BIO/CHEMICAL ANALYIS OF SEDIMENTS FROM THE ELBE RIVER, THE NORTH SEA AND FROM SEVERAL TRIBUTARIES

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Introduction

More than 1000 mixed halogenated PXDD/Fs, PXBs, PXNs and X-PAHs (X= Cl, Br, J and F) bind significantly to the Ah receptor. Many of them may also classify as persistent organic pollutant (POP), while only 29 PCDD/PCDF/dl-PCB congeners are routinely measured and monitored. Cell based bioassays such as the CALUX technology have been evaluated, accepted and used in National regulations for sediments and dredged materials analysis for the presence of dioxins and related compounds in e.g. the Netherlands (50 ng CALUX-TEQ/kg d.w.), Norway (25 ng CALUX-TEQ/kg d.w.), Japan (JIS K 0463; 150 ng CALUX-TEQ/kg d.w) or the USA (EPA 4435).

In this study we compare in a blind fashion the Total-TEQ measured by DR CALUX® bioassay to the WHO-TEQ levels (from 17 PCDD/Fs and 12 DL-PCB congeners) measured by chemical HRGC/HRMS analysis in sediments from 15 different locations from the European river Elbe as well as from several locations in the North Sea and specific tributaries.

Methods and materials

Sediment samples: All 23 dried sediment samples were received from the IES-JRC in December 2009. They have been analyzed by HRGC/HRMS in the laboratory of JRC and by DR CALUX® bioassay in the laboratory of BDS. Characteristic and representative samples of sediments were selected from the river Elbe, the North Sea and several specific tributaries. This cross-validation study between DR CALUX® bioassay versus chemical HRGC/HRMS analysis, was executed in blind fashion by both laboratories.

Sample extraction and clean-up for DR CALUX® bioassay: The procedure for the DR CALUX® bioassay by BDS is described in detail previously. Briefly, the dry sediment samples were extracted with toluene/acetone by ASE. Approximately five gram dried sediment was used for the clean-up. TBA was necessary to remove sulfur. The clean-up was conducted firstly by multilayer silica gel chromatography. The fractions were carefully evaporated by a stream of nitrogen, and replaced with 50 µL of dimethylsulfoxide (DMSO).

DR CALUX® bioassay measurement: The procedure for the DR CALUX® bioassay is described in detail previously. All requirements from the EC directives for cell based technologies have been fulfilled (such as below 1% false negatives, LOQ of 0.2 ng Total-TEQ/kg dw, repeatability and reproducibility below 15% and 30%; R2 of 2,3,7,8-TCDD higher than 0.98) by the ISO17025 accredited service laboratory of BioDetection Systems bv (Amsterdam, The Netherlands).

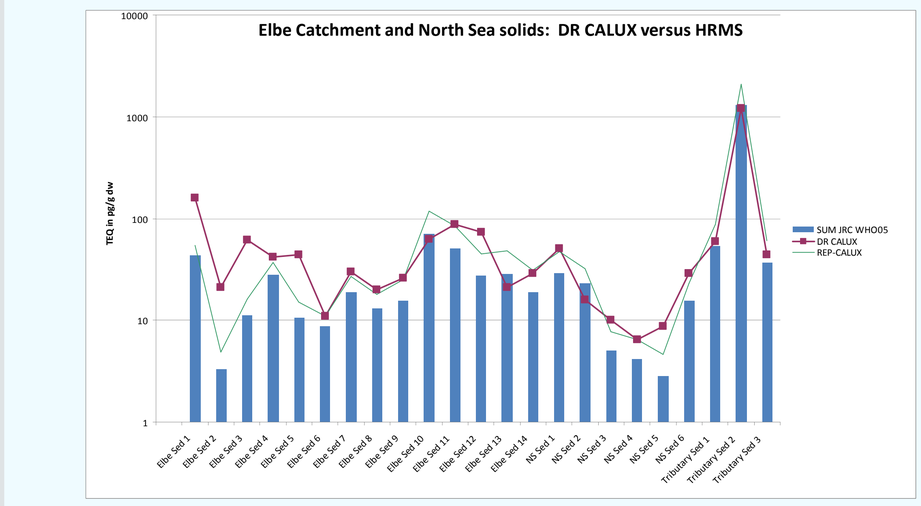
Chemical HRGC/HRMS analysis: Please see at the paper of Umlauf et al (Organohalogen Compounds DIOXIN 2010).

Results and Discussion

In sediments from the a) Elbe River from an area of about 1000 km, b) several North Sea sediments as well as c) tributaries, we observed an excellent correlation between the Total-TEQ by DR CALUX® and the WHO29-TEQ2005 (R^2 of 0.99). The correlation could be even improved in case we used the REP values of the DR CALUX® instead of the WHO-TEF2005 (R^2 of 0.9999). The Total-TEQ by DR CALUX® and the WHO2005-PCDD/PCDF/dl-PCB-TEQs ranged from 8.7 to 1200 respectively from 2.8 to 1290 ng TEQ/kg dw with a mean value of all samples of 92 respectively 79 ng TEQ/kg dw. In case of the Elbe sediments the Total-TEQ by DR CALUX® and the WHO2005-PCDD/PCDF/dl-PCB-TEQs ranged from 11 to 160 respectively from 3.3 to 71 ng TEQ/kg dw with a mean value of 49 respectively 25 ng TEQ/kg dw. In case of the North Sea sediments the Total-TEQ by DR CALUX® and the WHO2005-PCDD/PCDF/dl-PCB-TEQs ranged from 8.7 to 51 respectively from 2.8 to 29 ng TEQ/kg dw with a mean value of 20 respectively 13 ng TEQ/kg dw (Table 1 and Graph 1). Overall the chemical analysis of 17 PCDD/Fs and 12 DL-PCB congeners could explain 66% of the by DR CALUX® bioassay analysed Total-TEQ.

The DR CALUX® bioassay fulfilled all requirements as specified in the EC directives. There was no false negative regarding the Dutch guidelines for dredged material of 50 ng TEQ/kg dry weight. Regarding the Safe Sediment value of 20 pg I-TEQ/g dw only one sample was measured by DR CALUX® below the result of the chemical analysis (one North Sea sediment), but both results are in the range of the measurement uncertainty (30%).

Figure 1: Comparison of DR CALUX® Total-TEQ and HRGC/HRMS WHO-29 congeners PCDD/PCDF/dl-PCB-TEQ analysis from several sediment samples from the Elbe river, North Sea and several tributaries.



In case of the Dutch or Norwegian regulated levels for risk assessment of Total-CALUX TEQ levels for sediments and dredged materials (50 respectively 25 ng CALUX-TEQ/kg dw) 40% respectively 68% of the here analyzed sediments would be higher as the proposed risk assessment limits.

Table 1: DR CALUX® and HRGC/HRMS analysis from several sediment samples from the Elbe river, North Sea and several tributaries. Individual sediment analysis results as well as the ratio of bio/chemical analysis $R_{b/a}$, the correlation factor R^2 and the percentage of the TEQ of 29 PCDD/PCDF/dl-PCB congeners by chemical analysis compared to the DR CALUX® Total-TEQ (in %). All results are in ng TEQ/kg dw.

Sample	PCDD/DF/dl-PCB-TEQ	DR CALUX-TEQ®	REP-CALUX-TEQ	$R_{b/a}$	%
Elbe Sed 1	43	160	54	3,7	27
Elbe Sed 2	3,3	21	4,9	6,4	16
Elbe Sed 3	11	62	16,2	5,6	18
Elbe Sed 4	28	42	37	1,5	67
Elbe Sed 5	11	44	15	4,2	24
Elbe Sed 6	8,8	11	11	1,3	80
Elbe Sed 7	19	30	27	1,6	63
Elbe Sed 8	13	20	18	1,5	65
Elbe Sed 9	16	26	25	1,7	60
Elbe Sed 10	71	63	118	0,9	113
Elbe Sed 11	51	88	84	1,7	58
Elbe Sed 12	27	74	45	2,7	37
Elbe Sed 13	29	21	48	0,7	136
Elbe Sed 14	19	29	31	1,5	65
NS Sed 1	29	51	47	1,8	56
NS Sed 2	23	16	32	0,7	143
NS Sed 3	5,1	10	7,7	2,0	51
NS Sed 4	4,2	6,5	6,5	1,5	65
NS Sed 5	2,8	8,7	4,6	3,1	32
NS Sed 6	16	29	23	1,8	54
Tributary Sed 1	54	60	88	1,1	90
Tributary Sed 2	1290	1200	2100	0,9	108
Tributary Sed 3	37	44	61	1,2	84
R^2		0,9878	0,9999	2,1	66

In an earlier study in the Netherlands 257 marine harbor sediment samples levels ranged 0.2-136 ng DR CALUX®-TEQ/kg dry weight. PCDD/Fs explained 50% of the DR CALUX® activity. In an earlier sediment survey of samples send to BDS it was observed that 11% of the sediments have exceeded the Dutch guidelines of 50 ng TEQ/kg dw. In sediments from Osaka Bay the values of DR CALUX® and chemical HRGC/HRMS analysis ranged between 3.7-139 respectively 1.8-92 ng TEQ/kg dw (mean value 49 respectively 31 ng TEQ/kg dw). Chemical analysis of the 29 WHO-PCDD/PCDF/dl-PCB congeners could explain 65% of the Total-TEQ by DR CALUX® analysed.

Conclusions

An excellent correlation was observed between the Total-TEQ analyzed by DR CALUX® and the WHO-TEQ analyzed by HRGC/HRMS (R^2 of 0.99). The chemical analysis of 29 PCDD/PCDF/dl-PCB-congener could on average explain 66% of the Total-TEQ measured by DR CALUX®.

Demand for monitoring for dredged materials/sediments will continually rise due to more international legislation. Our results shows that the DR CALUX® bioassay for screening of dioxins/dl-PCBs and not yet regulated new dioxin-like compounds (such as PXDD/Fs and PXBs) in river and open sea sediments is an important tool to separate the bulk of unpolluted samples from the few percentage of polluted samples exceeding limit values.