Science of the Total Environment 631–632 (2018) 822–828

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Signatures of chlorinated dioxins and furans along the exposure path – The relation between vegetation and soil

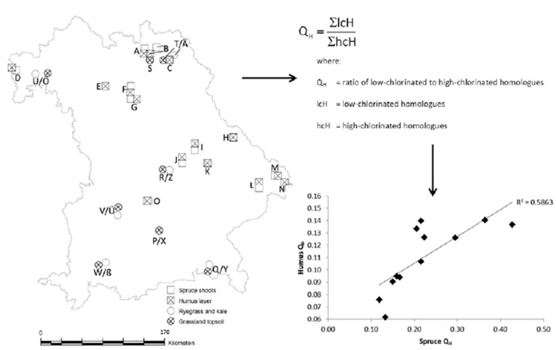
Edzard Hangen [a,*], Stefan Gonser [b], Jutta Köhler [b]

[a] *Dep. of Preventive Soil Protection and Soil Monitoring, Bavarian Environment Agency, Hans-Högn Strasse 12, 95030 Hof, Germany*
[b] *Dep. of Intermedia Environmental Monitoring, Bavarian Environment Agency, Schloss Steinenhausen, 95326 Kulmbach, Germany*

HIGHLIGHTS

- Ratio between low- and high-chlorinated homologues of PCDD/F is a robust fingerprint.
- These PCDD/F fingerprints are consistent across environmental compartments.
- PCDD/F signature of immission is stored in top soil's memory.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 February 2018
Received in revised form 7 March 2018
Accepted 9 March 2018
Available online xxxx

Editor: Jay Gan

Keywords:
Congener fingerprint
Spruce
Ryegrass
Curly kale
Forest humus layer
Grassland topsoil

ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) belong to the most toxic persistent organic environmental pollutants. Therefore, knowledge about their fate along the exposure path is of special concern. In order to comprehend the transfer of PCDD/Fs across different environmental compartments, PCDD/F concentrations in plants and in soil were evaluated. Pairs of soil and plant samples were selected according to the shortest distance between sampling points. At 15 sites PCDD/F concentrations in spruce needles and in forest humus layers where compared. Summer conditions were evaluated on the basis of 8 sites with ryegrass- and grassland topsoil samples. Autumn conditions were addressed using 7 sites with curly kale and topsoil samples under grassland. Correlation analyses of the PCDD/F congener profiles for plant- and soil samples were conducted. The correlations were compared to influencing site (e.g. local temperature) and spatial as well as temporal offset parameters. No governing parameter that decisively influenced the similarity between plant and soil signature became evident. By means of the toxicity factors of TEQ-WHO, tetra- and penta-PCDD/F homologues were assigned to the group of low-chlorinated homologues (lcH), and hexa-, hepta- and octa-PCDD/F homologues to the high-chlorinated homologues (hcH). lcH and hcH are presumed to differ in solubility, volatility and rate of degradation. The ratio of lcH/hcH revealed characteristic fingerprints that enabled the differentiation of the individual PCDD/F-plant and -soil pairs. Spruce-humus pairs showed a close relation during winter exposure times, while the lower summer concentrations were not reflected in the humus layer. Kale was exposed at the beginning of the season with elevated PCDD/F immissions, and showed a closer relation to grassland topsoil than did ryegrass. lcH/hcH proved as a simple criterion that can reveal related PCDD/F fingerprints of different environmental compartments despite signal attenuation due to decomposition, volatilization and particulate transport.

* Corresponding author at: Dep. of Preventive Soil Protection and Soil Monitoring, Bavarian Environment Agency, Hans-Högn Strasse 12, Hof, Germany.
E-mail address: edzard.hangen@lfu.bayern.de (E. Hangen).

https://doi.org/10.1016/j.scitotenv.2018.03.110
0048-9697/

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzo-furans (PCDD/Fs) are majorly generated during combustion processes, house firing and other thermal processes (Kulkarni et al., 2008). They are also undesired by-products in the production of chloro-organic chemicals (Hagenmaier et al., 1995), e.g. pentachlorophenol (timber preservative) and herbicides, as well as the manufacture of bleached paper and pulp. Some PCDD/Fs are carcino- and teratogenic (e.g. Fiedler et al., 1994; Marquardt and Schäfer, 1994). The most toxic dioxin is 2,3,7,8-tetrachloro-*p*-dibenzodioxin ("Seveso toxin") (Mocarelli, 2001), which is enriched along the food chain (Fernández-González et al., 2015). PCDD/F deposition is linked largely to airborne dust particles. They show limited tendency towards volatilization (US EPA, 1984) and displacement (McLachlan et al., 1996). In Bavaria, southern Germany, PCDD/F contents in soil in terms of international toxicity equivalents range from below detection limit up to 230 ng I-TEQ kg^{-1} of dry mass at brownfield sites (Joneck and Prinz, 1991). The Bavarian Environment Agency is collecting data on the effects of air pollutants on indicator plants. The assessment by vegetal accumulation indicators such as ryegrass, curly kale or spruce needle shows deposition-related inputs into ecosystems and may indicate risks for plants, animals and humans (VDI, 2016). These risks are also emphasized in legal regulations for soils, e.g. the Soil Protection Ordinance (BMU, 1999), in terms of restrictive threshold values. Thus, more information about the origin and import of airborne PCDD/Fs into soils should be derived by evaluating the combination of available plant and soil data. In Bavaria, there is no network that monitors PCDD/F contents continuously across different environmental compartments. Therefore, PCDD/F measurements of different compartments at sites with close spatial proximity should serve as a surrogate to characterize the contaminant's fate. For Bavaria the PCDD/F signatures in indicator plants at long-term monitoring sites as well as soil data from nearby sampling sites shall be compared. Regional fingerprints in response to specific contamination sources shall be identified.

2. Material and methods

In order to compare PCDD/F concentrations in soil and bioindicator plants from different sampling sites, measuring points closest to each other were paired using ArcMap 10.4.1 (Esri Inc.) (Fig. 1). Only plant data older than soil data was used to ensure temporal consistency of the PCDD/F input. As soil samples are presumed to integrate the PCDD/F input of several years, PCDD/F contents of all preceding plant sampling campaigns were averaged. Spruce needles are eventually accumulated in the forest humus layers. Thus, there is a direct link between both compartments, which induced us to contrast the spruce needle PCDD/F concentrations against those of the forest humus layers. Grassland vegetation resembles the receiving surface of ryegrass. Therefore, grassland topsoil was assumed to potentially mirror PCDD/F concentrations of ryegrass and kale, which were exposed at open field. Hence, PCDD/F concentrations of grassland topsoil were compared to those of ryegrass and kale, respectively.

2.1. Plant data

The Bavarian long-term monitoring network with bioindicator plants comprises different approaches: accumulation of PCDD/Fs in natural vegetation is assessed by a spruce monitoring network (passive monitoring). The locations of the sampled trees (*Picea abies*) were chosen depending on PCDD/F sources, e.g. house firing. Sampling of spruce needles was carried out according to VDI (2007), newly grown shoots are sampled after 6 months (autumn) and again after 12 months (spring) of exposure. Therefore, PCDD/F concentrations in spruce needles can be attributed to summer periods (autumn samples) and whole year periods (spring samples). The whole year periods are strongly dominated by the winter exposure, as PCDD/F immissions are higher during winter, while evaporation and photodegradation processes are lower. Therefore, the whole year exposure will be referred to as winter exposure in the following. Long-term active biomonitoring comprises the assessment by cultured bioindicator plants, which were exposed at chosen sites. Cultures of ryegrass (*Lolium italicum*) during summer and cultures of curly kale (*Brassica oleracea*) during autumn were used. Ryegrass cultures are exposed for five consecutive 4-week periods from May through September; curly kale is exposed for one 8-week period during October and November. After exposure the plants are sampled according to VDI (2016) and VDI (2008), respectively. The freeze-dried and homogenized samples were spiked with a prescribed mixture of C^{13}-labelled and 2,3,7,8-substituted dioxins and furans. After 24 h Soxhlet-toluol extraction the samples were analyzed using high-resolved gas chromatography and mass spectrometry (HRGC/HRMS) (LfU, 2007).

2.2. Soil data

Between 1997 and 2004 soils were sampled in an 8 × 8 km grid across the whole of Bavaria to derive background values of contaminants (Joneck et al., 2006). Composite soil samples included 8 individual samples within a 180 m^2-area. The state-wide inventory investigated forest-, arable and grassland soils. In the study presented here, only the humus layer of forest sites and the topsoils of grasslands are investigated further. Deep-frozen soil samples were analyzed for PCDD/Fs according to DIN (2000) and VDI (2003) using HRGC/HRMS.

Paired samples that served for further evaluations are characterized (Table 1). To address site parameters that might act upon the fate of PCDD/Fs, annual temperature and annual precipitation depth were included in Table 1. As further influencing factors for the correspondence of plant and soil PCDD/F concentrations the average temporal offset including all individual plant sampling campaigns and the spatial offset between the plant sampling and the soil sampling were added.

2.3. Similarity of individual plant- and soil-data pairs

Individual plant data were averaged to yield a singular set of PCDD/F congener values, which could be compared with the singular soil data. To classify the relationship between plant- and soil data of each pair, congener concentrations were transformed into TEQ-WHO PCDD/F values applying the toxicity equivalency factors (TEFs) of van den Berg et al. (2006). TEQ-WHO PCDD/F values of the 17 congeners of the plant data were compared to those of the soil data. The correlation coefficient, r, was calculated (SPSS Statistics 23, IBM Inc.) and used as measure of relation between plant- and soil signature (Eq. (1)).

$$r = \frac{\sum\left(Pl_j - \overline{Pl}\right) \cdot \left(So_j - \overline{So}\right)}{\sqrt{\left(Pl_j - \overline{Pl}\right)^2} \cdot \sqrt{\left(So_j - \overline{So}\right)^2}} \tag{1}$$

where:
r = correlation coefficient
j = index for individual congener
Pl = index for "plant TEQ-WHO PCDD/F"
So = index for "soil TEQ-WHO PCDD/F"

To attribute the similarity of plant- and soil TEQ-WHO PCDD/F congener profiles to influencing parameters, the r-value (Eq. (1), Table 2) was contrasted against the soil site's long-term temperature and precipitation as well as against the spatial and temporal offset between the plant- and the soil sampling (Table 3).