PCDD/Fs IN DANUBE RIVER SEDIMENTS FROM GERMANY TO THE BLACK SEA

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Introduction

The Second Joint Danube Survey (JDS2)[1] was the world's biggest river research expedition in 2007. Its main goal was to produce highly comparable and reliable information on water quality and pollution for the Danube River and many of its tributaries. The Secretariat of the International Commission for the Protection of the Danube River (ICPDR) coordinates the implementation of JDS2. Launched on August 2007 from Regensburg, Germany, the three boats of the JDS2 travelled 2,375 km downstream the Danube River, through 10 countries, to the Danube Delta in Romania and Ukraine. During the cruise water, suspended particulate matter, bottom sediment, mussel and fish were sampled at 95 sites. Here, we report here results of dioxin in sediment from 23 different sites.

Materials and Methods

Sediment samples were taken with a kick and sweep sampler (top 5 cm of the sediment sampled with a net normally used for macrozoobenthos sampling) at 23 different sites during JDS2 Cruise. Sediments were sampled at 14 sites on both left and right side of the Danube River. The sampling sites are reported on Figure 1. The sample codes are those used during JDS2 from ICPDR. More details are reported on the JDS2 web site[1].
The samples were wet sieved < 63 µm on the boat and frozen. Subsequently they were freeze dried; 20 g dry weight samples were Soxhlet-extracted for 24 h using n-hexane/acetone (220/30). The applied methodology follows USEPA method 1613. Prior to the extraction 16 carbon-13 isotope labeled internal standards were added (400 pg each, except OCDD with 800 pg). Extracts were evaporated to near dryness, refilled to 10 mL with n-hexane, and purified with an automated clean-up system (Fluid Management Systems, USA) operating with three different columns (a silica/sulfuric acid, a basic alumina and a carbon-column[2]) Purified extracts were evaporated to nearly dryness using nitrogen (Turbovap, Zymark, USA) and filled up with 30 µL of toluene. Prior to injection, two C^{13}-labeled recovery standards were added.

Quantification was carried out with a high resolution gas chromatograph (HRGC) (Hewlett-Packard/Agilent, Germany) with split/split less injection. Chromatographic column was a 60 m BPX-DXN (SGE, Australia) with 0.25 mm inner diameter and 25µm film thickness. The HRGC was coupled with a high resolution mass spectrometer (HRMS) (Autospec, Micromass/Waters, USA), working in the electron impact mode at 34 eV and with an average resolution of 10 000. For parent congener and corresponding labeled standards two ions each were registered.

Quality assurance and quality control were carried out by determining laboratory blanks together with each batch of 15 samples, running reference samples in parallel and calibrating the HRGC/HRMS with certified PCDD/F standard mixtures (CS from Welligton Laboratories, USA). All solvents (Sigma Aldrich/ Switzerland) and gas (Alphagaz/Italy) used were ultrapure grade suitable for PCDD/F analysis.

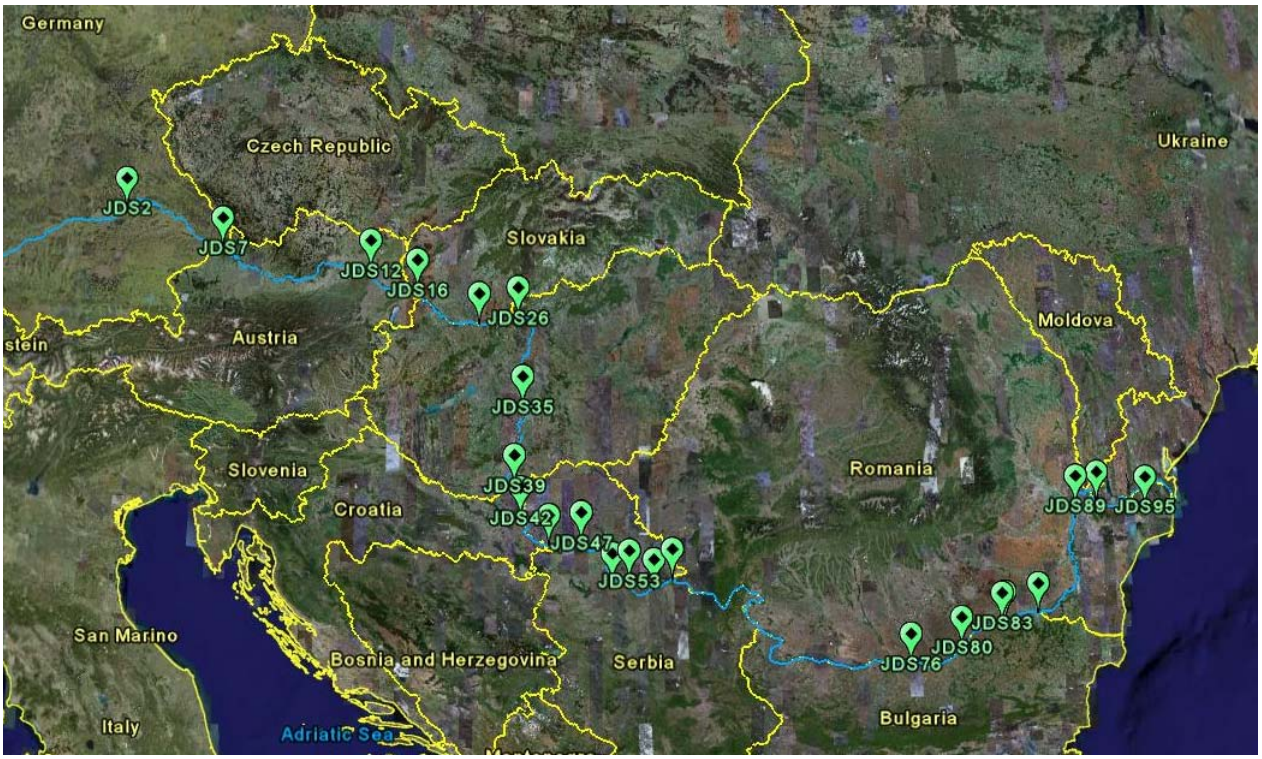

Figure 1: River Danube with the 23 sampling sites where sediments were analyzed for dioxins.

Results

The PCDD/Fs were detected in all sediments analyzed. Figure 2 shows the PCDD/Fs concentrations recorded in all right and left sampled sites on Danube River. The WHO-TEQ$_{(1998)}$ concentrations average was 0.003 ng/g and ranged from a minimum of 0.001 ng/g to a maximum of 0.022 ng/g. Higher concentrations were recorded at site JDS2 (0.004 ng/g) and from JDS39 to JDS53 sites, ranging between 0.002 to 0.006 ng/g. The highest with 0.022 ng/g was JDS53 sampled on the left side of the Danube River.

The PCDD/Fs levels reported from river sediments of other European countries are in the same level of magnitude of those recorded in this study. The River Po, the main Italian River draining one of the most populated and industrialized regions in Italy showed a concentration range from 0.001 to 0.013 WHO-TEQ$_{(1998)}$ ng/g[3]. In Spain, the PCDD/Fs were detected in three different river basins. One, Ebro River, located in the Northeast, was sampled at three different sites. The total WHO-TEQ values, including PCDDs, PCDFs and DL-PCBs, for sediment samples from Barbastro, Monzón and Flix were 0.0007, 0.010 and 0.189, ng/g respectively. However, the DL-PCBs contribution to the total calculated toxicity were 40%, 60% and 69% for Barbastro, Monzón and Flix, respectively[4]. The second and the third river, Tinto and Odiel, are located in the southwest and they showed level of ∑2,3,7,8-PCDD/Fs ranging from 0.002 to 0.237 ng/g[5]. In this study, we detected, the ∑2,3,7,8-PCDD/Fs in a range from 0.070 to 0.463 ng/g. In Germany, the WHO-TEQs$_{(1998)}$,were detected on Elbe River and the concentrations ranging from 0.010 to 0.080 ng/g[6].

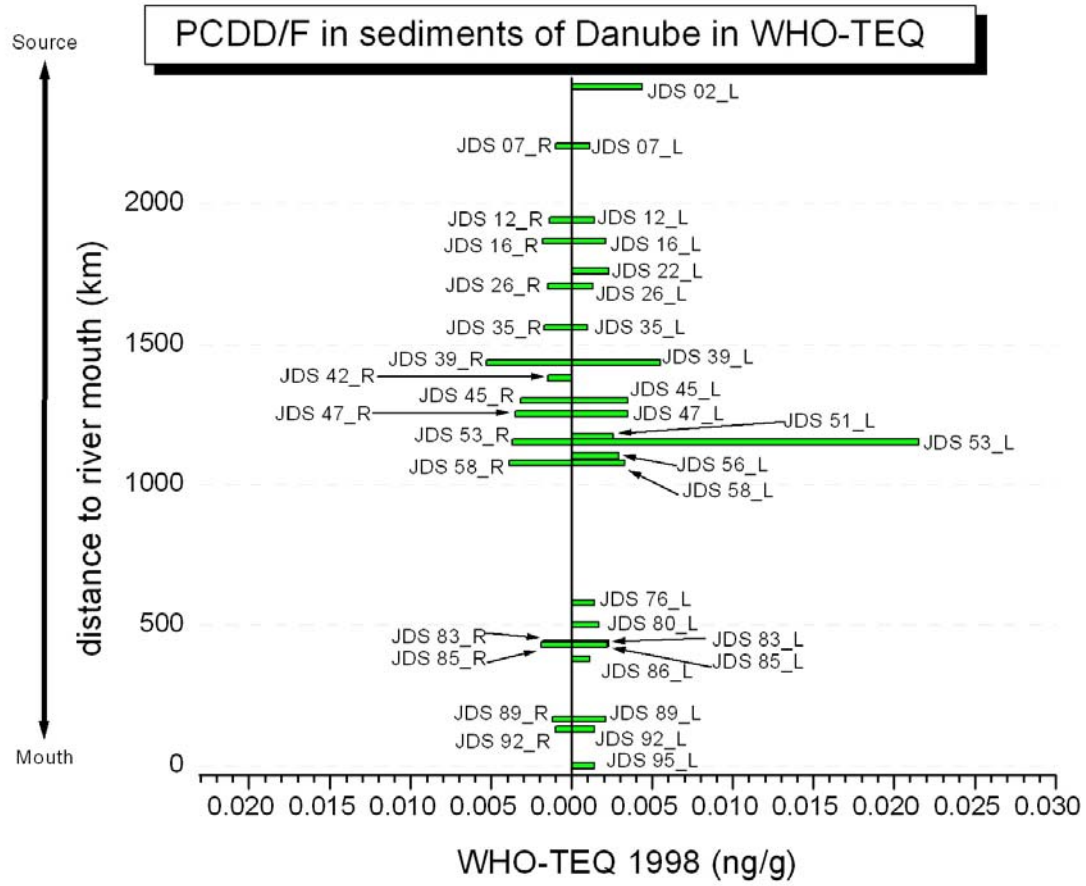

Figure 2: PCDD/Fs concentrations recorded in all right and left sampled sites on Danube River.

Conclusion:

In this paper, we have presented the preliminary results on the PCDD/F level Danube River sediments. More detailed data elaboration will be done with focus on congener patterns and source identification. The PCDD/F concentrations recorded in Danube sediments in this study ranged at the lower end compared to recent literature on PCDD/F levels in European River basins.

Acknowledgements:

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