

STUDY ON THE USE OF MOSSES AS BIOMONITORS TO EVALUATE THE ENVIRONMENTAL IMPACT OF PCDDs/PCDFs FROM COMBUSTION PROCESSES - PRELIMINARY RESULTS -

E. Abad, J. Caixach and Josep Rivera*

Mass Spectrometry Lab., Dept. of Ecotechnologies, IIQAB-CSIC

Jordi Girona 18-26, 08034 Barcelona (Spain).

Fax: 34-93-204.59.04, E-mail: jraeco@cid.csic.es

C. Real, J. Aboal, A. Fernández and A. Carballeira

Grupo de Ecotoxicología, Área de Ecología, Facultad de Biología, Universidad de Santiago de Compostela

López Gómez de Marzoa s/n. Campus Universitario Sur. 15782 Santiago de Compostela (Spain).

Fax: 34-981.59.69.04, E-mail: bfalejo@usc.es

Introduction

Up to now, evidence of the use of terrestrial mosses as biomonitors for atmospheric contamination has been extensively reported owing to their particular properties to accumulate contaminants^{1,2,3,4,5}. These organisms have been applied to the study of heavy metals and radioactive elements. Moreover, other studies also include the use of mosses to evaluate the presence of persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs)^{6,7,8,9,10,11}. However, data about their usefulness in biomonitoring polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is rather scarce.

The use of mosses as biomonitors presents numerous advantages^{12,13,14}, the most important of which are the following : (1) they usually lack a protective cuticle and epidermal cells with thick cell walls, therefore their tissues are permeable to water and minerals, including metal ions; (2) they obtain their mineral nutrition mainly via wet and dry deposition, and not from the substrate on which they grow; (3) many species are very abundant and widespread in different habitats; (4) they are easy to handle and their use as biomonitors is inexpensive; (5) they lack a well developed vascular system, therefore the transfer of contaminants to internal tissues is prevented.

This study aims to evaluate the use of mosses as biomonitors to get overall contamination information of PCDDs/PCDFs. To this end, moss samples from different sites potentially affected by well-known sources of dioxins were collected and analysed. In order to establish a background level, samples from control sites were also taken. Finally, as part of the preliminary assessment on the environmental impact of a new municipal waste management plant (MWMP), an evaluation of the current atmospheric load of PCDDs/PCDFs by using a passive sampler such as mosses in the neighbourhood of the facility was also conducted.

Methods and Materials

Moss samples were collected between November 2000 and January 2001 for PCDDs/PCDFs analyses. A preliminary campaign aiming to evaluate evidence mosses could be useful as a realistic bioindicator to identify point sources of PCDDs/PCDFs. Thus, four samples were collected as follows: two samples in a clean site, one as a first control sample collected in the surroundings of a new MWMP, before the activity was started and one more sample in a contaminated site (a landfill where the urban waste is frequently burned).

Prior to the extraction process, the samples have been lyophilized and spiked with known amounts of a ¹³C₁₂-PCDDs/PCDFs standards as described in EPA 1613. The analytes were removed from the matrices by Soxhlet extraction using toluene for 48 h. After which, the toluene extracts were transferred to n-hexane and the organic matrix was removed by a sulphuric acid treatment, whereas PCDDs/PCDFs remained in the n-hexane fraction.

Cleanup procedure was based on use of the Power PrepTM system (FMS Inc., MA). The automated clean up system is based multilayer silica, basic alumina and PX_21 carbon adsorbents, prepackaged in columns made of Teflon and hermetically sealed (FMS Inc. Boston, USA)¹⁵.

Purified extracts were analyzed by HRGC_HRMS on a GC 8000 series gas chromatograph (Carlo Erba Instruments, Milan, Italy) equipped with a CTC A 200S autosampler and coupled to an Autospec Ultima mass spectrometer (Micromass, Manchester, UK), using a positive electron ionization (EI+) source and operating in the SIM mode at 10000 resolving power (10% valley definition). Chromatographic separation was achieved with a DB_5 (J&W Scientific, CA, USA) fused_silica capillary column (60 m x 0.25 mm ID, 0.25 :m film thickness) with helium as carrier gas in the splitless injection mode (1_2 :L).

Quality assurance criteria were based on the application of quality control and quality assurance (QC/QA) measures. Other performance checks such as MS sensitivity and resolution or GC separation were performed as a current practice of the laboratory policy.

Results and Discussion

PCDDs/PCDFs were detected and quantified in almost all samples analyzed from tetra- to octachlorinated congeners. Table 1 gives the results of the analysis of the four samples. The levels of PCDDs/PCDFs determined in four samples from three different sites were 2.12, 2.44, 0.86 and 38.97 pg I-TEQ/g respectively. Sample 1 was a control site and the levels should be assumed as a background contamination. Samples 2 and 3 were collected in the surroundings of a new MWMP before the start of its operation activities. Finally, sample 4 was collected in a landfill where usually thermal processes occur. As expected, this sample presented the highest levels. The congener-specific distribution presents typical combustion pattern (figure 1). Moreover, the ratio between PCDFs and PCDDs, expressed in TEQ, is about 2.45, which is in accordance with the hypothetical ratio of 3 generally reported for combustion processes. In contrast, the ratio between furans and dioxins, also expressed in TEQ, found in all the other samples was about 1.3¹⁶.

As a preliminary conclusion, these results indicate that mosses can be presumably used as biomonitors of PCDDs/PCDFs. The analysis of 10 g dried sample allows to achieve a well-defined chromatogram as shows figure 1. Moreover, in the existence of a point source, the pattern of the PCDDs/PCDFs resembles the distribution of the compounds which occur as from the combustion-derived pattern and is distinctly different from those non-exposed organisms suggesting no alterations in the congener profile occur due to metabolic effects or transport within the organism (figure 2).

Table 1. Levels of PCDDs/PCDFs in moss samples at different sites.

ID	PCDDs/PCDFs (pg I-TEQ/g)	Ratio PCDD/F-TEQ	Sample Location
1	2.12	1.27	Control site -blank-
2	2.44	0.35	In the surroundings of the MWMP
3	0.86	1.14	In the surroundings of the MWMP
4	38.97	2.45	Landfill where waste is burned

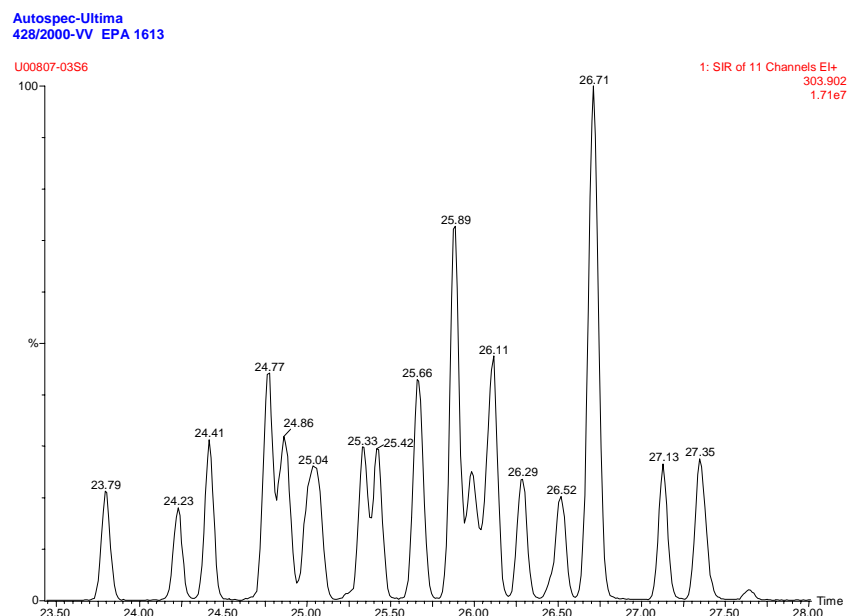


Figure 1. HRGC(DB-5)-HRMS(EI+) chromatogram of TCDF of a moss sample.

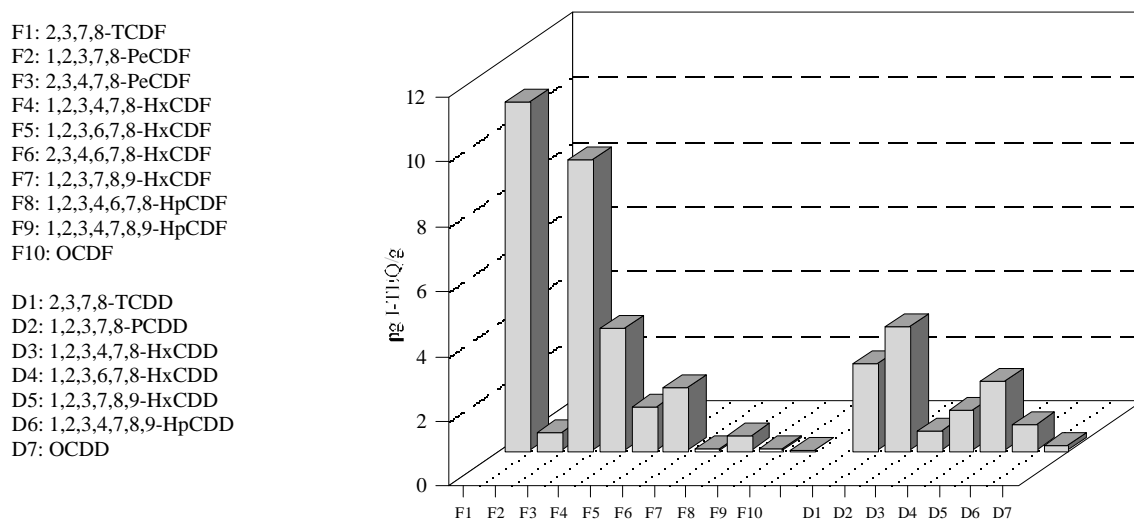


Figure 2. Congener specific 2,3,7,8-PCDD/F distribution of moss sample after thermal process.

Acknowledgments

The authors wish to thank M^a Generosa Martrat, Jordi Sauló, M.A. Agradós and José J. Llerena for their contribution to the preparation of this work.

References

1. Rühling, A. and Tyler, G. (1968). *Botaniska Notiser* 122, 248.
2. Aboal, J.R., Fernández, J.A. and A. Carballeira. (2001). *Enviro. Poll.* 115, 313.
3. Bargagli, R. (1998). *Trace elements in terrestrial plants*. Springer Verlag, Berlin.
4. Couto, J.A., Fernández, J.A., Aboal, J.R. and Carballeira, A. Submitted to *Atmospheric Environment*.

5. Fernández, J.A., Aboal, J.R., Couto, J.A. and Carballeira, A. (2002). *Atmospheric Environment* 36, 1163.
6. Wegener, J.W.M., van Schaik, M.J.M. and Aiking, H. (1992). *Enviro. Poll.* 76, 15.
7. Knulst, J.C., Westling, H.O. and Brorström-Lundén, E. (1995). *Environ. Monitoring and Assessment* 36, 75.
8. Lead, W.A., Steinnes, E. and Jones, K. (1996). *Environ. Sci. & Technol.* 30, 524.
9. Wilcke, W., Amelung, W. and Zech, W. (1997). *Z. Pflanzenernähr. Bodenk.* 160, 369.
10. Gerdol, R., Bragazza, L., Marchesini, R., Medici, A., Pedrini, P., Benedetti, S., Bovolenta, A. and Coppi, S. (2002). *Atmospheric Environ.* 36, 4069.
11. Orlinski, R. (2002). *Chemosphere* 48, 181
12. Berg, T. and Steinnes, E. (1997). *Enviro. Poll.* 98, 61.
13. Thöni, L., Schnyder, N. and Krieg, F. (1996). *Fresenius J. of Anal. Chem.* 354, 703.
14. Tyler, G. (1990). *Botanical Journal of the Linnean Society* 104, 231.
15. Abad E., Sauló J., Caixach J., Rivera J. (2000) *J. of Chromatogr. A* 893, 383.
16. Rappe C. (1994) *Fresenius J. Anal. Chem.* 348, 63.