New Dioxins: Diversity and Danger

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1. Introduction

The analysis of dioxins and especially dioxin-like compounds is restricted to considering of their structural diversity[1,2] .

There are three series of well known chlorine hazardous compounds: polychlorinated dibenzo-p-dioxins (PCDDs, 75 individual compounds), dibenzofurans (PCDFs, 135 compounds) and biphenyls (PCBs, 209) - 419 individual compounds in all. Among PCDDs and PCDFs there are 17 extremely toxic isomers, containing 2,3,7,8-substituted fragment, for instance, the tetrachloro (2,3,7,8-TCDD/TCDF) and pentachloro compounds (1,2,3,7,8- and 2,3,4,7,8-PeCDD/PeCDF).

Polybrominated analogues of the above mentioned ecotoxicants are more rare in *environment: PBDDs, PBDFs and PBBs (also in all 419 individual compounds)*[3]. *High toxicity* was shown for 2,3,7,8-TBDD/TBDF.

Nowadays only little published information is available on corresponding polyfluorinated compounds - PFDDs, PFDFs and PFBs (419 individual compounds)[4]. The same concerns mixed Br,Cl-compounds PBCDDs (the total number is 1700 compounds, including PBDDs and PCDDs) and PBCDFs (3320 compounds, including PBDFs and PCDFs)[3].

2.Discussion

Practically nothing is known about the environmental occurrence of mixed Cl,F- (PCFDDs, PCFDF and PCFB) and especially more complex Br,Cl,F-compounds (PBCFDDs, PBCFDFs and PBCFBs).

Potentially, reactions between chloro and sulfur compounds could be of environmental significance and lead to the formation of polychlorothianthrenes (PCTAs), sulfur analogues of the PCDDs, and polychlorodibenzothiophenes (PCDTs), sulfur analogues of PCDFs[5].

But there is no published information about other types of the polyhalogenated thianthrenes and thiophenes: substituted with Br (PBTAs and PBDTs), F (PFTAs and PFDTs) and with combinations of Br/Cl, Cl/F, Br/Cl/F.

Polybrominated pollutants seem to have similar or even higher toxicity, and recent environmental monitoring efforts demonstrated the presence PBDDs and PBDFs in fly ash samples[6]. The 2,3,7,8-tetrachlorothianthrene, the sulfur analogue of 2,3,7,8-TCDD, was reported to have high biological activity in a bioassay for PCDDs[7].

Structural consideration and biological activity of the other mentioned dioxin-like O- (mixed Br/Cl, Cl/F and Br/Cl/F compounds -DDs and DFs) and S-pollutants (PBTAs, PFTAs, PCDTs, PBDTs, PFDTs and mixed PBCTAs, PCFTAs, PBCFTAs, PBCDTs, PCFDTs, PBCFDTs and so on) indicate the toxicity similar to chlorine analogues[3].

Mixed halogenated (Br/Cl, Cl/F or Br/Cl/F) dioxin-like O- and S-compounds are expected in those processes where Br/Cl, Cl/F or Br/Cl/F containing compounds are present together, for instance during a chemical waste incineration.

For these reasons we had analyzed the real situation in connection with "industrial possibilities" of Russian chemical industry[2,8,9].

Table 1. The possibility of the formation of traditional and non-traditional dioxin-like pollutants on Russian chemical plants

Town	Name of plant	Type of dioxin-like pollutant						
		Cl	Br	F	Br/Cl	Cl/F	Br/Cl/F	S
Ufa	Khimprom	+						+
Cheboksary	Khimprom	+						+
Dzerdzhinsk	Kaprolactam	+						+
Usolje	Khimprom	+	+		+			
Dzerdzhinsk	Synthesis	+	+		+			+
Dzerdzhinsk	Orgsteklo	+		+		+		
Sterlitamak	Kaustic	+		+		+		
Volgograd	Khimprom	+		+		+		+
Chapaevsk	Plant of chemical fertilizer	+	+	+	+	+	+	
Kirovo-Chepetsk	Chemical plant	+	+	+	+	+	+	
Perm	Halogen	+	+	+	+	+	+	+
Slavgorod	Altaiikhimprom	+	+	+	+	+	+	+

Table 1 shows the result of consideration of the last 30-40 years of production of 12 Russian chemical plants with archaic approach to the disposal of chemical waste. It demonstrates the anticipated (and, as it turns out, the real) possibility of finding many of unknown dioxin-like pollutants in fly ash samples from chemical incinerators. Since incineration is one of the main sources for the environment occurrence of PCDDs/PCDFs and PBDDs/PBDFs, we can additionally expect:

- PFDDs, PFDFs, PCFDDs and PCFDFs (in Dzerdzhinsk, Sterlitamak, Volgograd, Chapaevsk, Kirovo-Chepetsk, Perm and Slavgorod),
- PBCFDDs and PBCFDFs (in Chapaevsk, Kirovo-Chepetsk, Perm and Slavgorod), and so on.

This also concerns different S-analogues of DD and DF:

- PCTAs and PCDTs (in Ufa and Cheboksary),
- PBTAs, PBDTs, PBCTAs and PBCDTs (in Dzerzhinsk),
- PFTAs, PFDTs, PCFTAs and PCFDTs (in Volgograd), and so on.

The reaction routes leading to the dioxin-like compounds in the fly ash are still unknown exactly. But it appears that these compounds originate from wastes incinerated, containing really large amounts of Cl-, Br-, F- and S-compounds (Table 1).

Bioaccumulation was shown to be especially important with the toxic and biologically most active 2,3,7,8-substituted isomers in dioxin-like compounds O- and S-types[1].

This primarily concerns the high toxic isomers in tetra- and pentahalocongeners.

Table 2. Number of 2,3,7,8-substituted isomers in tetra- and pentahalogenated dibenzo-p-dioxins (OO), dibenzofurans (O), dibenzothiophens (S), thianthrenes (SS) and mixed compounds (OS)

Types of compounds	Hal_4-isomers					Types of compounds	Hal_5-isomers				
	OO	O	SS	OS	S		OO	O	SS	OS	S
F_4	1	1	1	1	1	F_5	1	2	1	2	2
Cl_4	1	1	1	1	1	Cl_5	1	2	1	2	2
Br_4	1	1	1	1	1	Br_5	1	2	1	2	2
FCl_3	1	2	1	2	2	FCl_4	5	10	5	10	10
F_2Cl_2	3	4	3	4	4	F_2Cl_3	10	20	10	20	20
						F_3Cl_2	10	20	10	20	20
F_3Cl	1	2	1	2	2	F_4Cl	5	10	5	10	10
FBr_3	1	2	1	2	2	FBr_4	5	10	5	10	10
F_2Br_2	3	4	3	4	4	F_2Br_3	10	20	10	20	20
						F_3Br_2	10	20	10	20	20
F_3Br	1	2	1	2	2	F_4Br	5	10	5	10	10
$ClBr_3$	1	2	1	2	2	$ClBr_4$	5	10	5	10	10
Cl_2Br_2	3	4	3	4	4	Cl_2Br_3	10	20	10	20	20
						Cl_3Br_2	10	20	10	20	20
Cl_3Br	1	2	1	2	2	Cl_4Br	5	10	5	10	10
$FClBr_2$	3	6	3	6	6	$FClBr_3$	12	24	12	24	24
						FCl_2Br_2	24	48	24	48	48
FCl_2Br	3	6	3	6	6	F_2Cl_2Br	24	48	24	48	48
						FCl_3Br	12	24	12	24	24
F_2ClBr	3	6	3	6	6	F_2ClBr_2	24	48	24	48	48
						F_3ClBr	12	24	12	24	24
Sum	**27**	**45**	**27**	**45**	**45**	**Sum**	**201**	**402**	**201**	**402**	**402**

Table 2 shows the number of 2,3,7,8-substituted tetra- and pentahalo isomers for various structural compositions in traditional O-compounds of DD and DF types and also in S-analogues of TA and DT types. The majority of the environmentally important and not (yet) known compounds are mixed halogenated.

The environmental and toxicological significance of the new types of dioxin-like compounds is still not realized. The formation of these compounds in chemical waste incineration (or in direct combustion) would pose an additional potential health risk to the public and a threat to the environment.

Of course, a lot of previous measurements that have been made on PCDDs and PCDFs only[3] should be reanalysed

For this purpose it is necessary to use a new strategy of analysis[10] including the NMR approach[11,12].

3.References

1)Polychlorinated dioxins and dibenzofurans. Eds C.Rappe, H.-R.Buser, B.Dodet, and I.K.O'Neill. Lyon: IARC, WHO, 1991. 426 p.
2 Fedorov L.A. Dioxins as ecological danger: retrospective and perspective, Moscow: Nauka, 1993. 266 p.
3) Buser H.-R. Chemosphere 1987; 16: 713-32.
4) Weber R and H.Hagenmaier. Organohalogen compounds 1994; 19: 7-11
5) Buser H.-R., I.S.Dolezal, M.Wolfensberger, and C.Rappe C. Environ. Sci Technol 1991; 25: 1637-43.
6) Donnelly J.R., and G.W.Sovocool, Chemosphere 1989; 20: 295-300.
7) Hilker D.R., K.M.Aldous, R.M.Smith, P.W.O'Keefe, J.F.Gierty, J.Jurusik, S.W.Hibbins, D.Spink, and R.J.Parillo, Chemosphere 1985; 14: 1275-84.
8) Fedorov L.A. Chemosphere 1993; 27: 91-5,477-81.
9) Fedorov L.A. Chemistry and life. 1994; N 10, 25-27.
10) Ballschmiter K. Organohalogen compounds 1993; 11: 1-4.
11) Fedorov L.A., V.I.Dostovalova, and B.A.Rudenko. Organohalogen compounds 1992; 8: 45-7.
12) Fedorov L.A. and V.I.Dostovalova. Organohalogen compounds 1994; 19: 77-9.