Environmental Risk Assessment Resulting from Sediment Contamination with Perfluoroalkyl Substances

Grażyna Gałęzowska, Justyna Rogowska *, Ewa Olkowska, Wojciech Ratajczyk and Lidia Wolska

Department of Environmental Toxicology, Faculty of Health Sciences, Medical University of Gdansk, Debowa Str. 23A, 80-204 Gdansk, Poland; grazyna.galezowska@gumed.edu.pl (G.G.); ewa.olkowska@gumed.edu.pl (E.O.); sinclair@gumed.edu.pl (W.R.); lidia.wolska@gumed.edu.pl (L.W.)
* Correspondance: justyna.rogowska@gumed.edu.pl; Tel.: +48-58-349-19-35

Table S1. PFASs concentrations in sea sediments around the world.

Location	Sample	Year	Compounds	Range [ng/g d.w.]	References
Semi-enclosed bays in Korea	Sediment cores	2018	Σ16 PFASs	0.0067–0.821	[4]
Coastal areas of the North and Baltic Seas	Surface sediments	2012	Σ29 PFASs	0.018–2.6	[17]
German Bight	Surface sediments	2015	∑16PFAS	0.056–7.4	[11]
the East China Sea	Surface sediments	2015	∑14PFAS	n.d.–34.8	[18]
the Baltic Proper	Surface sediments	2016	∑24PFAS	1.33[1]	[20]
the Jiulong Estuary-Xiamen Bay	Surface sediments	2019	∑24PFAS	3.0-5.4	[19]
the Seto Inland Sea, Japan	Surface sediments	2020	Σ13 PFASs	0.05–0.67	[21]
the Bering Sea and the western Arctic	Surface sediments	2020	∑9PFAS	0.06–1.73	[22]
the Truckee River, USA	Surface sediments	2021	∑17PFAS	272.9[1]	[23]
the Las Vegas wash, USA	Surface sediments		∑17PFAS	345.7[1]	
the Gulf of Gdańsk	Surface sediments	2020	∑17PFAS	0.0403–40.6	This study
the Gulf of Gdańsk, the Vistula estuary	Surface sediments	2020	∑17PFAS	0.509–614	This study

[1]average value
d.w.- dry weight.

Table S2. Correlation coefficient of different PFASs in sediment from the Gulf of Gdansk (correlation is significant at $p<0.05$, dark green color – strong correlation, individual analysis of sampling points)

Vistula	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	PFHxDA	PFODA	PFBS	PFDS	PFHxS	PFOS
PFPeA	-0.182																
PFHxA	-0.123	-0.047															
PFHpA	-0.069	-0.131	0.933														
PFOA	-0.066	-0.149	0.953	0.991													
PFNA	-0.090	-0.153	0.946	0.984	0.991												
PFDA	-0.142	0.051	-0.106	-0.191	-0.183	-0.135											
PFUdA	-0.083	-0.208	0.065	-0.022	0.000	0.038	0.433										
PFDoA	-0.069	-0.180	0.870	0.835	0.854	0.855	0.140	0.082									
PFTrDA	-0.084	-0.226	0.627	0.518	0.543	0.585	-0.032	0.389	0.548								
PFTeDA	-0.102	-0.115	0.808	0.733	0.755	0.762	0.188	0.137	0.967	0.533							
PFHxDA	-0.105	-0.041	0.845	0.761	0.784	0.789	0.198	0.196	0.947	0.490	0.974						
PFODA	-0.078	0.252	0.119	-0.094	-0.065	-0.046	0.590	0.374	0.304	0.032	0.479	0.533					
PFBS	0.731	-0.272	-0.123	-0.079	-0.077	-0.091	0.048	0.354	-0.086	-0.014	-0.071	-0.066	0.065				
PFDS	-0.087	-0.105	0.037	-0.045	-0.039	-0.019	0.549	0.512	0.383	0.057	0.512	0.499	0.741	0.129			
PFHxS	-0.108	0.223	0.100	-0.050	-0.030	-0.029	0.388	0.619	-0.029	-0.067	0.036	0.189	0.576	0.189	0.301		
PFOS	-0.058	0.205	-0.102	0.048	-0.004	0.080	0.231	-0.065	-0.026	-0.062	0.021	0.022	0.049	-0.118	0.019	-0.081	
∑PFASs	0.028507	0.109304	0.114818	-0.02273	-0.00421	-0.00042	0.476396	0.717736	0.110026	-0.01275	0.199738	0.323694	0.698521	0.38102	0.553845	0.939075	-0.0791
WTP I	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	PFHxDA	PFODA	PFBS	PFDS	PFHxS	PFOS
PFPeA	0.188																
PFHxA	-0.312	-0.144															
PFHpA	-0.296	-0.220	-0.109														
PFOA	-0.312	0.068	-0.284	0.646													
PFNA	0.775	0.297	0.041	-0.371	-0.069												
PFDA	0.753	0.267	-0.368	-0.364	-0.159	0.717											
PFUdA	0.052	0.370	0.201	-0.439	0.080	0.492	0.552										
PFDoA	0.095	0.288	-0.243	-0.327	0.195	0.207	0.122	0.094									
PFTrDA	0.361	0.346	-0.501	0.359	0.540	0.283	0.295	0.106	-0.191								
PFTeDA	-0.028	0.241	-0.485	0.759	0.674	-0.097	0.150	-0.023	-0.249	0.691							
PFHxDA	0.130	0.251	-0.577	0.590	0.730	0.156	0.205	0.018	-0.150	0.819	0.881						
PFODA	0.588	0.349	-0.341	-0.438	-0.322	0.521	0.913	0.491	0.193	0.008	0.076	0.036					
PFBS	0.188	ND	-0.144	-0.220	0.068	0.297	0.267	0.370	0.288	0.346	0.241	0.251	0.349				
PFDS	-0.188	0.125	-0.345	0.899	0.691	-0.297	-0.267	-0.370	-0.288	0.629	0.885	0.799	-0.349	0.125			
PFHxS	-0.225	0.135	-0.304	0.884	0.668	-0.331	-0.319	-0.373	-0.330	0.631	0.858	0.773	-0.402	0.135	0.996		
PFOS	0.393	0.226	-0.306	-0.332	0.234	0.662	0.813	0.792	0.240	0.335	0.173	0.348	0.672	0.226	-0.226	-0.271	
∑PFASs	-0.2399	-0.00084	0.051993	0.929932	0.695549	-0.14006	0.2588	-0.16639	-0.36201	0.479398	0.787606	0.658811	-0.38017	-0.00084	0.880544	0.873676	-0.16593
WTP II	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	PFHxDA	PFODA	PFBS	PFDS	PFHxS	PFOS
PFPeA	0.229015																
PFHxA	0.241	-0.021															
PFHpA	ND	0.229	0.241														
PFOA	0.182	0.976	-0.070	0.182													
PFNA	0.189	0.938	0.007	0.189	0.975												
PFDA	0.129	0.850	-0.248	0.129	0.837	0.694											
PFUdA	ND	0.229	0.241	ND	0.182	0.189	0.129										
PFDoA	0.214	0.953	-0.197	0.214	0.944	0.883	0.879	0.214									
PFTrDA	0.092	0.688	0.182	0.092	0.650	0.501	0.865	0.092	0.659								
PFTeDA	0.216	0.704	0.240	0.216	0.659	0.518	0.852	0.216	0.674	0.990							
PFHxDA	-0.018	0.445	0.686	-0.018	0.387	0.327	0.436	-0.018	0.309	0.800	0.799						
PFODA	0.326	0.723	0.434	0.326	0.657	0.558	0.747	0.326	0.664	0.926	0.962	0.850					
PFBS	-0.014	-0.121	-0.293	-0.014	-0.181	-0.156	-0.206	-0.014	0.091	-0.367	-0.344	-0.425	-0.277				
PFDS	ND	0.229	0.241	ND	0.182	0.189	0.129	ND	0.214	0.092	0.216	-0.018	0.326	-0.014			
PFHxS	0.125	0.853	-0.241	0.125	0.840	0.698	1.000	0.125	0.882	0.869	0.855	0.446	0.752	-0.200	0.125		
PFOS	0.125	0.853	-0.241	0.125	0.840	0.698	1.000	0.125	0.882	0.869	0.855	0.446	0.752	-0.200	0.125	1.000	
∑PFASs	0.277036	0.884195	0.410694	0.277036	0.85116	0.818956	0.734687	0.277036	0.782383	0.813517	0.844817	0.777442	0.91461	0.29749	0.277036	0.740962	0.740962
WTP III	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	PFHxDA	PFODA	PFBS	PFDS	PFHxS	
PFPeA	0.145																
PFHxA	0.166	0.922															
PFHpA	ND	0.145	0.166														
PFOA	0.125	-0.145	-0.166	0.125													
PFNA	ND	0.145	0.166	ND	0.125												
PFDA	0.187	-0.107	-0.248	0.187	-0.187	0.187											
PFUdA	ND	0.145	0.166	ND	0.125	ND	0.187										
PFDoA	ND	0.145	0.166	ND	0.125	ND	0.187	ND									
PFTrDA	-0.645	0.630	0.641	-0.645	-0.232	-0.645	-0.290	-0.645	-0.645								
PFTeDA	0.176	0.867	0.991	0.176	-0.176	0.176	-0.264	0.176	0.176	0.618							
PFHxDA	-0.394	0.571	0.730	-0.394	-0.315	-0.394	-0.444	-0.394	-0.394	0.843	0.753						
PFODA	-0.185	-0.082	-0.046	-0.185	-0.325	-0.185	-0.546	-0.185	-0.185	0.082	-0.052	0.259					
PFBS	-0.885	-0.223	-0.266	-0.885	-0.177	-0.885	-0.260	-0.885	-0.885	0.478	-0.283	0.184	0.411				
PFDS	ND	0.145	0.166	ND	0.125	0.143	0.187	ND	ND	-0.645	0.176	-0.394	-0.185	-0.885			
PFHxS	ND	0.145	0.166	ND	0.125	0.143	0.187	ND	ND	-0.645	0.176	-0.394	-0.185	-0.885	ND		
PFOS	ND	0.145	0.166	ND	0.125	0.143	0.187	ND	ND	-0.645	0.176	-0.394	-0.185	-0.885	ND	ND	
∑PFASs	-0.00816	0.928951	0.974507	-0.00816	0.22398	-0.00816	0.3187	-0.00816	-0.00816	0.760305	0.953247	0.797972	0.096264	0.07183	-0.00816	-0.00816	-0.00816
WTP IV	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUdA	PFDoA	PFTrDA	PFTeDA	PFHxDA	PFODA	PFBS	PFDS	PFHxS	
PFPeA	0.195																
PFHxA	0.200	1.000															
PFHpA	1.000	0.195	0.200														
PFOA	0.253	0.135	0.142	0.253													
PFNA	0.200	1.000	1.000	0.200	0.142												
PFDA	0.127	0.997	0.996	0.127	0.102	0.996											
PFUdA	1.000	0.195	0.200	ND	0.253	0.200	0.127										
PFDoA	0.200	1.000	1.000	0.200	0.142	1.000	0.996	0.200									
PFTrDA	0.259	0.949	0.951	0.259	0.441	0.951	0.935	0.259	0.951								
PFTeDA	0.200	1.000	1.000	0.200	0.142	1.000	0.996	0.200	1.000	0.951							
PFHxDA	0.249	0.968	0.970	0.249	0.379	0.970	0.957	0.249	0.970	0.998	0.970						
PFODA	0.284	0.423	0.429	0.284	0.955	0.429	0.393	0.284	0.429	0.688	0.429	0.637					
PFBS	1.000	0.195	0.200	ND	0.253	0.200	0.127	ND	0.200	0.259	0.200	0.249	0.284				
PFDS	1.000	0.195	0.200	ND	0.253	0.200	0.127	ND	0.200	0.259	0.200	0.249	0.284	ND			
PFHxS	0.200	1.000	1.000	0.200	0.142	1.000	0.996	0.200	1.000	0.951	1.000	0.970	0.429	0.200	0.200		
PFOS	0.200	1.000	1.000	0.200	0.142	1.000	0.996	0.200	1.000	0.951	1.000	0.970	0.429	0.200	0.200	1.000	
∑PFASs	0.224171	0.992073	0.992929	0.224171	0.258006	0.992929	0.984902	0.224171	0.992929	0.980927	0.992929	0.991879	0.533576	0.224171	0.224171	0.992929	0.992929

ND = not detected both analytes, if one detected used as zero in calculating ½ method limit detection (MDL)
WTP-wastewater treatment plant

PFBA-perfluoro-*n*-butanoic acid, PFPeA-perfluoro-*n*-pentanoic acid, PFHxA-perfluoro-*n*-hexanoic acid, PFHpA-perfluoro-*n*-heptanoic acid, PFOA-perfluoro-*n*-octanoic acid, PFNA-perfluoro-*n*-nonanoic acid, PFDA-perfluoro-*n*-decanoic acid, PFUdA-perfluoro-*n*-undecanoic acid, PFDoA-perfluoro-*n*-dodecanoic acid, PFTrDA-perfluoro-*n*-tridecanoic acid, PFTeDA-perfluoro-*n*-tetra-decanoic acid, PFHxDA-perfluoro-*n*-hexadecanoic acid, PFODA-perfluoro-*n*-octadecanoic acid, PFBS-potassium perfluoro-1-butanesulfonate, PFHxS-sodium perfluoro-1-hexanesulfonate, PFOS-sodium perfluoro-1-octanesulfonate, PFDS-sodium perfluoro-1-decanesulfonate

Table S3. Sediment characteristic

Sampling area	f_{oc} [%]: min. – max. (average mean)[1]	Type of sediment[2]
The Vistula river	4.2 – 9.0 (7.7)	medium grain sand and fine grain sand except: silt - W4,W6-W8,W24,W27 and very fine grain sand - W18-19,W25
WTP I	2.1 – 6.1 (2.8)	coarse grain sand – GA2, GB1, GB3 medium grain and fine grain sand - G0, GA3, GB2 silt - GA1, GB1, GB4
WTP II	2.2 – 5.7 (2.7)	medium grain and fine grain sand
WTP III	1.1 – 6.7 (5.1)	medium grain sand and fine grain sand except: silt - XA3, XB2, XB3
WTP IV	1.6 – 6.8 (5.3)	medium grain sand

f_{oc} - fraction of organic matter

[1]data obtained from previous research in area of the Baltic Sea

[2] sediment samples were classified based on the Unified Soil Classification System

Estimation of environmental risk parameters

To estimate the Predicted No Effect Concentration (PNECs) values (Eq. (S1)), the lowest recorded toxicity data for all species of aquatic animals were collected from the literature [54].

$$\mathrm{PNEC} = \frac{\mathrm{NOEC\ or\ L(E)C50}}{AF} \quad \text{(S1)}$$

where:

NOEC—no observed effect concentration,

EC50—the concentration of compound at which the organism gives half-maximal response,

LC50—the concentration of compound where 50% of the organisms die,

AF—an appropriate standard assessment factor (the assessment factor value is corresponded with availability of number of trophic levels of NOEC).

Because of insufficient data on toxicity of PFASs to sediments, the lowest toxicological values for water phase ($PNEC_{water}$) have been collected from literature (See Table S4). Additionally, in Table S4, assessment factors are presented, which in all cases were estimated as 1000 (the overall AF generally consists of the following 10-fold factors: extrapolation toxic parameter for acute to chronic effects (10×), across species extrapolation (10x), uncertainty in the overall estimation of effects (10×) [61]). For PFTrDA, PFTeDA, PFHxDA and PFODA, experimental values of $PNEC_{water}$ are not available and in these cases ToxTram QSAR or advisory guideline values were applied (recommended by the Department of Health and Human Services in North Carolina). To extrapolate $PNEC_{water}$ values for marine samples, an additional 10-fold factor was used. Investigation is still needed regarding ecotoxicological data on aquatic organisms (especially marine water and sediment) to introduce unified threshold values that allow the comparison of different ecosystems. For example, the following values of $PNEC_{water}$ for PFOA used in risk assessment protocols were found in the literature: 1428 ng/L (freshwater), 20,000 ng/L (freshwater), 100,000 ng/L (freshwater), 570,000 ng/L, 119000000 ng/L [54,62–65].

After collection of $PNEC_{water}$ data, the equilibrium partitioning method (EqPM) was used to calculate the $PNEC_{sediment}$, according to the Technical Guidance Document of the European Union (Eq. (S2)) [54,65]. Additionally, for substances with a log K_{ow} >5 the $PNEC_{sediment}$ calculated value needs to be decreased by a factor of 10 [55].

$$PNEC_{sediment} = (0.783 + 0.0217 \times K_{oc}) \times PNEC_{water} \quad (S2)$$

where:
$PNEC_{sediment}$—predicted no effect concentration for marine water
K_{oc}—the organic carbon partitioning coefficient
$PNEC_{water}$ —predicted no effect concentration for sea water.

Risk quotient (RQs) values for the PFASs occurring in sea sediment and water phase were calculated for aquatic organisms by comparing the measured environmental concentration (MEC) in the sea samples to the predicted no-effect concentration (PNEC) according to equation (S3) [53,54,66]:

$$RQ = \frac{MEC_x}{PNEC_x} \quad (S3)$$

where:
MECx – measured environmental concentration [ng/L or ng/kg d.w. – dry weight],
PNECx – predicted no effect concentration [ng/L or ng/kg],
x – values for water or sediment.

Table S4. Information on perfluoroalkyl substances used in the environmental risk assessment

CAS	Compound name	Compound acronym	log Kow [L/kg][1]	log Koc [L/kg][1]	log Kd [L/kg][2]	Type of toxic parameter used to estimate $PNEC_{water}$[3]	AF used to estimate $PNEC_{water}$ [3]	$PNEC_{water}$ [ng/L][3]	$PNEC_{sediment}$ [ng/kg][4]
375-22-4	perfluoro-n-butanoic acid	PFBA	2.14	1.813	0.26[1]	LC50	1000	110000	241316
2706-90-3	perfluoro-n-pentanoic acid	PFPeA	2.81	2.464	0.91[1]	LC50/EC50	1000	32000	227176
307-24-4	perfluoro-n-hexanoic acid	PFHxA	3.48	3.116	2.78	LC50/EC50	1000	97000	2825310
375-85-9	perfluoro-n-heptanoic acid	PFHpA	4.15	3.767	2.63	LC50	1000	7852	1002563
335-67-1	perfluoro-n-octanoic acid	PFOA	4.81	4.419	2.49	LC50	1000	1428	814300
375-95-1	perfluoro-n-nonanoic acid	PFNA	5.48	5.071	3.25	LC50/EC50	1000	1000000	255618796
335-76-2	perfluoro-n-decanoic acid	PFDA	6.15	5.722	3.95	LC50	1000	45	51488
2058-94-8	perfluoro-n-undecanoic acid	PFUdA	6.82	6.374	4.72	LC50	1000	8	41073
307-55-1	perfluoro-n-dodecanoic acid	PFDoA	7.49	7.026	3.31	LC50	1000	1	32024
72629-94-8	perfluoro-n-tridecanoic acid	PFTrDA	8.16	7.677	3.59	lack of PNEC – use of ToxTram QSAR value		103	10644855
376-06-7	perluoro-n-tetra-decanoic acid	PFTeDA	8.83	8.329	3.19	lack of PNEC – use of ToxTram QSAR value		83	38325704
67905-19-5	perfluoro-n-hexadecanoic acid	PFHxDA	10.17	9.632	8.08[1]	lack of PNEC – use of ToxTram QSAR value		77	716061729
16517-11-6	perfluoro-n-octadecanoic acid	PFODA	11.51	10.94	9.38[1]	lack of PNEC – use of recommended value (the Department of Health and Human Services in North Carolina)		140	26156990202
375-73-5	potassium perfluoro-1-butanesulfonate	PFBS	1.82	2.249	0.26	EC50	1000	372000	1723473
3871-99-6	sodium perfluoro-1-decanesulfonate	PFDS	1.01	3.552	2.00[1]	LC50	1000	15400	1203247
2795-39-3	sodium perfluoro-1-hexanesulfonate	PFHxS	2.35	4.855	1.34	EC50	1000	250000	388703550

1763-23-1	sodium per-fluoro-1-oc-tanesulfonate	PFOS	4.49	4.855	2.94	LC50	1000	610	948437

K_{ow} – octanol water partitioning coefficient; K_{oc} – organic carbon partitioning coefficient; K_d - sediment/water distribution coefficient, NOEC – no observed effect concentration; EC50 – the concentration of compound at which the organism gives half-maximal response; LC50 – the concentration of compound where 50% of the organisms die; AF – assessment factor; PNEC – predicted no effect concentration

[1] data obtained from the EPI Suite™ model, in case of log Kd additionally data on fraction of organic carbon in sediment were used

[2] [20]

[3] [40,41,54,61,62,67,68]

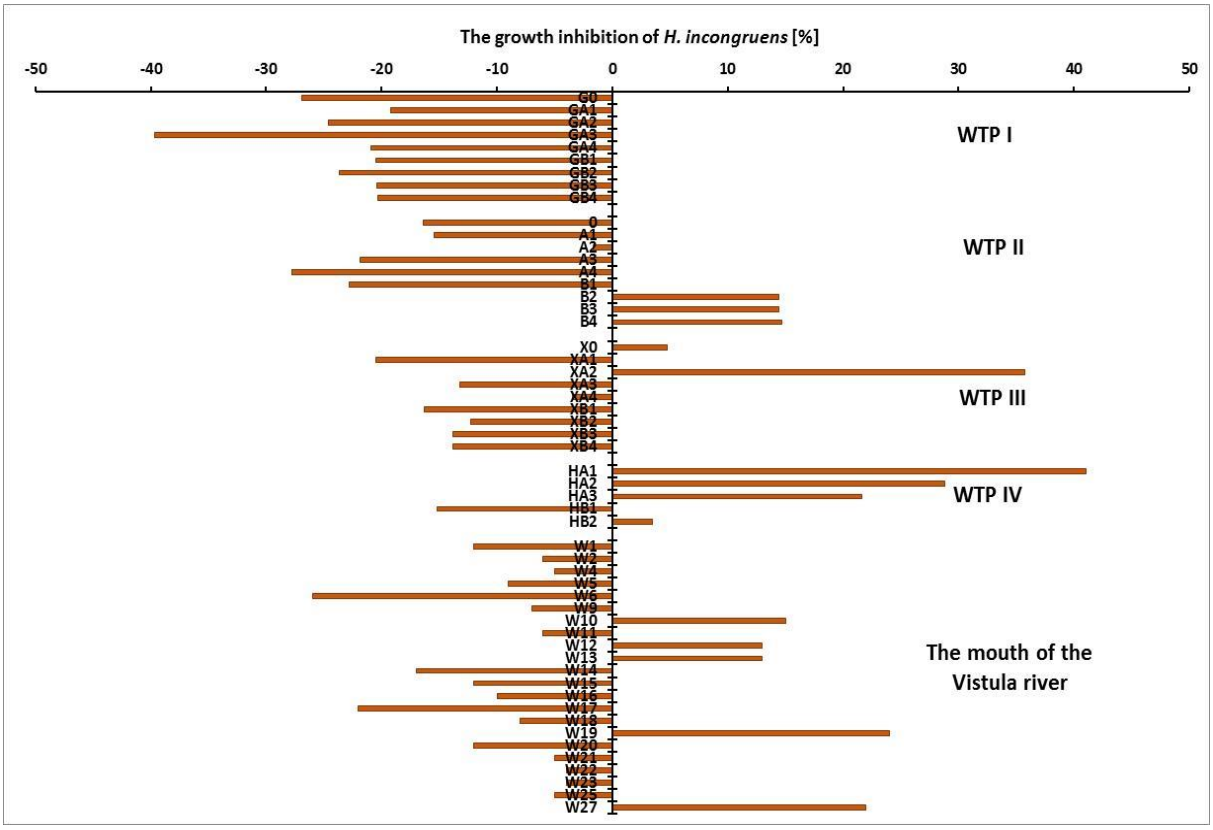
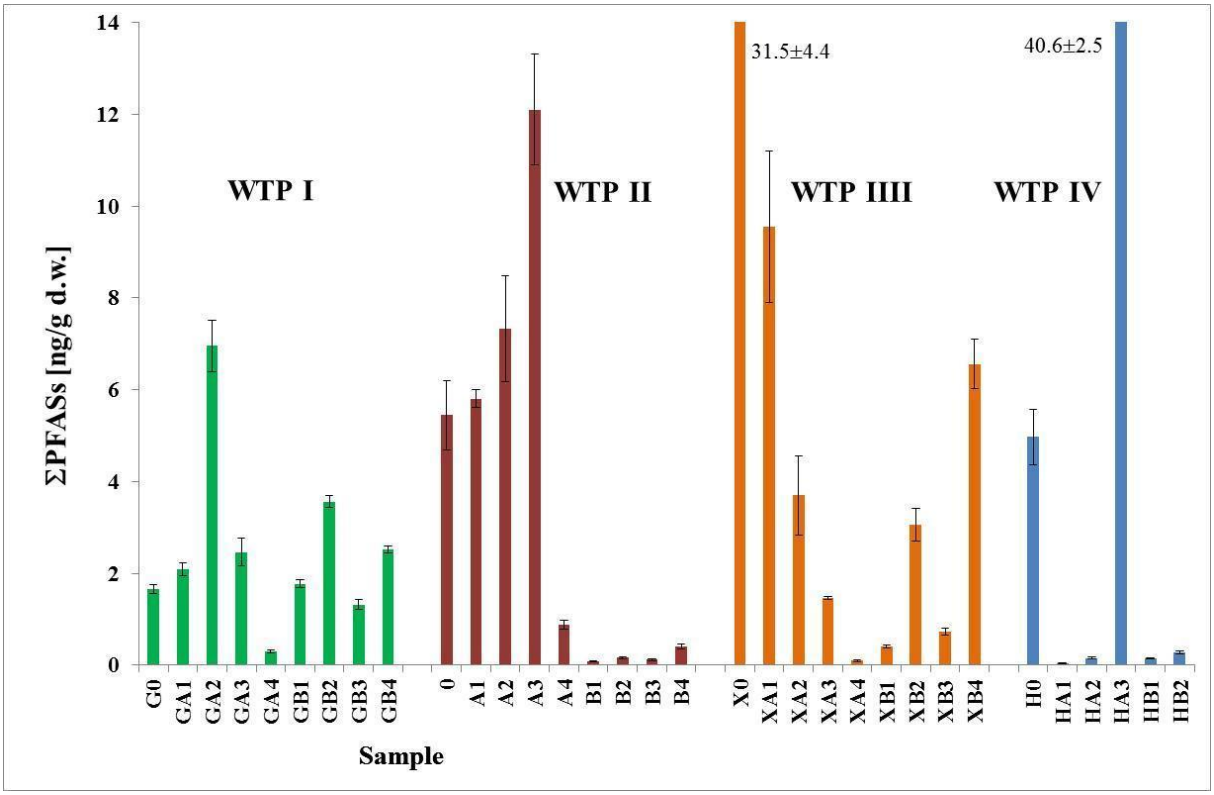
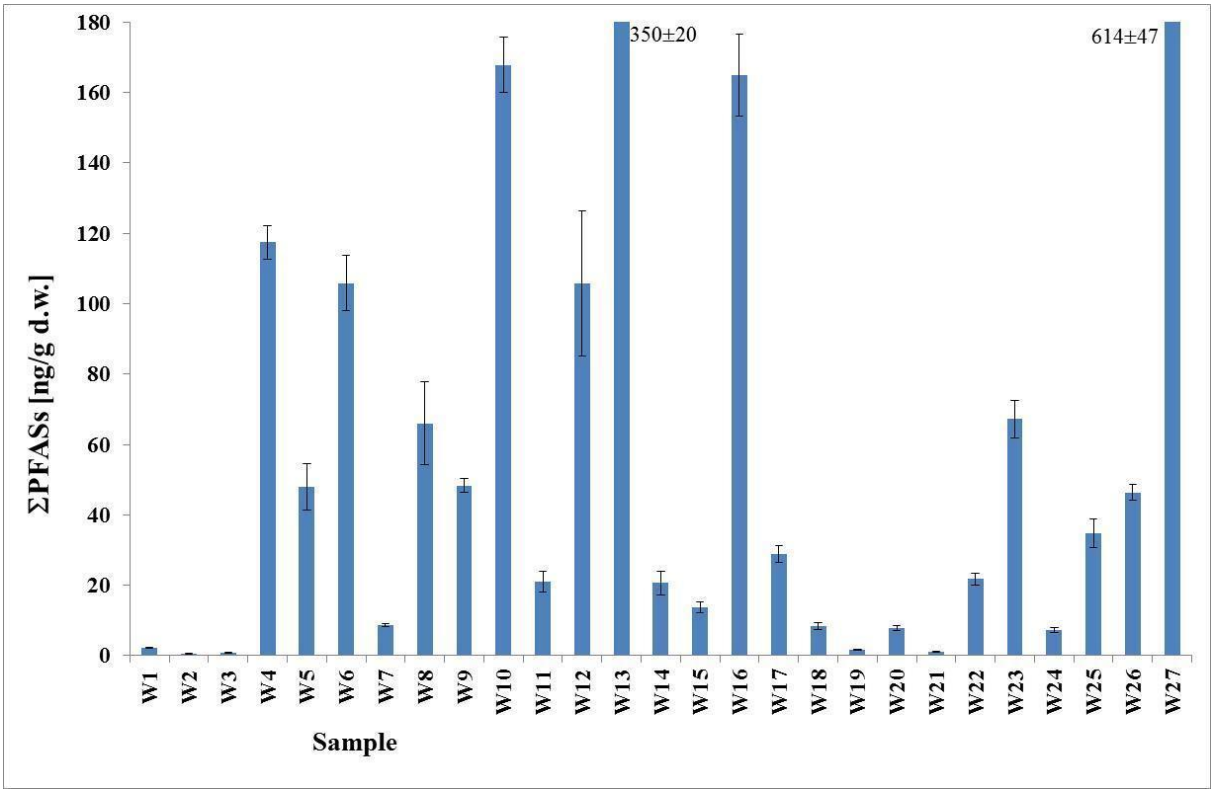


Figure S1. The results of the growth inhibition of H. incongruens in samples taken around the sewage collectors' outlets from wastewater treatment plants (WTP I-WTP IV) and from the mouth of Vistula



(a)



(b)

Figure S2. The results of the determination of PFASs in samples taken around the sewage collectors' outlets from wastewater treatment plants (WTP I-WTP IV) (a) and from the mouth of Vistula (b)