HCHs IN SOLID MATTER FROM THE RIVER ELBE, ITS TRIBUTARIES AND THE NORTH SEA

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Introduction:

The River Elbe (Czech: *Labe*) is one of the major rivers of Central Europe. It originates in the Krkonoše Mountains of northwestern Czech Republic before traversing Bohemia (Czech Republic), then Germany and flowing into the North Sea at Cuxhaven, 110 km northwest of Hamburg. Its total length is 1,094 km. The Elbe's major tributaries are the Vltava (German: *Moldau*), Saale, Havel, Mulde, SchwarzeElster, and Ohre rivers. The Elbe River basin, comprising the Elbe and its tributaries, has a catchment area of 148,268 km^2, the fourth largest in Europe. The basin spans four countries, with its largest parts in Germany (65.5%) and the Czech Republic (33.7%). Much smaller parts lie in Austria (0.6%) and Poland (0.2%). The basin is inhabited by 24.5 million people **(**1**).**
Organochlorine pesticides are man-made organics chemicals. Hexachlorocyclohexanes (HCHs) have been extensively used and are therefore found widely distributed in the environment. HCHs are listed under the Stockholm Convention on POPs (persistent organic compound) and are included into the priority list of Water Frame Directive.
Here we show the results of HCHs in solids matter of 35 different sites along the River Elbe, selected tributaries, and the North Sea

Sampling sites and sampling

In the period from September to October 2008 a total of 35 solid samples (sediments, composite samples of freshly deposed sediments (FDS) and suspended particulate matter (SPM) were taken from the Elbe, its tributaries Vltava, Mulde, Saale, Stör, Spittelwasser and Bode (tributaries of the Mulde resp. Saale) and the North Sea (see Figure 1). Samples from the Elbe are indicated in red, in the tributaries in yellow, and in the North Sea in black. The sampling sites in the North Sea are located in the vicinity of a dumping site for dredged sediments in the south of the island Helgoland. The two sites KS8 and KS11 represent the area where sewage sludge from Hamburg used to be dumped in the past. For comparison 2 samples were taken in a distance of 2 and 12 km from the dumping site and from a reference site as well.
Sediment sampling was carried out by a Van-Veen-Grap; depth 0-12 cm. Care was taken to ensure that the surface layer of the sediment was selected for the samples, so that the results reflected the current contamination situation. The FDS samples were collected for 4 weeks in a basin placed inside a monitoring station SPM was collected with a centrifuge.

Material and Method

All organics solvents used were trace analysis grade (Sigma-Aldrich, Buchs SG, Switzerland). 2g Alunina –B/5g Florosil custom columns were obtained from Supelchem.
Native and ^{13}C-labelled OCPs internal standards were obtained from Cambridge Isotope Laboratories. Isotope labelled α - HCH, γ-HCH were used as internal standardsand ^{13}C-labelled β – HCH, was used as recovery standards.

Analytical determinations*:*

Samples were Soxhlet extracted with n-hexane/acetone (220/30) for 48 h after being spiked with internal standards.
Copper powder was added to the solvent during the extraction to remove Sulphur.
The 90% of the extract collected was concentrated under nitrogen flow until 0.5ml and then diluted with n-hexane to 5ml. These 5ml was submitted to an automated clean up using acid silica/neutral silica, basic alumina and active carbon columns for the analysis of PCDD/Fs, PCBs and PBDEs (data not reported here).
The remaining 10 % was concentrated under nitrogen flow and dedicated to the OCPs analysis. The extract was loaded on 2g Alumina–B/5g Florisil SPE column and eluted with 35ml of n-hexane/ethyl acetate (80/20). The clean-up was performed using an automated clean up system with autosampler (AccuPrep MPS^{TM}) and three solid phase module (J2 Scientific (Missouri, USA). The system processes the samples in sequence.
Finally the sample was concentrated and spiked with OCP recovery standards. The final volume of 100 µl was submitted to instrumental analysis for OCPs.
HCHs were analysed using isotope dilution with HRGC-HRMS for the quantification on the basis of an in house method.

HCHs were analyzed on double HRGC (Thermo Trace GC Ultra, ThermoElectron, Bremen, Germany) coupled with a DFS high resolution mass spectrometer HRMS (ThermoElectron, Bremen, Germany) operating in EI-mode at 45 eV with a resolution of >10000. The two most abundant ions of the isotopic molecular cluster were recorded for both native and labelled congeners.The compounds were identified through comparison of retention times of the corresponding standards and the isotopic ratio of the two ions recorded.
Gas chromatographic conditions for HCHs were: Split/splitless injector at 250 °C, constant flow at 1.0 ml $min^{-1}$of He, GC-MS interface at 270 °C and a GC program rate: 100 °C with a 1 min hold, then 10 °C min^{-1} to 300 °C and a final hold at 300 °C for 9 min.

Results

The concentrations of the sum-HCHs (Figure 2) in the Elbe River solid matter ranging from a minimum of 0.69 ng/g at Lysa nad Labem (km -151) to a maximum of 104 ng/g at Cerinovskokm (km -115) with an average of 15 ng/g. The beta isomer was the most abundant followed by the alpha isomer (Figure 3).
The results were in accordance with the concentrations detected in the Elbe River by other authors (2) in 2002. When comparing the average levels with those of a Danube survey in 2008 they result more than one order the magnitude higher (3).
The highest concentration of the sum-HCHs (7070 ng/g) was recorded in the Spittelwasser River that spills the contamination into the Mulde River (224 ng/g), an Elbe tributary with a well known contamination history. In these Elbe tributaries the distribution of the HCH isomers was dominated by the beta isomer contributing 87% to the total HCH concentration (Figure 3).
The spatial concentration trend of the sum-HCHs across the Elbe River displays a strong increase after the confluence of the tributary Mulde, thus pointing to a high pollution potential of the River Mulde and Spittelwasser, as demonstrated earlier e.g. for PCDD/Fs (4).
This is confirmed by the change of the relative distribution of the different HCHs isomers (Figure 3). The average distribution upstream of River Mulde is dominated to 47% by the beta isomer followed by the alpha (22%) and gamma (20%) isomers. After the Mulde River confluence, from Magdeburg (km 318) to Seemannshöft (km 629), the beta isomer increases to 62% and the alpha and gamma isomers decrease to the 19% and 8 % respectively in the Elbe solids. In the final segment of the Elbe River (where the total HCH concentrations are < 5ng/g) from Grauerort (km 661) to the mouth at Cuxhaven (km 725), the relative distribution returns quite similar to the upper stretch of the Elbe with the beta isomer at 47% followed by the alpha and gamma isomers with 21% and 15 respectively.
The other tributaries, Vltava, Saale, Stör, and Bode displayed low concentration of the total HCHs in the range of the low contaminated sections of the River Elbe.
In the North Sea the concentration of sum-HCHs at the sites KS8 and KS11 were 4.26 ng/g and 1.21 ng/g respectively, the other sites were below detection limit.

Acknowledgement

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References:

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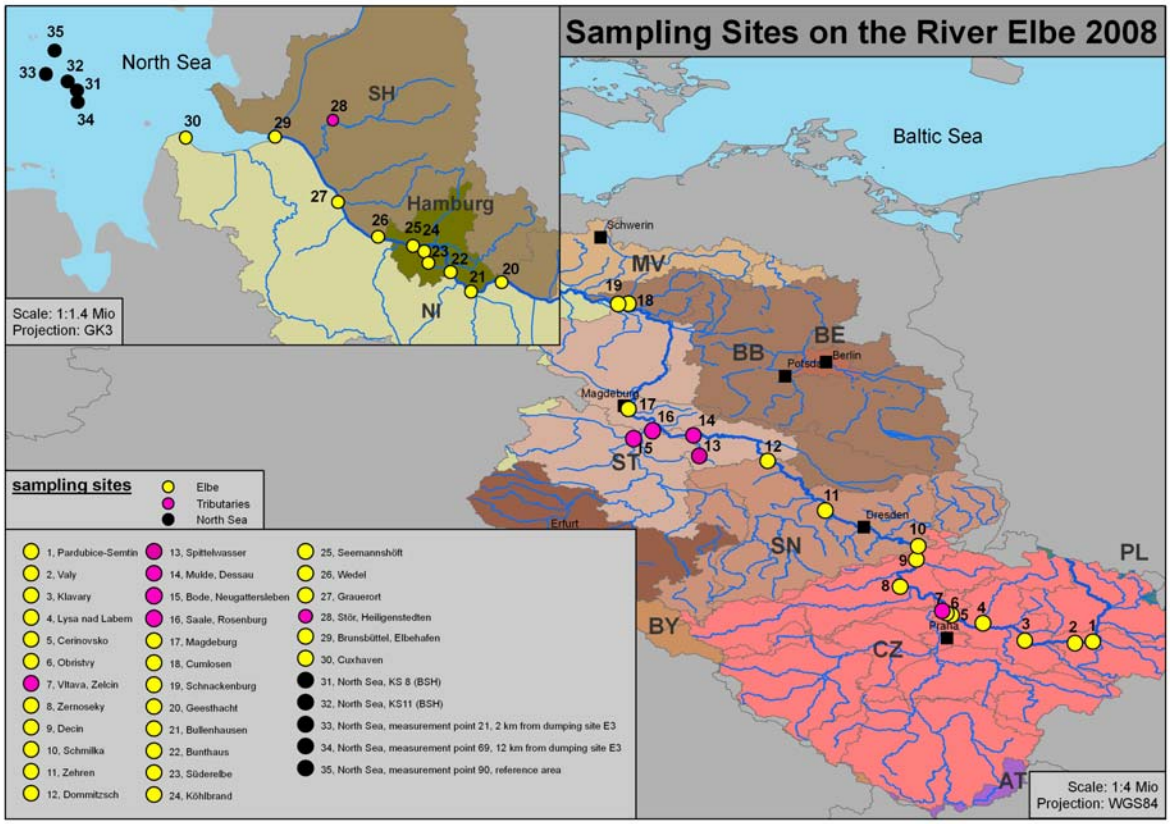

Figure 1: Sampling sites

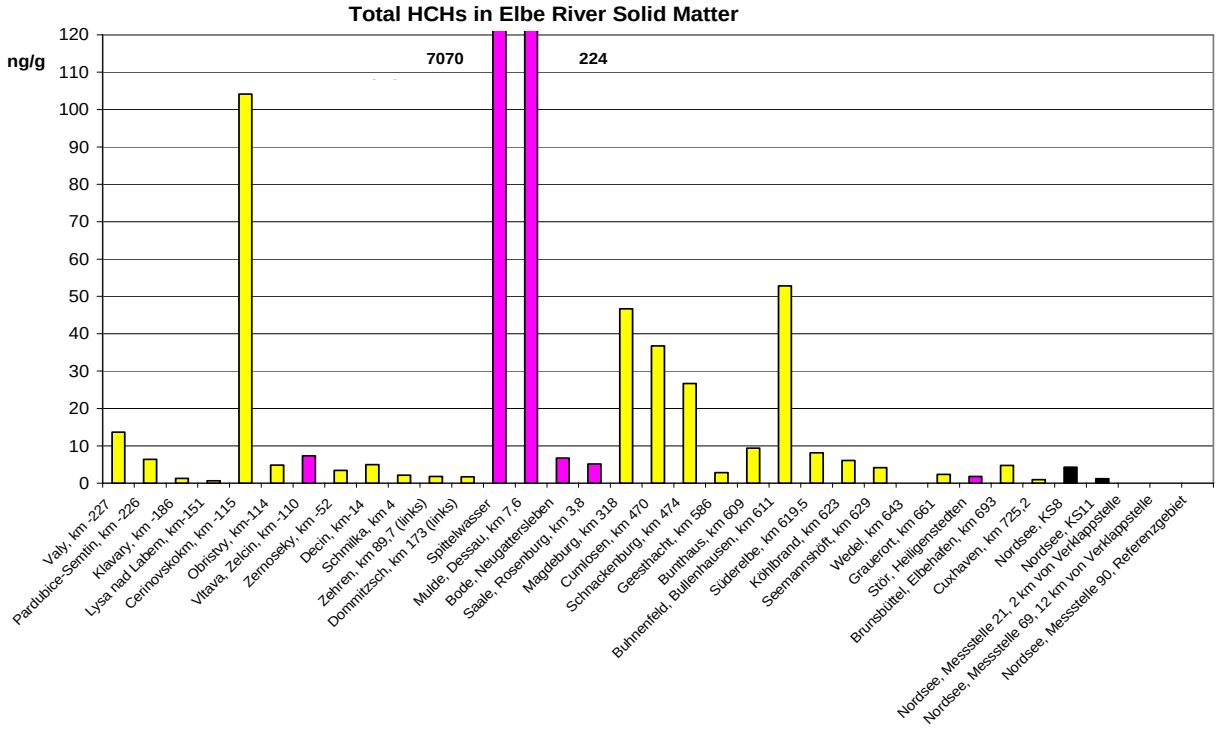

Figure 2: Sum-HCHs in solids from the River Elbe, its tributaries, and the North Sea.

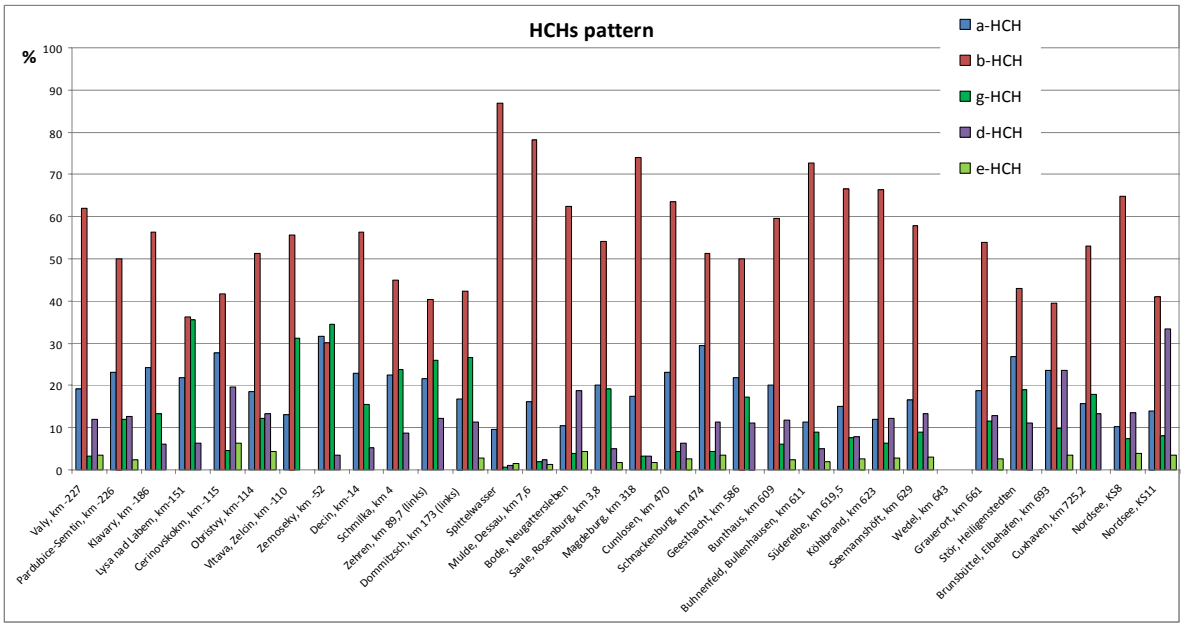

Figure 3: distribution (%) of HCHs in solids from the River Elbe, its tributaries, and the North Sea.