DIOXIN PATTERN OF ENVIRONMENTAL SAMPLES, FEED AND FOOD IN POLLUTED SITES IN SLOVAKIA

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs, 75 congeners) and dibenzofurans (PCDFs, 135 congeners), commonly referred to as dioxins (PCDDs/Fs), are widely dispersed environmental contaminants belonging to the group of persistent organic pollutants (POPs) included in the Stockholm Convention on POPs. They are well known as toxic and lipophilic compounds with environmental and biological resistance leading to significant bioaccumulation in living organisms and through the food chain to humans. Various biochemical and toxic responses to POPs were studied and described previously: endocrine disruption, immune dysfunction, thyroid disorders, breast cancer, reproduction and dental defects, hearing loss, etc.[1-5]. Dioxins are produced unintentionally due to incomplete combustion and as by-products during production of some chlorinated substances. The main environmental pollution sources are: metallurgical industry, burning of hospital, hazardous and municipal waste, non-industrial diffuse sources like automobile emissions, domestic combustion of fossil fuels, forest fires, smouldering of copper cables, cement kilns, pulp and paper production based on chlorine bleaching. Uncontrolled combustion of household and garden waste also belong to important dioxin sources[6-8].

It was found that the exposure of the general population to POPs occurs mainly through consumption of contaminated food, mainly high-fat foods of animal origin, such as milk and dairy products, animal meat, liver and fat from fatted cattle and wild game, some fish meat and eggs[7,9, 10]. The exposure of animals depends on the state of environment in the given area. The relationship between emissions and ground level pollutant concentrations is very complex. Imission monitoring is often carried out as a complement to the measurement of emissions[11].

The previously published data confirm that the most polluted region with PCDDs/Fs in Slovakia, from the ones selected for this study, was the Krompachy region. In contrast to other regions, the very high POP levels in cow´s milk from small family farms in Krompachy did not differ from big farms, since the animals grazed freely on the same meadows. This clearly illustrates the pollution of the local environment with dioxins[6, 12-14]. Now, after a few years the question of dioxin pollution in Krompachy region was raised again by the National Focal Point of Slovak Republic for Scientific and Technical Matters for EFSA – Ministry of Agriculture and Rural Development of the Slovak Republic. The need for detailed monitoring of this area and investigation of pollution sources was expressed as important task for the near future. Similar activities are also carried out by the Network of European Union Reference Laboratory (EURL) for Halogenated Persistent Organic Pollutants in Feed and Food and National Reference Laboratories[15].

Materials and Methods

Sampling areas and sample collection
Within our study four potentially contaminated areas were selected (Košice – metallurgical plant, municipal waste incinerator, Krompachy – metallurgical plant, Nemecká – refinery, waste incineration, Šaľa – chemical plant, hazardous waste incineration) and the neighbourhood of the Starina water reservoir in the north-east of Slovakia was chosen as a background area. In total, 20 ambient air, 32 soil, 34 sediment, 86 feed, 45 game, 37 fish and 161 food samples were collected in 2007. The air samples were simultaneously collected during two campaigns in March (winter) and June (summer) according to USEPA Method TO-9 at sites 1 - 5 kilometres from the pollution source using high-volume samplers GPS-1 (Graseby Andersen, USA). Soil samples were obtained from 0-20 cm (plowed soil) and 0-10 cm (not-plowed soil) depth with 6-10 sub-samples several metres far from each other at all locations. Bottom sediment samples were collected in co-operation with the Water Research Institute by standardised methods. Biota samples from big farms were collected by Regional Veterinary and Food Administrations. Food samples originating from small family farms were collected by our research team. A global positioning system (GPS) was used for precise localization of almost all sampling points.

Chemical analysis
All samples were analysed by HRGC/HRMS (USEPA 1613 and 1668 isotope dilution methods) using $^{13}C_{12}$-labelled PCDD and PCDF extraction standards added prior to extraction. Environmental samples, feedstuffs and food samples requiring lyophilisation were extracted using ASE®300 extractor (Dionex, USA). Other food samples were homogenised, mixed with anhydrous sodium sulphate and the fat was extracted on column with hexane. Isolated fat was treated with silica-H_2SO_4 column and extracts were cleaned-up and fractionated by FMS PowerPrep™ system (Fluid Management Systems, USA). PCDDs/Fs were separated by HP 6890 gas chromatograph (Hewlett-Packard, Palo Alto, California, USA) operating in splitless mode on DB-5MS (60 m, 0.25 mm i.d., 0.25 µm ft) and Rtx-2330 (60 m, 0.25 mm i.d., 0.1 µm ft) capillary columns and determined by MAT95XP mass spectrometer (Thermo Finnigan, Bremen, Germany).

Results and Discussion
POP levels in almost all samples mentioned above were described previously[6, 12-14]. In this paper we focused on the mean dioxin congener patterns and their possible use for identification of typical local patterns of PCDD/F pollution of environment and biota especially in the polluted site of Krompachy region. We compared the dioxin profiles in environmental compartments (air, soil, sediment) with feedstuffs and selected foodstuffs (hen eggs, cow´s milk, fish). Comparison of two approaches were made: dioxin profiles calculated on the amount of drawn air / dry weight of soil, sediment, feed / lipid basis for food or wet weight for fish, and calculation of the levels of the dioxin congeners as relative contribution (%) to the toxic equivalent (WHO-PCDD/F-TEQ) according to Malisch[16]. In all cases a totally different dioxin profile arose comparing these two approaches.

Dioxin pattern calculated on product basis
In the background area of Starina water reservoir air samples have different dioxin profile in winter and summer. In summer, especially tetra- through hexachlorinated dibenzofurans have the same high levels as other congeners in contrast to the winter values. However, by this approach the predominant pollutants in the samples of sediment, soil, feed and eggs were OCDD and 1,2,3,4,6,7,8-HpCDD with very similar dioxin profile. Dioxin pattern in milk was completely different with predominance of 2,3,4,7,8-PeCDF. The dioxin patterns in Krompachy samples showd different congener profile for soil, milk and especially eggs and fish. Identical dioxin profile was found in air, sediment and feed. The predominant congener in winter air campaigne was OCDF and in summer 1,2,3,4,6,7,8-HpCDF followed by OCDD and 1,2,3,4,6,7,8-HpCDD.

Relative contribution (%) to WHO-PCDD/F-TEQ

When approach by Malisch is used[16], dioxin profiles in Starina air, sediment, soil, hen eggs and partially milk seems to be the same with predominance of 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, TCDD and TCDF. Feed and especially fish has different congener profile. Comparing the patterns in Krompachy samples calculated as relative contribution (%) to WHO-PCDD/F-TEQ we can see the same profile for all environmental and food samples except fish. It is in contrast with findings mentioned above. It clearly illustrates the contribution of the polluted local environment to the contamination of biota. The different congener profile in fish samples can be caused by different metabolization process in fish compared to terrestrial animals. The predominant pollutants in all fish samples were 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF whether the dioxin pattern has been calculated on sample amount or as % contribution to TEQ.

In conclusion, it can be said that the dioxin patterns in air samples can be assessed as different for winter and summer (Figure 1). The seasonal variations in dioxin concentration shows that the levels of PCDDs/Fs in ambient air in winter are almost 10-times higher than in summer. In Slovakia majority of family houses in rural areas use residential heating based on fossil fuels during winter. It is known that combustion of biomass increases dioxin emissions into the air. Combustion of garden and household waste also occurs in Slovakia despite the ban. The influence of emissions from household heating systems is unambiguous and should not be underestimated[6,17,18], especially as a possible pollution source of local feedstuffs in rural areas (Figure 2).

According to Malisch, identification of contamination sources is a very complex and difficult issue. There are many examples that illustrate the detective work and scientific aspects for identification of the source. All these findings can support the performance of monitoring programs and risk management in polluted sites[16]. Since the request from the Slovak state administration is up to date, it will be necessary to look more closely at all results from Krompachy region available in Slovakia.

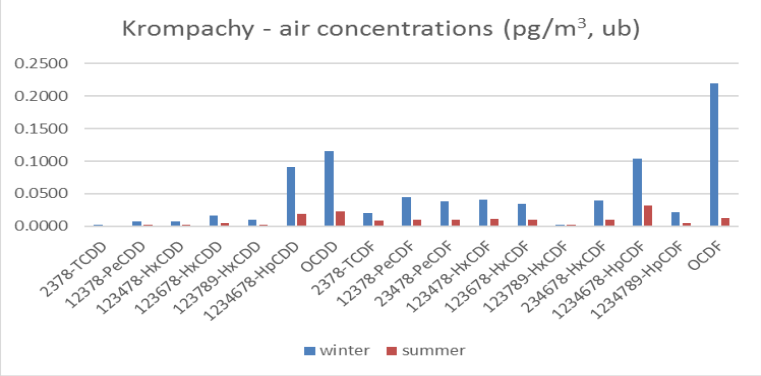

Figure 1: Dioxin pattern of ambient air from Krompachy region in pg/m^3 (ub = upper-bound levels).

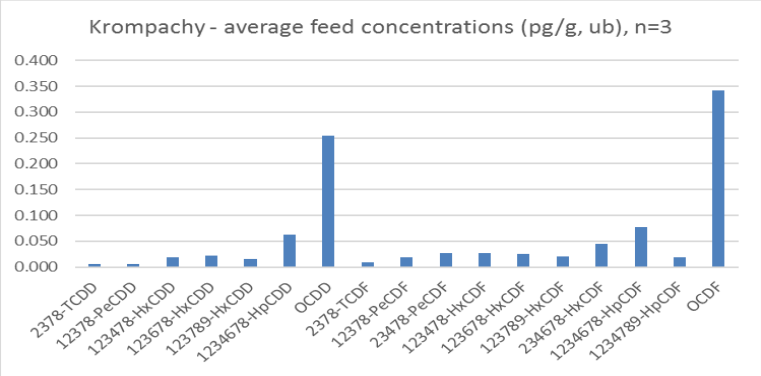

Figure 2: Dioxin pattern of feed from Krompachy region in pg/g (ub = upper-bound levels).

Acknowledgements

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-21-004205. This article was created by the realisation of the project "Centre of excellence of environmental health", ITMS No. 26240120033, based on the supporting operational Research and development program financed from the European Regional Development Fund.

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