DIFFERENCE IN THE RATIOS OF PCDD/PCDF TOXIC CONGENERS IN ORGANIC AND INORGANIC MATRICES. STATISTICAL EVALUATION OF ANALYTICAL MEASUREMENTS

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Introduction

It has been proposed in works[1,2] that there is a common mechanism exists for the formation of quasi-stationary mixture of 17 toxic PCDD/F congeners. They are formed via the electrofilic chlorination of original 2,3,7,8-tetrachlorodibenzo-*p*-dioxins/dibenzofurans (TCDD/F). If the electrofilic chlorination mechanism (ECM) really takes place in the formation of congener mixtures then, without any further assumptions, it makes possible an accurate evaluation of the ratios between 7 pairs of neighboring (Table 1) congeners: 3 < 4; 4 > 5; 9 < 11; 11 > 12; 12 > 13; 16 < 14; 15 > 16.

Processing more than 900 datapoints, which come from different works[2] the assumption on the significant contribution of ECM in the formation of congener mixtures in thermal sources has been proven. It allows to use the «statistical scale» (SS) (Fig. 1) for the determination of deviations in each tabulated mixture of congeners from ECM requirements, or for the estimation of errors, which arise from the concentration determination for each of 17 congeners included in this list (formed by ECM). Obviously, if 3 > 4, 9 > 10, or 16 < 15 in the mixture formed, then it requires further explanations. In this case, either another mechanism (not ECM) occurs, or these are the measurement errors (or even misprints), or these ratio changes are caused by the external differential factors (selective adsorption, selective decomposition, losses due to volatility, etc.). In all cases, an investigator should take into account the possibility of deviation from the mixture content defined by ECM. In the present work we apply the SS for the detailed analysis of congener mixtures.

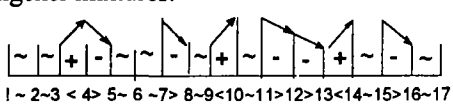


Fig.1 Statistical scale. The arrows point at the changes in the concentrations of neighboring congeners, which conform to ECM.

Processing of the data from Tables 2 and 3 allows to add the following expressions with a high degree of probability: 1 < 2 (>70%), 2 > 3 (90% for éå, *there is a reverse relationship for IM in 60% of cases considered*), 5 < 6 (100%), 6 < 7 (90%), 10 > 11 (90% for éå, *there is a reverse relationship for IM in 80% of cases considered*), 14 < 15 (90%), 16 < 17 (100%).

Methods and Materials

Two matrix tables 16x16 have been used for analysis (Tables 2 and 3), which contain data from the works published in Dioxin-98 and -99 symposia proceedings. The data conform to the following requirements:

1. Reported in works data on the mixture content should include all 17 toxic congeners (Table 1).
2. The data, in which the congener concentrations are characterized as (nd), (<), (>), (≅), etc. have not been considered.

3. The data for each object should not contain the same values for either pair of neighboring congeners. In this case, the concentration deviations in the second decimal digit have not been considered as a difference, so these data are not included in matrices.
4. To extend the monitoring, no more than 2 mixtures for different matrices (usually only one mixture) have been taken from any single work.
5. If the mixture content does not conform to the SS by more than 4 positions this mixture has been considered controversial and rejected. Only two mixtures are of this kind.
Note: The common statistics are even improved by the inclusion of additive tables (mixtures), it is well seen from the previous works[1,2] where the deviation percentage was under 4% at the procession of 900 datapoints. These considerations are consistent with the data of [4,5] where there has been a large data file analyzed by the principle component analysis (PCA) technique, as well as it has been shown that the first principle component of PCA set contains 91-98% information of isomer-distribution. The second principal component contains only 7% of the information.
6. Organic (OM) and inorganic (IM) matrices have been equally considered. Each table (matrix) includes 16 mixtures and 16 columns, which report the differences between the concentrations («more-less» slopes) of neighboring congeners (see Fig. 1).

Resualts and Discussion

Considering the matrix tables obtained one may notice some difference between the mixture content in OM and IM. It should not occur because OMs are contaminated by IMs. Therefore, there should be the differential factor during the transfer from IMs to OMs.
Tables 2 and 3 suggest that at the probability of no less than 80% for all the congeners, and not depending on the matrix type, there is a good correspondence in the ratios of neighboring congeners, though there are also some stable deviations. The concentration of D61 in OMs is usually higher than that of D5. It is in contrast with the conger ratio in IMs where the D61 concentration is usually higher than that of D5. The difference between OMs and IMs is even more pronounced in the case of $F6_1$. The F61 congener is always (70%) in a lower amount in OMs than F52, whereas F61 prevails over F52 in IMs. There is also some inconsistency in the congener content in OMs and IMs for two more congeners. In our opinion, the cause of deviation in the congener content in OMs comparing to IMs is probably the abrupt decrease in water solubility (more than 30-fold) for D61 comparing to D5, and for F61 comparing to F52. Such a decrease is less pronounced for D7:D8 and F4:F51 pairs and vaguely appears on the «more-less» plots. It is obvious that some chlorination steps may significantly change the dipole moment (polarity and polarization) of a molecule due to the full chlorination of one of aromatic rings (1,2,3,4-position) therefore shifting the solvatation (hydration) of a molecule.

Table 1

No.	Codes	Congeners	Solubility ng/l	Log(Kow)
1	D4	2378-TCDD	200	6.8
2	D5	12378-PeCDD	120	(6.64)
3	D6(1)	123478-HxCDD	4.4	7.8
4	D6(2)	123678-HxCDD	(4.4)	(7.3)
5	D6(3)	123679-HxCDD	(4.4)	(7.3)
6	D7	1234678-HpCDD	2.4	8.0
7	D8	OCDD	0.4	8.1 (7.59)
8	F4	2378-TCDF	419	5.8 (6.53)
9	F5(1)	12378-PeCDF	(240)	6.79 (6.4)
10	F5(2)	23478-PeCDF	236	(6.92)
11	F6(1)	123478-HxCDF	8.2	[7.5]
12	F6(2)	123678-HxCDF	18	[7.5]
13	F6(3)	123789-HxCDF	(13)	[7.5]
14	F6(4)	234678-HxCDF	(13)	[7.5]
15	F7(1)	1234678-HpCDF	1.4	(7.92)
16	F7(2)	1234789-HpCDF	1.4	(7.9)
17	F8	OCDF	1.2	11 (8.78)

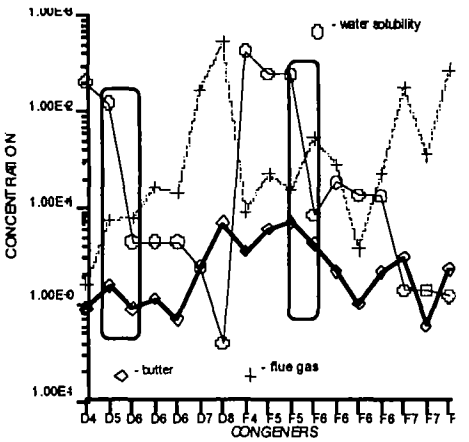
Table 2. Inorganic matrices (IM). "+" – concentration rises; "–" – concentration decreases for the corresponding congeners on the plots like Fig. 2.

‹	Congeners: / Matrix	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	outlet gases[1]	+	+	+	–	+	+	–	–	+	+	–	+	–	+	–	+
2	sediments[2]	+	–	+	–	+	+	–	+	–	+	–	–	–	+	–	+
3	sediments[2]	+	+	+	+	+	+	–	+	–	+	–	–	–	+	–	+
4	soil[3]	+	+	+	–	+	+	–	+	+	+	+	–	+	+	–	+
5	soil[3]	+	+	+	–	+	+	–	+	+	+	+	–	+	+	–	+
6	furnaces[4]	+	+	+	–	+	+	–	–	+	+	–	–	+	+	–	+
7	fly ash[5]	+	+	+	–	+	+	–	+	+	+	+	+	–	+	–	+
8	sludge[6]	+	–	+	–	+	+	–	–	+	+	+	–	+	+	–	+
9	soil[7]	–	+	+	–	+	+	–	+	–	+	–	–	+	+	–	+
10	outlet gases[8]	+	–	+	–	+	+	–	+	+	+	+	+	–	+	–	+
11	outlet gases[8]	+	+	+	–	+	+	–	+	+	–	+	+	–	+	–	+
12	outlet gases[9]	+	+	+	–	+	+	–	–	+	+	–	–	+	+	–	+
13	fly ash[9]	+	+	+	+	+	+	–	–	+	–	+	–	+	+	–	+
14	outlet gases[10]	+	–	+	–	+	+	–	–	+	–	–	–	+	+	–	+
15	outlet gases[11]	+	–	+	–	+	+	–	+	–	+	–	–	+	+	–	+
16	outlet gases[11]	+	+	+	–	+	+	–	+	–	+	–	–	+	+	–	+
Nos. of deviations from 16		1	5	0	2	0	0	0	6	5	3	7	4	6	0	0	0

Table 3. Organic matrices (OM).

‹	Congener: / Matrix	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
1	butter[1]	+	–	+	–	+	+	–	+	+	–	–	–	+	+	–	+
2	blood[2]	+	–	+	–	+	+	–	–	+	–	–	–	+	+	–	+
3	fat tissues[3]	+	–	+	–	+	+	–	–	+	–	–	–	+	+	–	+
4	blood[4]	+	–	+	–	+	+	–	–	+	–	+	–	–	+	–	+
5	milk[5]	+	–	+	–	+	+	–	–	+	–	–	–	+	+	–	+
6	sperm[6]	+	–	+	–	+	+	–	+	+	+	–	–	–	+	–	+
7	milk[7]	–	+	–	–	+	+	–	+	+	–	–	–	+	+	–	+
8	blood[8]	+	–	+	–	+	+	–	–	+	–	+	–	–	+	–	+
9	milk[8]	+	–	+	–	+	+	–	–	+	–	–	–	+	–	–	+
10	blood[9]	–	+	+	–	+	+	–	–	+	–	–	–	+	+	–	+
11	milk[9]	–	–	+	–	+	+	–	+	+	–	–	–	+	+	–	+
12	serum[10]	+	–	+	–	+	+	–	–	+	–	+	–	–	+	–	+
13	plasm[11]	+	–	+	–	+	+	–	–	+	–	+	–	–	+	–	+
14	deer liver[12]	+	+	+	–	+	–	–	–	+	–	–	–	–	+	–	+
15	blood[13]	+	–	+	–	+	+	–	–	+	–	–	–	+	+	–	+
16	milk[14]	–	–	+	–	+	+	–	–	+	+	–	+	–	+	–	+
Nos. of deviations from 16		4	3	1	0	0	1	0	4	0	2	4	1	7	1	0	0

Obviously, such an abrupt change of molecular properties may lead to the change in the rate of congener transfer into living tissue. In either case, it is clear that the mixture content of toxic congeners (at least for two of them) is changed significantly during the transfer from OM to IM. Tables 2 and 3 show that there is a genetic link between dioxins and furans. It is reflected in the constancy of the D8-F4 ratio for all the considered cases. Since dioxins and furans belong to the absolutely different classes of organic compounds, there should not be such a link between them. If it is observed, then either they have a common ancestor, or there is a possibility for extension



(furan → dioxin) or shrinking (dioxin → furan) of the oxygen containing ring in the original DD/DF. It is possible in the reduction conditions due to the elimination of oxygen atom or in the oxidation conditions due to the reverse reaction (C-C bond rapture). The second route, formation of dioxins and furans from a common ancestor, requires the ratio ΣD : ΣF to be constant (or close) that is not observed.

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Figure 2. Comparison of the data on the content of congener mixture for OM (butter) and for IM (outlet gases) with the solubility of the corresponding congeners in water. The deviations are marked in segment; it is shown that the concentration ratio of neighboring congeners in these areas corresponds to the behavior of the solubility curve for OM, while it does not for IM.

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