POLYCHLORINATED DIBENZO-P-DIOXINES AND DIBENZOFURANS IN FLOODPLAIN SOILS OF THE CZECH REPUBLIC

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Introduction

Floodplains are a dynamic ecosystem where the interaction among various environmental media occurs. A characteristic feature of floodplain systems is a high spatio-temporal heterogeneity which is reproduced by the interactions among processes of erosion, transportation and accumulation of material together with anthropogenic landscape transformation. Due to the chemical properties (persistence and low mobility in soil), the bulk of polychlorinated dibenzo-p-dioxines and dibenzofurans (PCDD/Fs) input is preserved in the surface layer of soils and concentrations in the soil are related to the cumulative input. As far as risky substances are concerned, riverine floodplains can adopt water quality properties during flooding periods[1]. When looking into the potential mobilization of POPs during the flooding, two principal contamination fluxes have to be taken into consideration:

- The remobilisation and redistribution of contaminated river sediments, subsequently deposited on the flooded areas, may have resulted in soil contamination.
- The contamination of waters and soils may have resulted from mobilization in contaminated terrestrial areas such as industrial sites, landfills, and sewage treatment plants, flooded during high water events.

The broad agriculture utilisation of floodplain soils with elevated risky substances concentrations can pose some threats to the food safety. The flooding of the land by water carrying POPs as well as by contaminated sediments seems to be an important source of the localized contamination and provides another transfer mechanism to the human food chain. It is generally thought that PCDD/Fs are adsorbed on soil organic matter so strongly that they are rarely transported to plant roots and into aboveground plant tissues. There was observed little correlation between soil and plant concentrations of PCDD/Fs in the literature[2,3], but some exceptions were proved for plant parts growing in the soil (e.g. unpeeled potato tubers, unpeeled carrots) and for the plants of the genus *Cucurbita*[2,4,5]. Another potential pathway was proved in the UK – the research provided strong evidence that flooding of pastureland can indeed result in elevated concentrations of PCDD/Fs and PCBs in milk (due to the ingestion of contaminated grass and soil) from the farms so affected[6].

The light substrate floodplain soils situated in a warm climatic region in the Czech Republic are suitable for vegetable production usually grown for direct consumption. Especially along the middle reaches of the river Elbe and lower reaches of the river Ohře, the vegetable production meets a higher probability of pollution exposure because of the cumulative effect of the pollution sources. For these reasons, the main aim of this study was to obtain an overview of the contamination spread in respect of PCDD/Fs in recent alluvial plains used for agricultural purposes in the Czech Republic. Soil samples were taken along the downstream profiles of the important Czech watercourses (namely from the water meadows, pastureland and arable land) and analysed for the above mentioned compounds.

Materials and methods

To identify target areas for sampling, we used a GIS-based approach using nationwide digital data on soil distribution, agriculture land use and hydrological floods in the Czech Republic. We focused on sampling of recent floodplain soils with a high frequency of flood events. Thus the sampling sites were preferably located in a spatial framework of 5-year flood inundation areas gathered from the Digital database of water management data (DIBAVOD). As for agricultural land use characteristics, these were determined using the Land Parcel Identification System (LPIS) compiled by the Ministry of Agriculture of the Czech Republic. For each sampling site, a mixed sample consisting of 10 individual samples from the area of 100 x 100 meters was used. The soil samples were taken during the period 2010-2013. The sample depth was 0-10 cm for pastures and 0–30 cm for arable land. In the soil samples from the alluvial plains, there was analysed a wide range of risky substances including 17 WHO-PCDD/Fs, seven indicator PCB congeners (28, 52, 101, 118, 138, 153, 180) and 7 risky elements (As, Cd, Cu, Hg, Ni, Pb and Zn). The basic soil properties (e.g. total organic carbon, soil texture characteristics) were determined.

Analytical methods

As for PCDD/Fs, the samples were homogenized and spiked with isotope-labelled surrogate standards and extracted in a Soxhlet extractor for 24 h using n-hexane/acetone. After the treatment of the raw extract with conc. H_2SO_4 extract, the purification was executed using a multi-layer silica column (acid/neutral) and basic alumina and carbon column combination. PCDD/Fs were analysed on a double high resolution mass spectrometer Autospec Ultima NT (Waters) coupled with an HP 6890 gas chromatograph (Agilent) and equipped with a CTC 200SA autosampler. The International toxicity equivalent (I-TEQ) is used for the PCDDs/Fs assessment because it has been used in the Research Institute for Soil and Water Conservation since 1999[7,8].

As for PCB, dry soil samples were extracted with dichloromethane in a Büchi System automatic extractor. Fractionation was achieved on sulphuric acidmodified silica gel columns. Samples were analysed on a GC-ECD HP 5890 using a Quadrex-fused silica column coated with 5% phenyl-methylpolysiloxane. Analytical details were described elsewhere[9].

The pseudototal contents of risky elements (As, Cd, Cu, Ni, Pb, and Zn) in an extract of aqua regia were analysed using the AAS method. The total content of Hg was assessed using an Advanced Mercury Analyzer (AMA). The pollution index (PLI) was calculated for risky elements in the floodplains following the definition of pollution load index for estuarine sediments[10].

$CF = C_{metal}/C_{background}$

$PLI = (CF_1 \text{ x } CF_2 \text{ x } \ldots\ldots CF_n)^{1/n}$

CF contamination factor, n number of metals

C_{metal} concentration of pollutant in a floodplain soil

$C_{background}$ upper limit of the variability of the element in the Czech soils

Results and discussion

The PCDD/F contents in all soil samples were low and ranged from 0.4 to 7.8 ng/kg I-TEQ with a median of 1.12 ng/kg. Concentrations of PCDDs/PCDFs in agricultural floodplain soils were not significantly correlated with organic carbon content. The TOC content ranged from 0.31% to 3.19% and displayed a high degree of divergence in respect of the soil type and land use. The dioxin results show a clear pattern – the highest concentration levels were found along the rivers in the old industrial areas of the North Bohemian and North Moravian regions. A spatial downstream gradient of some hazardous substances was proved for the rivers transecting these regions. The cumulative effect of pollution was proved for the samples especially in the Czech section of the river Elbe – a high spatial association was proved for ITEQ values for PCDD/Fs and ∑PCBs. Both aggregation measures resemble the spatial distribution of main potential pollution sources along the river Elbe (see Figure 1). The main sources of the river Elbe pollution are as follows:

- Pardubice, situated 100 km east of Prague, can be considered to be an important industrial centre with a chemical factory of Alliachem Synthesia, an oil refinery and a heavy machinery manufacturer. The Synthesia factory grounds are contaminated with a broad range of substances (simple aromatics, chlorinated aromatics, Hg, As, PCBs, organochlorinepesticides)[11].
- The town of Neratovice is located about 25 km north of Prague. The main risks have resulted from the past production of the Spolana chemical plant that manufactured a broader range of substances (e.g.linearolefins, viscosestaple and chlorinated pesticides). The chemical plant grounds were contaminated with dioxins, mercury, chlorinatedaliphatic hydrocarbons and OCPs[12].
- The river Ohře drains the North-Western Bohemian region, well known for its brown coal fields and high industrial activity. The high load of the region is related to a spatial coincidence of various pollution sources connected with a high concentration of industry, high urbanisation rate as well as with an elevated geochemical background for some risky elements (As, Be).
- The town of Usti nad Labem is located at the lower reaches of the river Elbe, where the Spolchemie chemical plant is situated. The production at the plant involves inorganic chemicals, syntheticresins,

and organic paints. Grounds of the chemical plant are contaminated with chlorinatedaliphatic hydrocarbons, simple aromatics, PAHs, PCBs, metals, organochlorinated pesticides and HCB[11].

As for the Elbe floodplains, a strong correlation was proved for the ITEQ values of PCDD/Fs with ∑PCBs (r=0.84), but contrary to that ITEQ values were weakly correlated with PLI. The pronounced correlation of PCDD/Fs and PCBs concentrations suggests that the sites are exposed to the similar mixture of pollutants resembling the sources along the river Elbe. Furthermore, there was proved a high effect of the affluent of the river Ohře on the pollution load index in the Elbe floodplains because of the catchment area of Ohře in the Nort-Western Bohemian region characterized by a high immision load. In the catchment of the river Ohře, there were recorded high values of pollution load index for risky elements together with high ITEQ values for PCDD/Fs, but no correlation with ∑PCBs,. These results confirmed the connection of the load to the historical pollution peak in the 80s of the 20th century when a high content of emission pollution was deposited to soils. As for other river systems of the Czech Republic, no significant spatial gradient in PCDD/Fs concentrations was evident and the ITEQ values were steady along the rivers with only minor influence of the local pollution sources.

Figure 1 Spatial gradient of risky substances and potential sources along the Czech section of the river Elbe

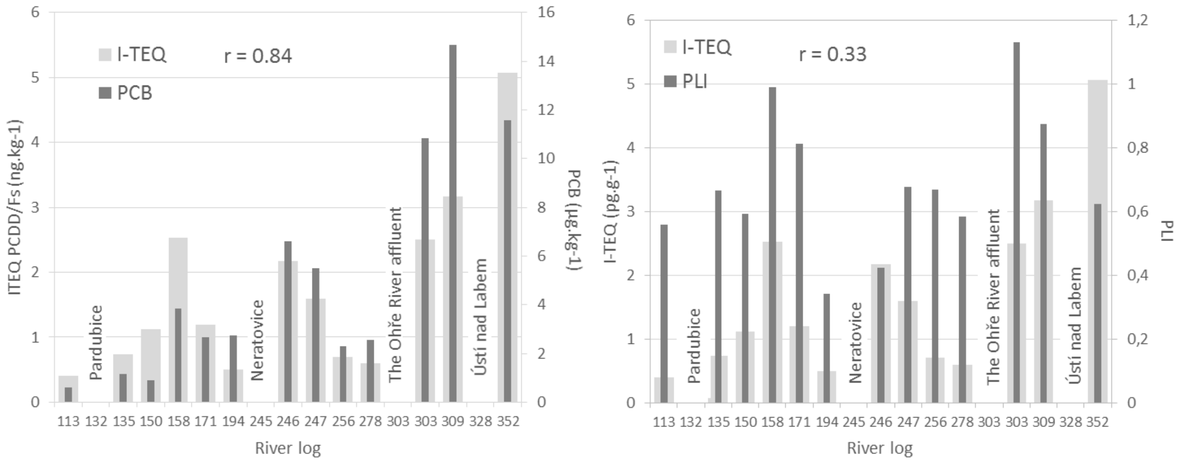
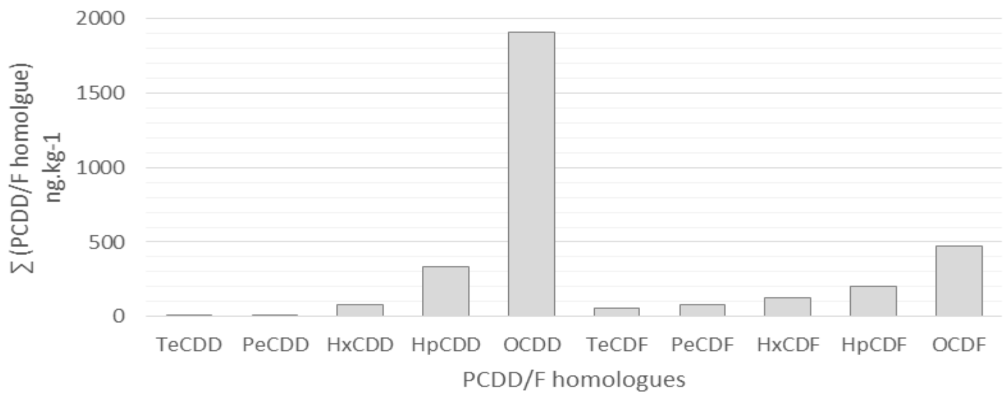
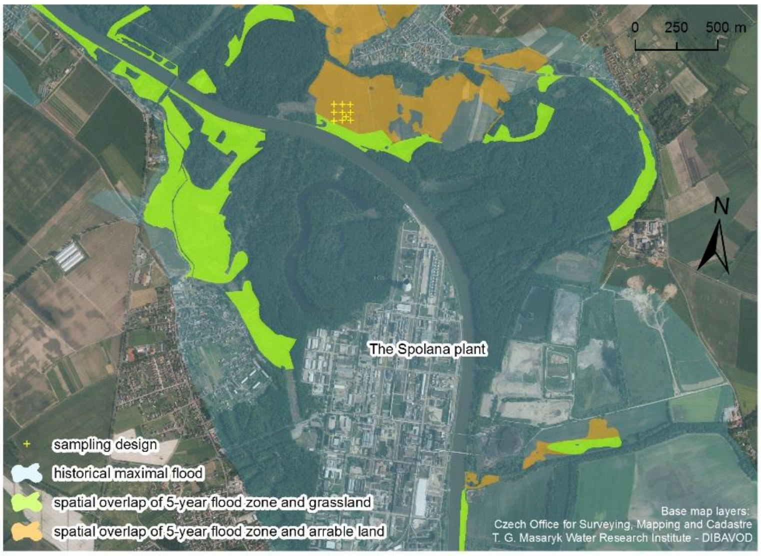


Figure 2 Relative contributions of the 17 PCDD/F congener homologues for 59 sites of the Czech floodplains



When only PCDD/Fs were considered, the homologue profiles for the majority of the individual sites were identical to that observed for all the sites together (OCDD > OCDF > HpCDD > HpCDF > HxCDF > HxCDD) (Figure 2). A number of sources were recognized in the soil samples via congener profiles, although similar congener profiles make it extremely difficult to distinguish among different sources. The cluster analysis of congener profiles of the floodplain sites determined 4 detached specific sites (singularities in a cluster tree) and 3 clusters where the main differentiating features were the homologous groups of OCDD, OCDF and HpCDF. Last but not least, a heavy and continuous precipitation in the Czech Republic and in South-East Germany led to an extreme flooding in June/July 2013. The extreme summer flood in August 2002 showed that polluted alluvial soils in the catchment can also act as sources for POPs under certain circumstances[12]. There is a major concern with a high public attention on the Spolana chemical plant due to the possibility that dioxins could be released into the environment during the flood. In view of the facts, the agricultural floodplain soils close connected to chemical plant were sampled in 2011 and immediately after the flood in 2013 (Figure 3). The PCDD/Fs fingerprint in samples suggests only a minor local impact from the production of the herbicide 2,4,5-T at the Spolana plant in the past, with no significant impact on the overall contamination of the Elbe with PCDD/Fs. There was observed a slight increase of PCDD/Fs load in the soil shortly after the high water event in 2013 (Figure 3).

Figure 3 Sampling of the agriculture land next to the Spolana plant (before and after the flood in 2013)



PCDD/Fs	17.10.2011	10.7.2013
2,3,7,8 TeCDD	0.5	0.1
1,2,3,7,8 PeCDD	ND	0.63
1,2,3,4,7,8 HxCDD	ND	0.39
1,2,3,6,7,8 HxCDD	ND	1.1
1,2,3,7,8,9 HxCDD	ND	0.95
1,2,3,4,6,7,8 HpCDD	5.7	16
OCDD	49.2	110
2,3,7,8 TeCDF	1.4	2.8
1,2,3,7,8 PeCDF	0.7	1.5
2,3,4,7,8 PeCDF	1	3
1,2,3,4,7,8 HxCDF	1.1	2.9
1,2,3,6,7,8 HxCDF	0.6	2.1
2,3,4,6,7,8 HxCDF	0.7	2.5
1,2,3,7,8,9 HxCDF	ND	0.1
1,2,3,4,6,7,8 HpCDF	3.6	9.8
1,2,3,4,7,8,9 HpCDF	ND	1.1
OCDF	7.4	13
I-TEQ	1.6	3.2
∑ PCB	5.52	27.756

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