixture in air and grass suggest that the different PCDD/Fs are scavenged by the grass from the atmosphere with similar efficiencies and that soil-borne PCDD/Fs could be making only a minor contribution to the herbage concentrations.

Introduction

This paper summarises data obtained during a year-long monitoring program undertaken in 1992/3 in Bolsover, Derbyshire, UK (1), in which congener/homolog-specific PCDD/F data were obtained from air, deposition and herbage sampled concurrently. The data provide clues as to how PCDD/Fs deposit from the atmosphere to the terrestrial surface.

Materials and Methods

Air sampling Samples were collected at 6 sites for about a year, from October 1992 using filter/polyurethane foam to trap particulates and vapours respectively. Data from just two sites, the local background site and the one nearest an industrial complex, will be discussed here. On 22 June 1993, 14 September 1993 and 30 October 1993 concurrent air, deposition and herbage samples were collected.

Bulk deposition and grass sampling Teflon coated 'Upturned Frisbee' bulk deposition collectors were deployed and grass was sampled at each site and the yield recorded. A 1 m^2 of grassland was fenced off in Feb. '93, to ensure no animals grazed on the area; it was not cut initially until 30 Mar.'93, but thereafter 3 samples were collected from each of the sites on the sampling dates given above.

Sample preparation and analysis The samples were spiked with a mixture of labelled PCDD/F internal standards to correct for analytical losses and ensure quality control. All the 2,3,7,8-substituted PCDD/Fs and the total homolog groups were quantified. Analysis was carried out using isotope dilution high resolution gas chromatography/mass spectrometry. Detection limits for the various 2,3,7,8-substituted PCDD/Fs varied between ~0.4 and 2.5 pg on column. This was equivalent to ~1.3 fg m^{-3} for air, ~0.13 ng kg^{-1} dry weight for vegetation and ~0.5 pg m^{-2} day^{-1} for deposition samples. Field blanks were always well below those detected in the corresponding batch of samples.

Results and Discussion

PCDD/F transfer velocities The data enabled calculation of transfer or deposition velocities (Vd) values across the range of congeners and site locations. Values for individual congeners/homologs throughout the whole study ranged between 0.034 - 0.82 cm sec^{-1} at the 2 sites, averaging 0.27 for ΣPCDD/Fs at the regional background site and 0.22 at the site closest to the industrial complex. The Vd values were similar across the range of congeners/homologs; even though a substantial proportion of the TCDD/F air burden is probably in the vapour phase and almost all of the OCDD/F burden is likely to be associated with the particles there were no systematic differences in Vd with chlorination level (although there appear to be some differences for selected congeners). This implies that vapour and particle-associated PCDD/Fs transfer to the bulk deposition collectors with similar efficiency.

Comparisons of the herbage data with the air and deposition data Vegetation receives inputs of airborne organic contaminants via gas phase deposition, particulate dry deposition and wet deposition. The concentration of compounds associated with the plant tissue is therefore affected by the rate at which compounds are supplied from the atmosphere, the diluting effects of plant growth, environmental variables - such as temperature and precipitation -and properties of the plant and sward. These factors will have influenced the concentrations measured for the 3 sampling intervals. The general trend at all sites was for higher concentrations of PCDD/Fs being measured in the samplings made on 22 June and the 30 October, with concentrations being lower in the 14 September sampling. Yields (g m^{-2}) for the different sampling intervals followed the sequence 22 June harvest > 14 September harvest > 30 October harvest at all sites.

As noted previously, the air and deposition patterns were very similar; herbage is similar again. This is an important observation, because - as for the deposition - it implies that the tetra- through to octa-CDD/Fs have transferred from air-to-herbage in this study with roughly equal efficiency. This is shown by a detailed comparison of the congener composition for the background and industrial sites in Table 1 and by Figure 1, where the concentrations of the different 2,3,7,8-substituted congeners in air and vegetation for both sites are plotted. Figure 1 shows a highly significant correlation between concentrations of different PCDD/Fs in air and vegetation at both sites.

The 'offtake' of PCDD/Fs could be calculated (i.e. the amount of compound per unit area of land surface), either as the total offtake per harvest (pg m^{-2}) or as the retention of PCDD/Fs by the grass per unit time (i.e. pg m^{-2} day^{-1}). Figure 2 shows the total offtake of each of the 17 2,3,7,8 -substituted PCDD/Fs for the 30 October harvests at the same two sites plotted against their bulk deposition flux. Again, the relationship is a strong linear one. Offtakes at the regional background site (C) were generally higher (by a factor of ~3) than at the site closest to the industrial complex (D) for a given bulk deposition flux, because the sward at the former site (plant productivity averaged 1.9 g dw m^{-2} day^{-1}) was much fuller than at the latter (0.9 g dw m^{-2} day^{-1}), and was therefore presumably a more efficient scavenger/retainer of the airborne PCDD/Fs. Site C was a well kept, fertilised lawn whilst site D was rough pasture for grazing. The ratio of the flux removed by grass per day (pg m^{-2} day^{-1}) to the bulk deposition flux (pg m^{-2} day^{-1}) was in the range 0.63-3.0 (average 1.1) at the regional background site and in the range 0.02 - 1.6 (0.38) at the site closest to the industrial complex. Schuler *et al.* (2) obtained values in the range 0.03 - 1.9 (0.4 for the ΣTEQ) for the same ratio in a study undertaken with a Bergerhoff deposition sampler in Switzerland and where the grass growth rate averaged ~2.5 g dw m^{-2} day^{-1}.

Comments on air-plant modelling of PCDD/Fs Lorber and co-workers (3, 4) presented a model of air-plant transfers of PCDD/Fs, considering the gas-phase and particle phase transfer processes separately. They postulated that gas-phase PCDD/Fs would be retained by the waxy surface of plant tissues, whilst particle-phase transfers would result in deposition of PCDD/Fs to the leaf surface which may be subsequently washed off. The implication of their model, subsequently adopted by others, is that a given mixture of PCDD/Fs would transfer with different efficiencies (dependent on the gas:particle phase partitioning), with the result that there would be a different

Figure 1: Air concentrations versus plant concentrations at two sites for one sampling interval (8 Dec. '92-5 Jan. '93).

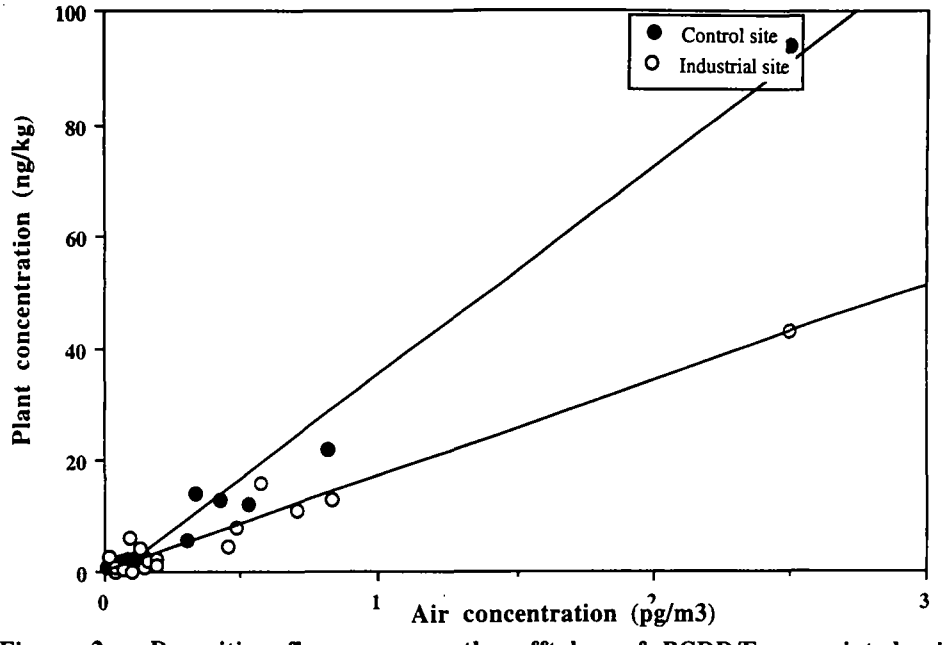
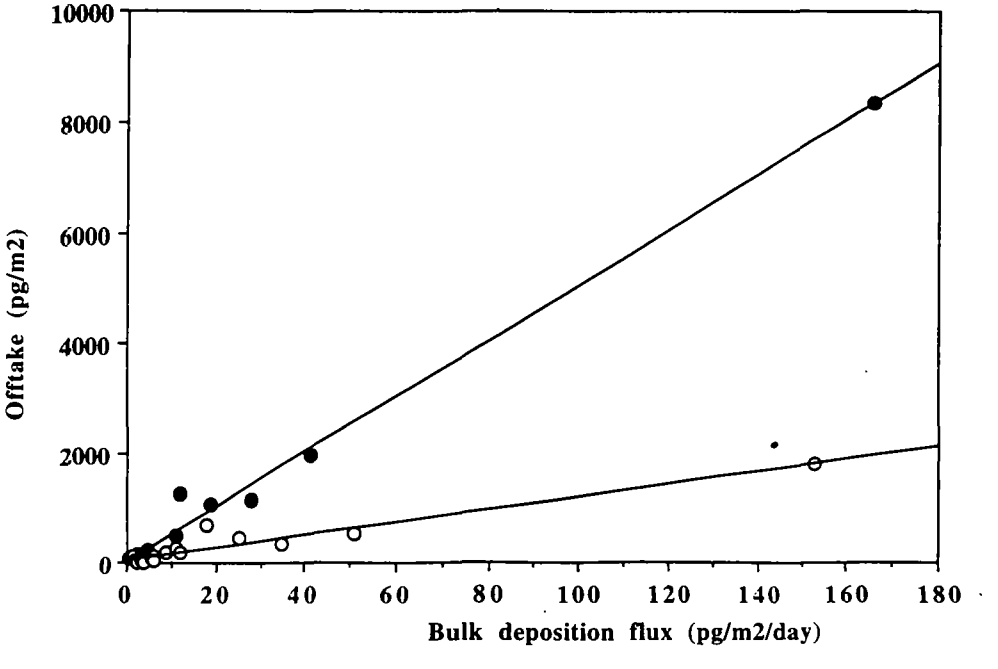


Figure 2: Deposition fluxes versus the offtakes of PCDD/Fs associated with vegetation at two sites for the final sampling interval. Solid circle is the regional background site: $y = 50x + 11$, $r^2 = 0.992$. Hollow circle is the site closest to the industrial complex: $y = 11x + 52$, $r^2 = 0.921$.



mixture of PCDD/Fs on the vegetation. The current dataset, and that obtained by Schuler *et al.* (2), does not support this model structure, because the sward has a quantitatively similar mixture of PCDD/Fs to that measured in the air. As McLachlan (5) noted, vegetation may not just scavenge the gas phase of a certain volume of air, but also the particle phase of an equal volume.

It is possible to derive estimates of the volumes of air 'scavenged' or 'cleaned' by vegetation in this study. At the site closest to the industrial complex, for example, 440 g dw of vegetation was harvested on the 22 June '93 and contained the PCDD/Fs from the equivalent of ~33 m^3 of air sampled over the 84 days since the previous harvest. On the 14 September the 176 g of vegetation contained the PCDD/Fs from the equivalent of ~11 m^3 of air sampled over the 84 days since the previous harvest and on the 30 October the 42 g of vegetation contained the PCDD/Fs from the equivalent of ~45 m^3 of air sampled over the 46 days since the previous harvest. From field measurements with meadow grass and corn McLachlan (5) estimated that the former scavenged the PCDD/Fs from the equivalent of 9 m^3 of air per g dry grass while the latter scavenged the equivalent of 4.5 m^3/g dw; he then developed a model to describe the accumulation of PCDD/Fs from air into cows milk based on 'vegetation scavenging' of PCDD/Fs. This was tested against a UK database of air, grass and cows milk concentrations and performed better across the range of congeners than other models (4).

Table 1: PCDD/Fs in air, deposition and herbage for the regional background site and the site closest to the industrial complex for the sampling interval 14 Sept-30 Oct 1993 (air in pg m^{-3}, deposition in pg m^{-2} day^{-1}, grass in ng kg^{-1} dry weight).

	Regional background site (C)			Industrial complex site (D)		
	Air	Deposition	Grass*	Air	Deposition	Grass*
2,3,7,8-TCDD	0.009	<0.46	0.72	0.017	1.6	2.8
1,2,3,7,8-PeCDD	0.03	2.3	1.3	0.04	3.8	<0.08
1,2,3,6,7,8-HxCDD	0.08	4.8	2.3	0.09	10.8	6.0
1,2,3,4,7,8-HxCDD	0.04	2.3	0.93	0.04	3.2	0.73
1,2,3,7,8,9-HxCDD	0.1	3.8	1.8	0.13	8.9	4.2
1,2,3,4,6,7,8-HpCDD	0.82	41	22	0.84	51	13
OCDD	2.5	166	94	2.5	153	43
TCDD	0.72	73	66	3.1	509	750
PeCDD	0.56	54	33	1.2	477	410
HxCDD	0.65	38	26	0.78	73	38
HpCDD	0.71	41	22	0.73	48	11
2,3,7,8-TCDF	0.33	12	14	0.57	18	16
1,2,3,7,8-PeCDF	0.06	2.5	1.8	0.10	2.2	<0.09
2,3,4,7,8-PeCDF	0.10	4.1	2.2	0.19	6.0	1.2
1,2,3,4,7,8-HxCDF	0.30	11	5.6	0.45	12	4.6
1,2,3,6,7,8-HxCDF	0.10	4.5	2.2	0.16	5.7	1.8
2,3,4,6,7,8-HCDF	0.14	4.8	2.6	0.19	6.0	2.4
1,2,3,7,8,9-HxCDF	0.02	1.8	0.61	0.07	1.9	0.54
1,2,3,4,6,7,8-HPCDF	0.53	19	12	0.71	25	11
1,2,3,4,7,8,9-HPCDF	0.11	2.9	1.1	0.14	3.2	0.89
OCDF	0.42	28	13	0.48	35	8.0
TCDF	1.6	24	93	3.3	131	290
PeCDF	0.84	27	31	2.3	64	21
HxCDF	0.45	18	13	1.4	26	19
HpCDF	0.22	<1.8	<0.22	0.43	<1.6	<0.31

* Yield were 89 and 42 g m^{-2} dry weight, respectively, at the two site

General comments It is appropriate to remember that although the processes of dry gaseous and dry particulate deposition of PCDD/Fs from air-vegetation have been studied experimentally, in the

temperate, maritime environment of the UK wet depositional inputs may be extremely important in supplying SOCs to terrestrial ecosystems. This may result in 'flushes' of inputs to the vegetation surface, supplying particulate and dissolved PCDD/Fs to the plant surface and presumably potentially washing off some previously deposited material. Wet deposition has been shown in mass balance studies to dominate the inputs of many SOCs to the Great Lakes, for example. The bulk deposition samplers used in this study also obviously receive and sample the wet deposition. The similarities in the mixtures of PCDD/Fs in the air, deposition and grass noted in this study may therefore be at least partly explained by the influence of wet deposition in moving PCDD/Fs out of the atmosphere to the terrestrial surface. The similarities in pattern are perhaps also indicating that gas phase PCCD/Fs in air are equilibrating with the plant in the time periods between harvesting in this study (see also ref. 7).

Acknowledgements We are grateful to SAL Ltd for chemical analysis of the air samples, various landowners for allowing us access to the field sites, Mr S. Holmes (Bolsover District Council) for his assistance, the Environment Agency for funding and Dr M. McLachlan for helpful discussions. The views expressed are those of the authors and do not necessarily reflect those of the Agency.

Literature cited

1. Jones, K. C.; Duarte-Davidson, R. *Environmental monitoring of dioxins and furans in air, deposition and herbage around the Coalite Works, Bolsover, Derbyshire.* Environment Agency Report (1997).
2. Schuler, F.; Schmid, P.; Schlatter, C.; *Organohalogen Cmpds*, 1995, 26, 59-62.
3. Lorber, M. N.; Cleverly, D.; Schaum, J.; Phillips, L.; Schweer, G.; Leighton, T. *Sci Total Environ.*, 1994, 156, 39-65.
4. Lorber, M. *Organohalogen Compounds* 1995, 24, 179-183.
5. McLachlan, M. S. *Organohalogen Compounds* 1995, 26, 105-108.
6. Douben, P. E. T.; Alcock, R. E.; Jones, K. C. *Environ. Pollut.* 1997, 95,333-344.
7. Thomas, G.; Sweetman, A.; Lead, W. A.; Jones, K. C. Proc. this conference.