VERTICAL DISTRIBUTION OF PCDD/FS IN FOREST SOIL FROM QUEENSLAND, AUSTRALIA

Joelle A. Prange[1,2], Caroline Gaus[1,2], Olaf Päpke[3], Roland Weber[4] and Jochen F. Müller[1]

[1]National Research Centre for Environmental Toxicology, 39 Kessels Road, Coopers Plains 4108, Queensland, Australia.
[2]School of Public Health, Griffith University, Nathan 4111 Queensland, Australia.
[3]Ergo Forschungsgesellschaft mbH, Geierstrasse 1, 22305 Hamburg, Germany
[4]Universität Tübingen, Inst. for Org. Chem., Auf der Morgenstelle 18, 72076 Tübingen, Germany

Introduction

A number of recent investigations in Queensland and elsewhere have identified elevated concentrations of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) in geological deposits, rural localities, archived soil and dated sediments from regions distant to industry and/or periods before industrialisation. The PCDD/F congener profile in most of these samples are dominated by PCDDs (in particular OCDD) with increasing concentrations of PCDDs with increasing chlorination, whereas PCDFs are low or below the limit of quantification. The source of the elevated PCDDs in each of these studies is currently unknown, and natural formation has been suggested as a potential source of this contamination.

Due to the physico-chemical properties of PCDD/Fs, such as a high affinity for organic carbon, the majority of PCDD/Fs in soils from contemporary sources are typically present in the top 0 –15 cm, and are generally considered not to diffuse into deeper layers. If a natural formation of PCDD/Fs in the soil from a historic source exists, then it would be expected that elevated PCDD/Fs are present in deeper soil layers. In Queensland, previous sampling of soils have focused on the surface (0 – 5 cm); therefore, in order to investigate the extent of the PCDD/F contamination, and to provide information on a the potential PCDD/F source in Queensland, a soil core sample was collected in a forest area in Queensland and analysed for PCDD/Fs.

Material and Methods

A soil core was collected from a remote eucalypt sclerophyll forest situated in the southeast region of Queensland, Australia. The soil core was collected with a hand soil auger with a head size of 70 mm with extensions to 3.5 m. The hand auger cored in 10 cm increment, each 10 cm was removed and homogenised using stainless steel sampling equipment. The samples were stored in aluminum foil and kept frozen prior to analysis. To avoid contamination during sampling, the soil corer was cleaned between each 10 cm increment and care was taken not to allow soil from the surface to fall into the deeper layers.

Samples from each 50 cm layer (0-10 cm, 50-60 cm, 100-110 cm, 150-160 cm, 200-210 cm, 250-260 cm, 300-310 cm and 340-350 cm) were analysed for 2,3,7,8-substituted congeners at ERGO Forschungsgesellschaft mbH, Germany, using standardized method[1]. The detailed analytical method is described elsewhere[2].

Results and Discussion

In this study PCDD/Fs were detected in all soil core layers analysed, the ΣPCDD/F concentrations ranged from 22 - 59 ng g^{-1} dw (3.2 – 15.9 pg g^{-1} dw WHO TEq). In all depth layers PCDDs dominated and the congener profile was consistently dominated by OCDD, contributing between 97.7 % and 99 % of Σ PCDD/Fs. The concentration of ΣPCDDs ranged from 22 – 59 ng g^{-1} dw, and concentration generally decreased with depth; however the deepest soil layer (3.5m) still contained elevated concentrations. In the deeper soil however, only HpCDD and OCDD were detected in substantial concentrations (with low concentrations of 1,2,3,4,6,7,8 HpCDF) and no other non-2,3,7,8 PCDD/Fs were identified. In contrast, the concentrations of ΣPCDFs decreased in concentration with increasing depth and elevated PCDFs (240 pg g^{-1} dw) were detected only in the surface soil (0 – 10 cm). In the deeper soil layers ΣPCDFs ranged from 12.6 – 4.2 pg g^{-1}dw. The D:F ratio reflects this strong decrease in PCDF concentration, ranging from 240 in the top layer to 12 000 in the bottom layer.

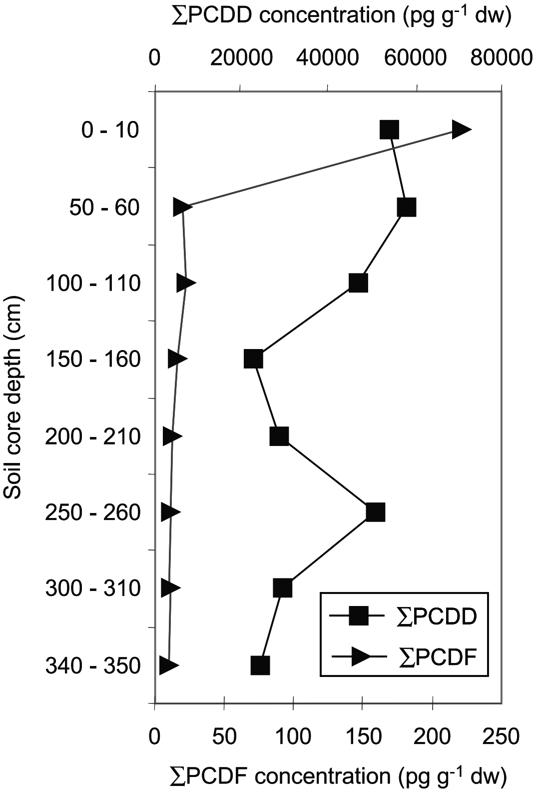

Figure 1. ΣPCDD (top axis) and ΣPCDF (bottom axis) at depth in the forest soil core

Due to the physico-chemical properties of PCDD/Fs, they are generally found to accumulate in the top 0 – 15cm and vertical migration in soils is typically considered negligible. However, similar to the present study, Brzuzy and Hites [3] report elevated PCDD/Fs to a depth of 90 cm (ΣPCDD/F ~16 ng g^{-1} at 90 cm) from a soil core collected from Mitchell, Indiana . The authors suggested that due to the low organic content of these soils, the holding capacity for PCDD/Fs may have been overloaded resulting in PCDD/F leaching to deeper soil layers. However, a vertical migration would be expected to be similar for both PCDD and PCDF homologues. In the present study, almost exclusively OCDD and HpCDD were found in deeper soil layers whereas PCDFs (including OCDF and HpCDF) decreased rapidly with increasing soil depth.

To the knowledge of the authors, no other studies have identified significant PCDD/F contamination to a depth of 3.5m in soils. Two possibility are discussed which could explain the elevated concentrations of PCDDs detected at this site; a) the contamination is due to a natural formation of PCDDs in the deep soil layers by a yet unidentified process and b) the migration of a PCDD precursor and subsequent transformation to PCDDs in the deeper soil.

In this study, elevated concentrations of almost exclusively HpCDD and OCDD were detected to 3.5 m depth in the soil core from this study. Similarly, in a study by Green et al., 2001, elevated PCDD/Fs were detected in archived soil samples from the Rothamsted Experimental station in the UK, from fields not subject to chemical application[4]. In this study they identified an increase in the concentration of OCDD and HpCDD with depth and suggested that if the contamination was not due to migration then the resulting OCDD may have been formed by poorly understood processes in the subsoil or remnants of an ancient OCDD source. Furthermore, in a recent study by Gaus et al., results from dated sediment cores from the coast of Queensland indicate that post depositional processes may have resulted in the specific PCDD/F profiles identified in ‘natural formation’ samples[5]. The authors suggested that the original source pattern is most likely predominately OCDD and/or HpCDD. The results from the present study have identified only OCDD and HpCDD at substantial concentration in the deeper soils. Therefore these results suggest that if natural formation processes are responsible for the PCDD/F contamination in Queensland, the PCDD pattern in the deeper soils may represent the original source profile and further investigation are necessary at this site to identify potential formation processes. In this respect it is interesting that the PCDD/F congeners detected in the deep soil samples in this study (OCDD, HpCDD and 1,2,3,4,6,7,8 HpCDF) have been produced in experiments by the enzymatically-mediated chlorination of humic substances[6], proposing a potential natural formation mechanism of PCDD/Fs.

However, in contrast to the deeper soil layers, the 0 – 10 cm soil contained elevated concentrations of PCDFs (ΣPCDF 241 pg g^{-1} dw). The PCDF congeners and isomers present in the surface soil are not typical for ‘natural formation’ samples and may provide further information on possible PCDD/F sources. For example the 1,2,4,6,8,9 HxCDF and 1,2,3,4,6,8,9 HpCDF are dominant PCDF isomers in the surface soil sample, which are considered a ‘marker’ of PCP (pentachlorophenol) contamination[7]. Chlorophenols, such as PCP are well known for high OCDD contamination, and furthermore a number of studies have identified the photochemical and biochemical transformation of chlorophenols to HpCDD and OCDD[8,9, 10]. Chlorophenols are relatively polar and therefore are able to migrate downwards in soil[11]. Subsequent conversion of chlorophenols (or dioxin pre-cursor) to OCDD and HpCDD in the deeper soil layers may therefore account for the contamination at this site.

The results from this study have identified contamination of predominately HpCDD and OCDD to a depth of at least 3.5 m at a site in the coast of Queensland. Although the origin of this contamination is still unknown, the results from this study support a PCDD/F source of predominately OCDD. Further analysis of soil with this dominating HpCDD and OCDD contamination in Queensland may elucidate the source of elevate PCDDs in Queensland. However, the results from this study suggest that if such vertical contamination is consistent for the entire coast of Queensland than a substantially greater contamination may be present in the Queensland coastal environment than originally estimated.

Acknowledgements

The authors would like to acknowledge the funding source for this project including ARC SPIRT, Queensland Health Scientific Services (QHSS), ERGO Forschungsgesselschaft, GBRMPA and NRCET (funded by QHSS). Special thanks must also be given to Simon Albert for spending many hours and energy collecting the soil core and to DNR for the loan of the soil auger.

References

1. Klärschlammverordnung, A. (1992) Abfallgesetz Stand 15.
2. Prange, J. A., Gaus, C., Päpke, O. and Müller, J. F. (2002) Chemosphere 46, 1335.
3. Brzuzy, L. P. and Hites, R. A. (1995) Environmental Science & Technology 29, 2090.
4. Green, N. J. L., Jones, J. L., Johnston, A. E. and Jones, K. C. (2001) Environmental Science and Technology 35, 1974.
5. Gaus, C., Prange, J. A., Connell, D. W., Brunskill, G. J., Päpke, O., Müller, J. F. and Weber, R. (this issue) Organohalogen Compounds
6. Vikelsoe, J., Lassen, P., Johansen, E. and Carlsen, L. (1994) Organohalogen Compounds 20, 351
7. Harrad, S. J. and Malloy, T. A. (1991) Chemosphere 23, 181.
8. Oeberg, L. G., Anersson, R. and Rappe, C. (1992) Organohalogen Compounds 9, 351.
9. Wittsiepe, J., Kullmann, Y., Schrey, P., Selenka, F. and Wilhelm, M. (1999) Toxicology Letters 106, 191
10. Wittsiepe, J., Kullmann, Y., Schrey, P., Wilhelm, M. and Selenka, F. (1998) Organohalogen Compounds 36, 351.
11. Kim, Y. and Lee, D. (2002) Journal of Hazardous Materials B91, 113