Sources of PCDD/Fs, PAHs and trace metal contamination of Upper-Scheldt and IJser river sediments.

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Objectives.

- What are the levels of PCDD/Fs, PAHs and trace metals in Upper-Scheldt and IJser river sediments?
- Are there similarities in contamination levels and congener profiles?
- What are the sources of the contaminants?
- Do we observe a reduction/increase in the contamination level with time?

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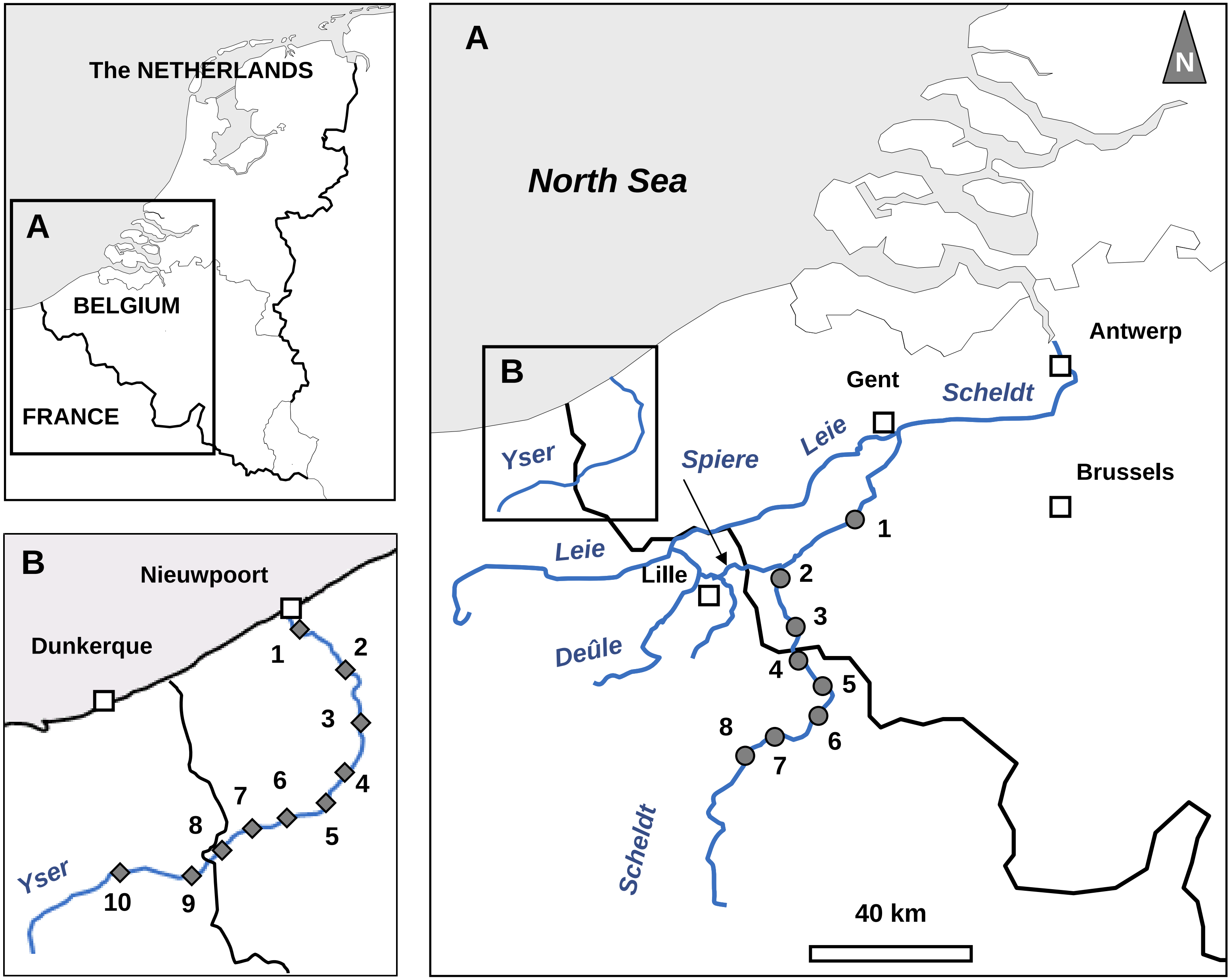


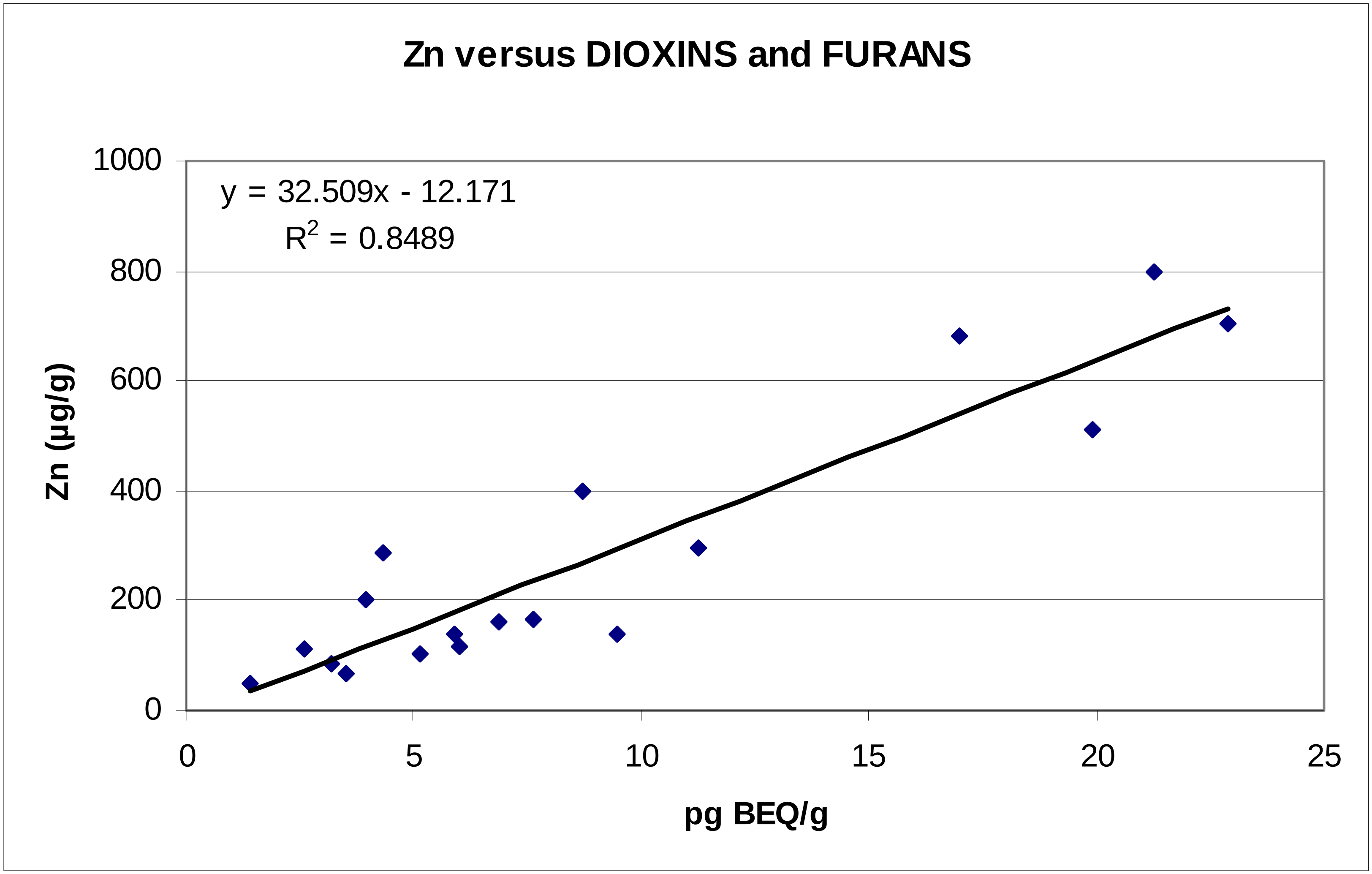
Concentrations of PAHs. PCDD/Fs. Dioxin-like PCBs and trace metals in sediments of both rivers

Sampling Station	km from the mouth	USEPA-PAH (µg/g)	PCDD/Fs (pg TEQ/g)	Dioxin-like PCBs (pg TEQ/g)	Cu (µg/g)	Zn (µg/g)	Pb (µg/g)	Cd (µg/g)	Al (mg/g)
Upper-Scheldt 1 (Oudenaarde)	185	1.80	1.43	0.79	16.2	201	47.8	1.95	8.3
Upper-Scheldt 2 (Spiere-Helkijn)	214	8.91	5.41	3.37	81.3	702	169	7.26	16.9
Upper-Scheldt 3 (Antoing)	232		2.70	1.29	39.5	400	156	2.88	10.7
Upper-Scheldt 4 (Mortagne du Nord)	241	2.80	3.94	1.75	39.7	296	101	2.07	13.5
Upper-Scheldt 5 (Vieux-Condé)	251	1.22	1.70	1.05	21.8	138	36.3	1.14	13.2
Upper-Scheldt 6 (Bruay sur l'Escaut)	261	6.81	5.72	5.08	47.9	510	99.9	2.71	10.9
Upper-Scheldt 7 (Lourches)	276	8.24	12.0	4.05	88.1	800	241	4.64	19.0
Upper-Scheldt 8 (Bassin Rond)	281	4.31	11.5	3.75	55.7	682	345	1.92	20.1
Yser 1 (Nieuwpoort)	1	1.93	0.77	0.23	12.4	111	21.3	0.244	28.7
Yser 2 (Diksmuide)	10	4.16	1.05	0.23	13.1	66.1	14.4	0.226	13.3
Yser 3 (Diksmuide)	16	3.35	1.74	0.67	25.4	116	23.4	0.321	20.2
Yser 4 (Diksmuide)	23	2.25	3.10	1.22	40.1	165	36.6	0.482	35.3
Yser 5 (Lo-Reninge)	26	1.14	1.46	0.38	26.3	105	23.5	0.312	31.5
Yser 6 (Lo-Reninge)	31	3.35	2.38	0.66	45.5	161	38.3	0.487	34.5
Yser 7 (Alveringem)	35	0.93	1.29	0.37	27.9	289	32.9	0.308	32.8
Yser 8 (Poperinge)	39	0.49	2.04	0.67	28.6	141	31.0	0.464	39.3
Yser 9 (Bambecque)	44	1.21	0.94	0.29	12.4	84.0	17.4	0.288	23.7
Yser 10 (La Cloche)	59	0.69	0.34	0.08	9.66	47.5	13.7	0.195	18.9

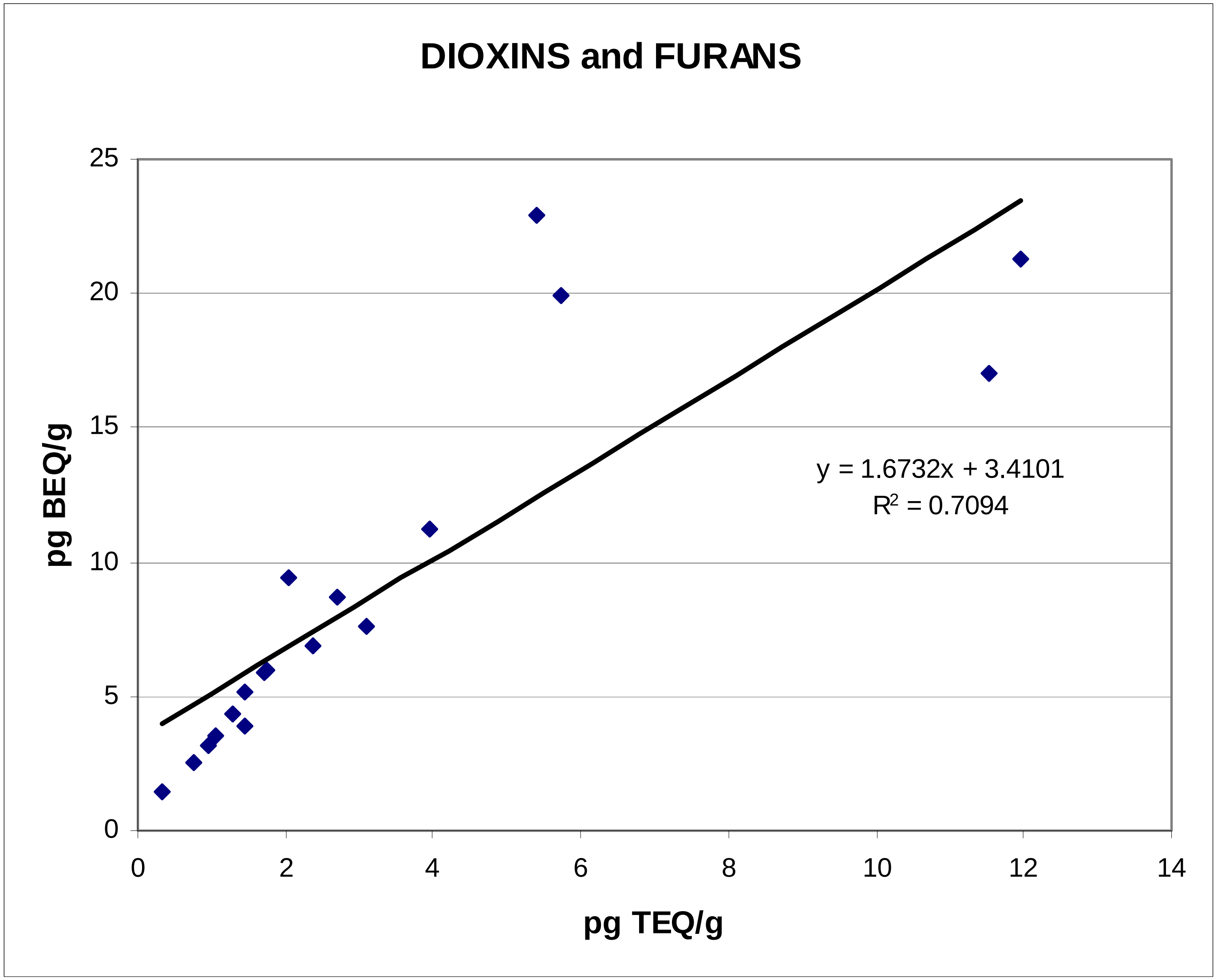
Spearman Rank Order correlation matrix for the whole parameter data set

	PCDDs TEQ (pg/g)	PCBs TEQ (pg/g)	Cu (µg/g)	Zn (µg/g)	Pb (µg/g)	Cd (µg/g)	Al (mg/g)
16 USEPA PAHs (µg/g)	0.679 *0.0025* (17)	0.637 *0.0058* (17)	0.630 *0.0066* (17)	0.588 *0.0128* (17)	0.603 *0.0103* (17)	0.618 *0.0081* (17)	-0.390 *0.119* (17)
PCDDs TEQ (pg/g)		0.938 *<0.001* (18)	0.953 *<0.001* (18)	0.862 *<0.001* (18)	0.886 *<0.001* (18)	0.853 *<0.001* (18)	-0.112 *0.650* (18)
PCBs TEQ (pg/g)			0.839 *<0.001* (18)	0.889 *<0.001* (18)	0.907 *<0.001* (18)	0.924 *<0.001* (18)	-0.342 *0.161* (18)
Cu (µg/g)				0.872 *<0.001* (18)	0.864 *<0.001* (18)	0.796 *<0.001* (18)	0.0485 *0.843* (18)
Zn (µg/g)					0.955 *<0.001* (18)	0.893 *<0.001* (18)	-0.236 *0.338* (18)
Pb (µg/g)						0.930 *<0.001* (18)	-0.292 *0.234* (18)
Cd (µg/g)							-0.432 *0.0713* (18)

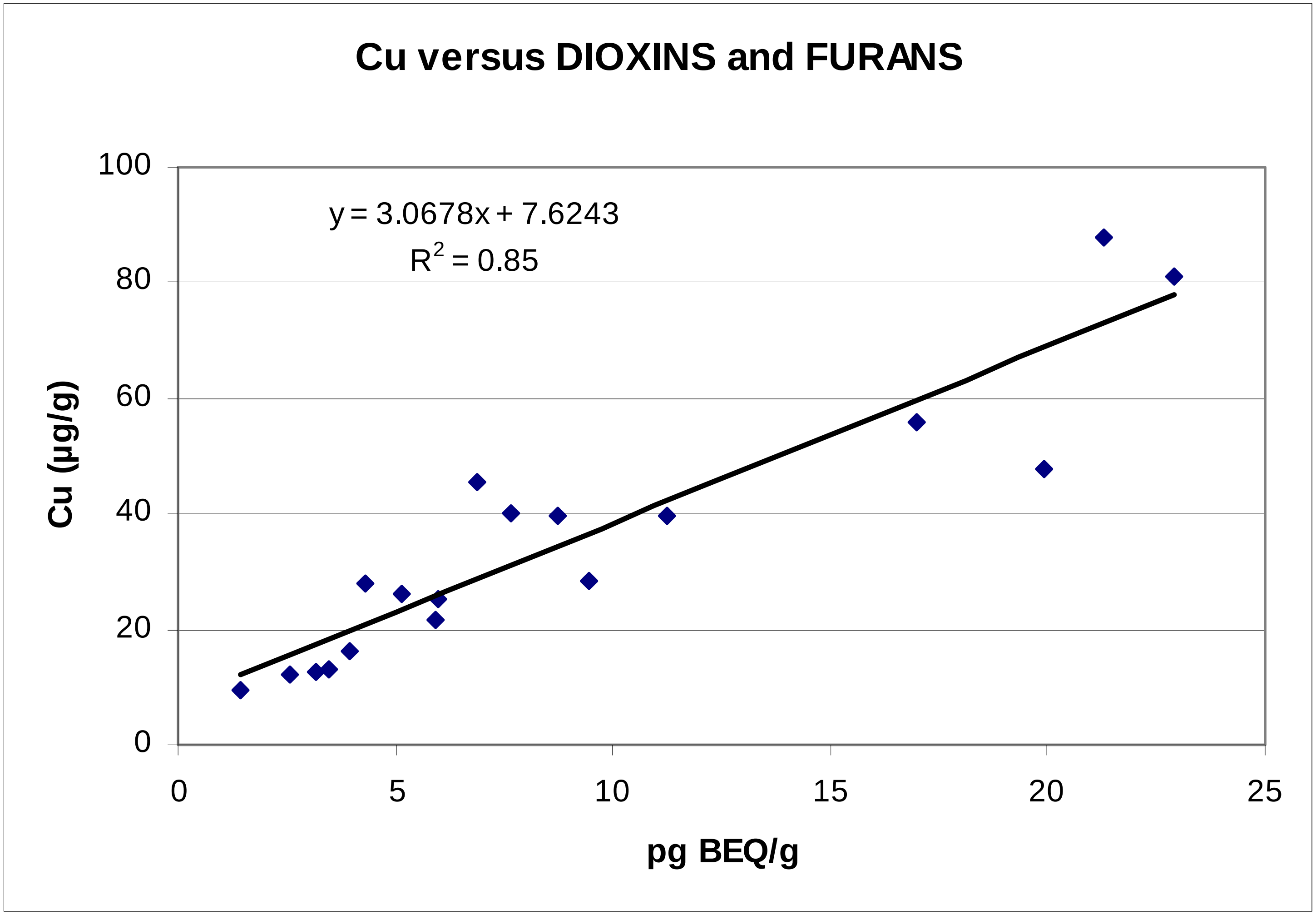
Correlation PCDD/F versus Zn



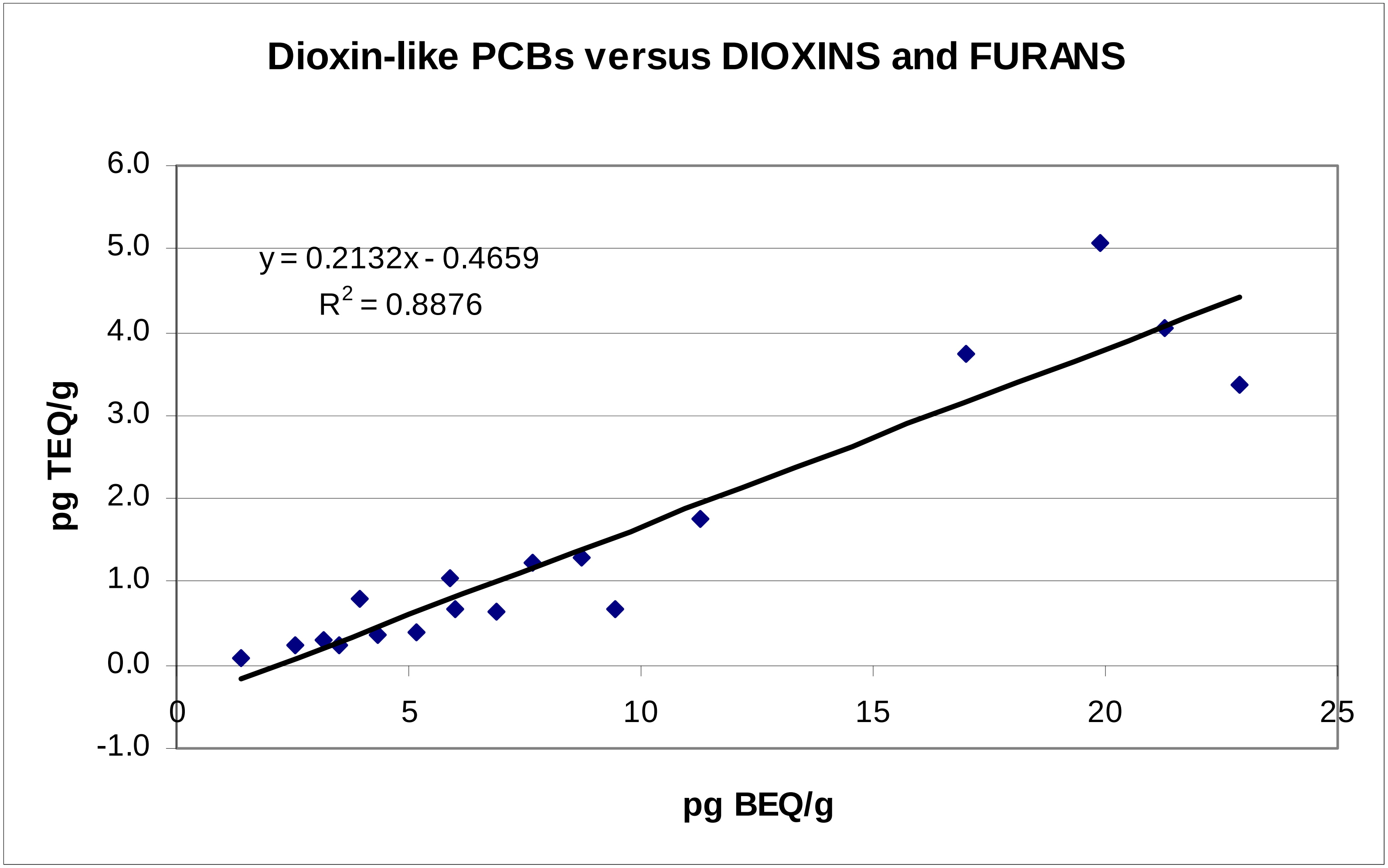
Correlation BEQ versus TEQ PCDD/F



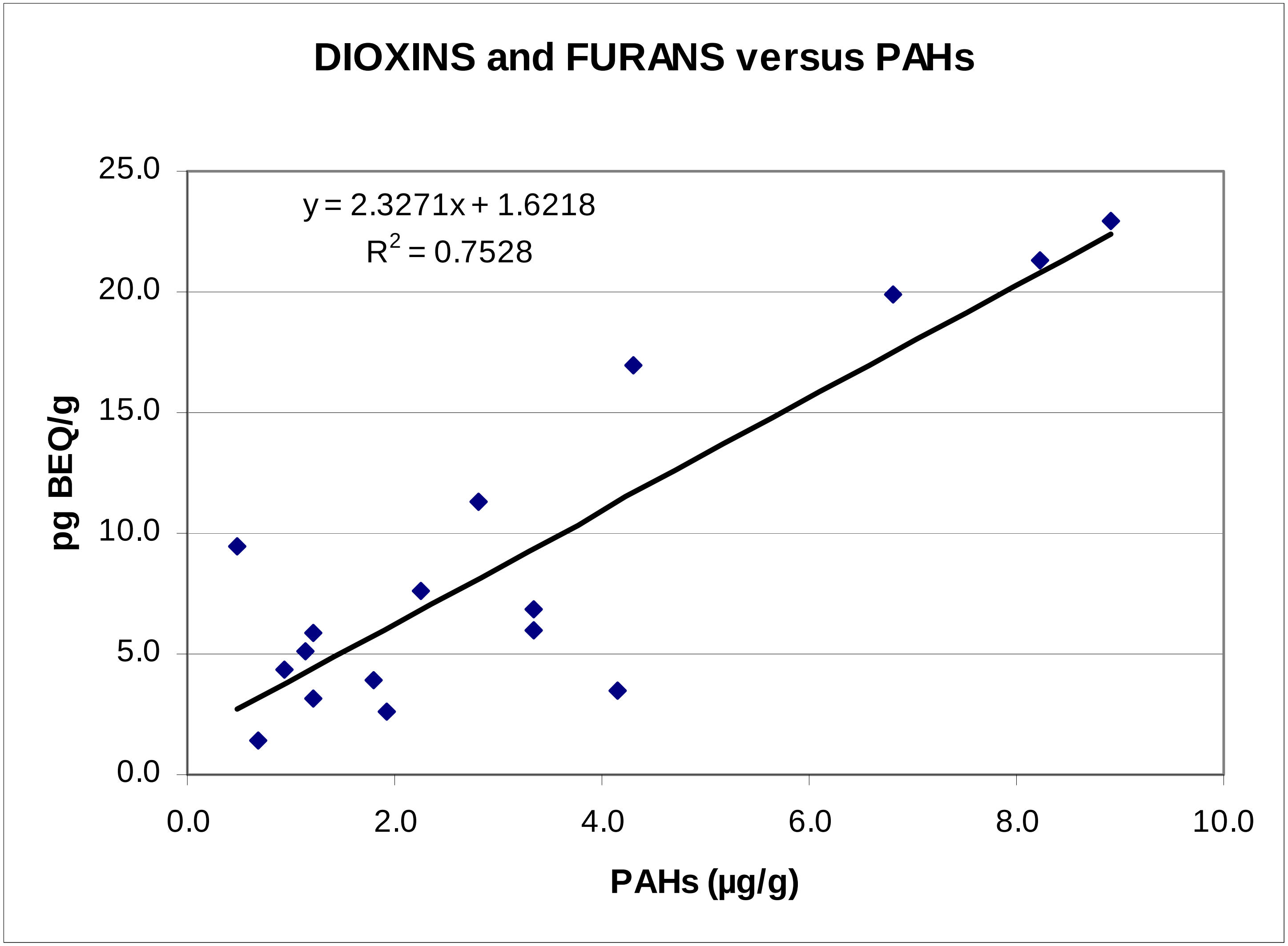
Correlation PCDD/F versus Cu



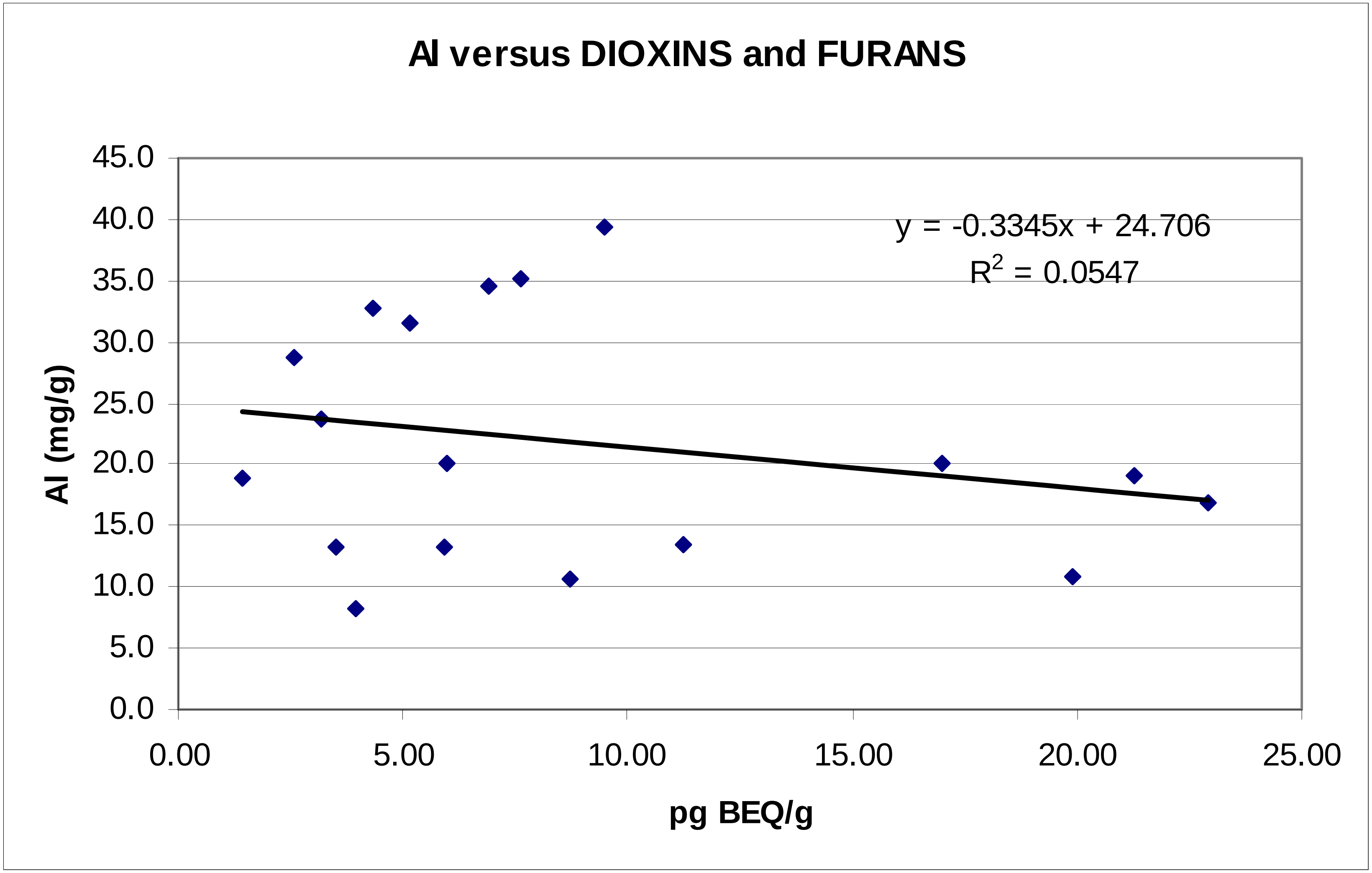
Correlation PCDD/F versus PCBs



Correlation PCDD/F versus PAHs

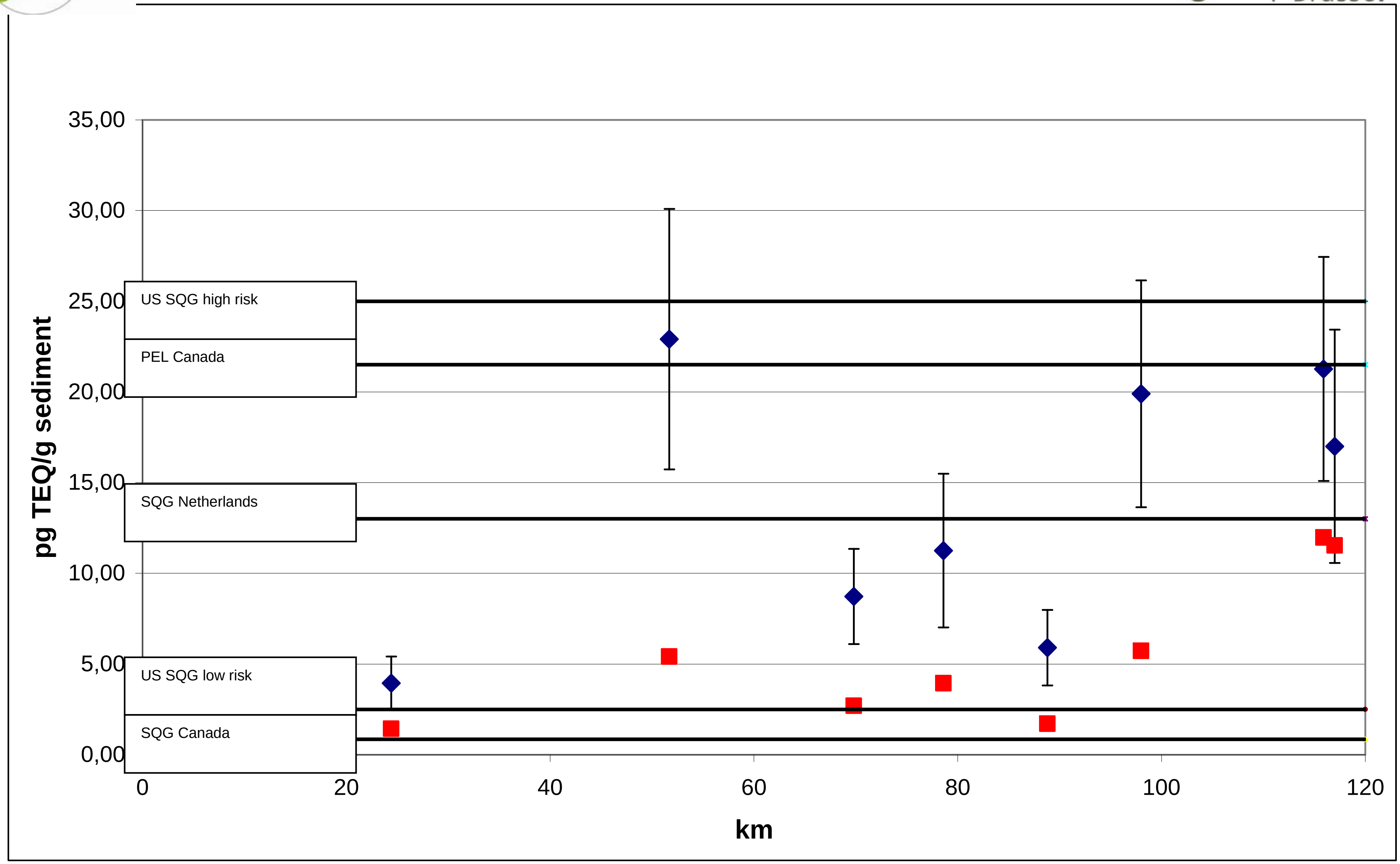


Correlation PCDD/F versus Al



Guidelines and norms SQG (Sediment Quality Guidelines) and PEL (Probable Effect Level) in pg-TEQ/g-sediment

SQG Canada	0.85	
PEL Canada	21.5	
SQG Nederland (enkel TCDD)	13	
SQG US (enkel TCDD)	2.5	mammals
guideline US high risk to sensitive species (enkel TCDD)	25	mammals



Dioxins Upper-Scheldt: Calux-BEQ (blue dots) and GCMS-TEQ (red dots)

Sources of contamination?

PAHs: looking to diagnostic ratios:

- When the HMW compounds (4 to 6 aromatic rings) dominate (LMW/HMW ratio is inferior to 1), a pyrolytic origin is suggested and vice versa
- The anthracene/(anthracene + phenanthrene) ratio indicates a pyrolytic origin when values are > 0.10.
- The same is true for the benzo[a]anthracene/(benzo[a]anthracene + chrysene) ratio although the boundaries are less clear: <0.20 suggests petrogenic and > 0.35 combustion origin.
- The indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene + benzo[ghi]perylene) ratio <0.20 indicates a petrogenic origin and a value > 0.50 grass, wood and coal combustion.

Sampling Station	km from the mouth	LMW[1]/HMW[2]	A[3]	B[4]	C[5]	D[6]
Sediment						
Upper-Scheldt 1 (Oudenaarde)	185	0.3	0.3	0.6	0.5	0.6
Upper-Scheldt 2 (Spiere-Helkijn)	214	0.6	0.3	0.6	0.5	0.6
Upper-Scheldt 3 (Antoing)	232	0.3	0.2	0.6	0.5	0.6
Upper-Scheldt 4 (Mortagne du Nord)	241	0.2	0.2	0.6	0.4	0.5
Upper-Scheldt 5 (Vieux-Condé)	251	0.2	0.2	0.6	0.5	0.5
Upper-Scheldt 6 (Bruay sur l'Escaut)	261	0.2	0.2	0.6	0.5	0.6
Upper-Scheldt 7 (Lourches)	276					
Upper-Scheldt 8 (Bassin Rond)	281	0.1	0.2	0.6	0.4	0.5
Yser 1 (Nieuwpoort)	1	0.3	0.3	0.6	0.5	0.5
Yser 2 (Diksmuide)	10	0.2	0.3	0.6	0.5	0.6
Yser 3 (Diksmuide)	16	0.2	0.2	0.6	0.5	0.6
Yser 4 (Diksmuide)	23	0.4	0.2	0.3	0.4	0.6
Yser 5 (Lo-Reninge)	26	0.3	0.3	0.6	0.4	0.5
Yser 6 (Lo-Reninge)	31	0.3	0.2	0.6	0.4	0.5
Yser 7 (Alveringem)	35	0.3	0.1	0.6	0.5	0.6
Yser 8 (Poperinge)	39	0.2	0.1	0.6	0.4	0.5
Yser 9 (Bambecque)	44	0.3	0.2	0.6	0.5	0.6
Yser 10 (La Cloche)	59	0.2	0.2	0.6	0.5	0.6
Atmosphere						
Zelzate 1				0.6	0.3	0.6
Zelzate 2				0.6	0.3	0.6

[1]LMW = Low Molecular Weight PAHs; [2]HMW = High Molecular Weight PAHs; [3]A = Anthracene/(Anthracene + Phenantrene); [4]B = Fluoranthene/(Fluoranthene + Pyrene); [5]C = Benzo[a]anthracene/(Benzo[a]anthracene + Chrysene); [6]D = Indeno[1,2,3,-cd]pyrene/(Indeno[1,2,3-cd]pyrene + Benzo[ghi]perylene)

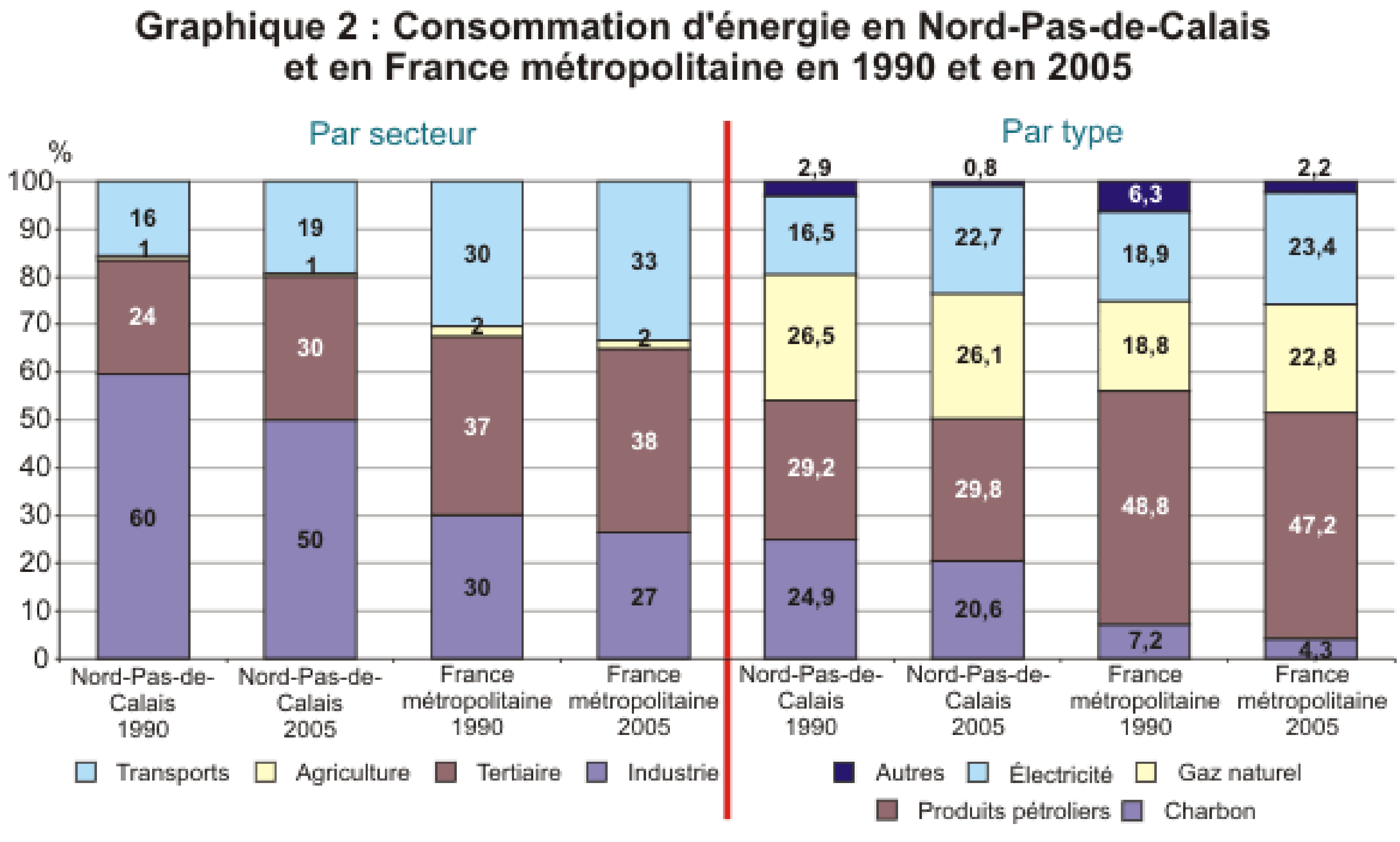
Les Houillères du Bassin du Nord et du Pas-de-Calais

2400 million tons extracted.

852 mines, 326 slag heaps, 13 cokes-ovens, 14 electric power plants

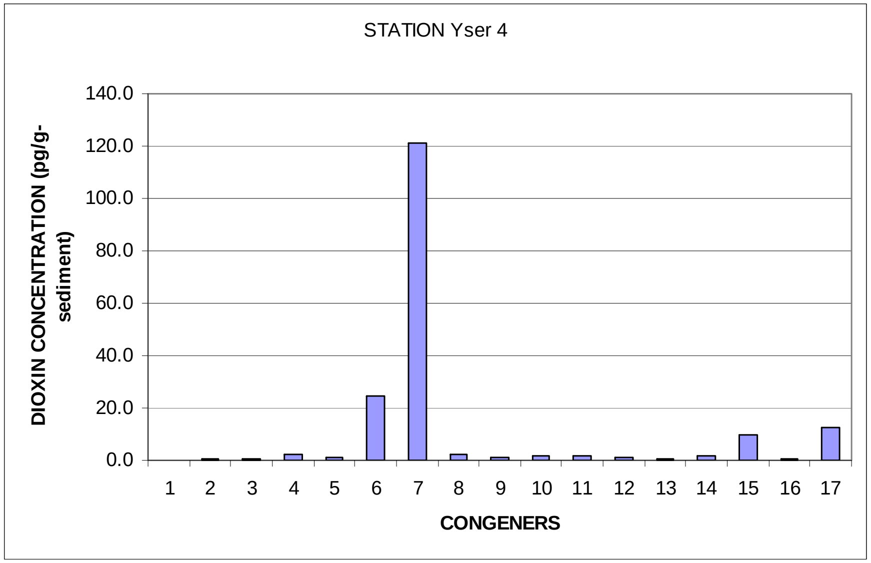
	1950	**1960**	**1970**	**1980**	**1990**	**2000**
Production (*in Million t)*	27,56	28,94	16,99	4,47	0,23	-

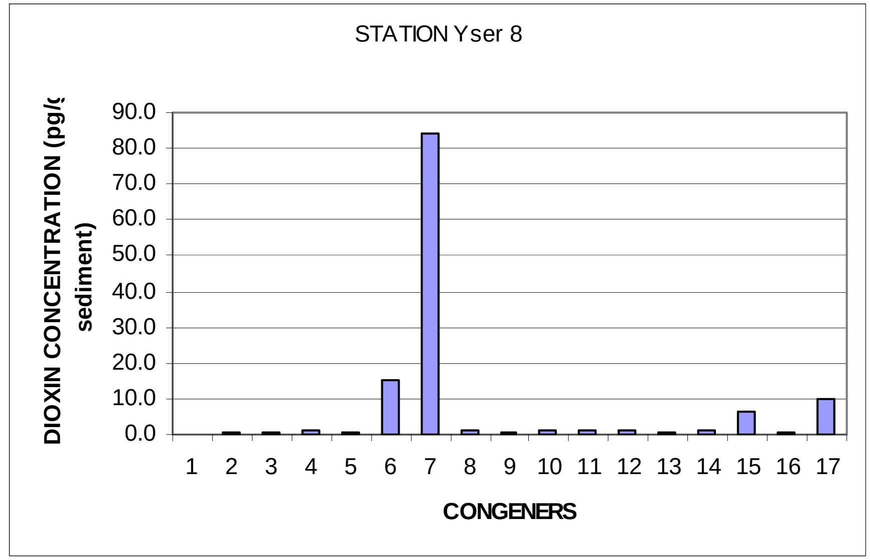
Power plants: coal utilization

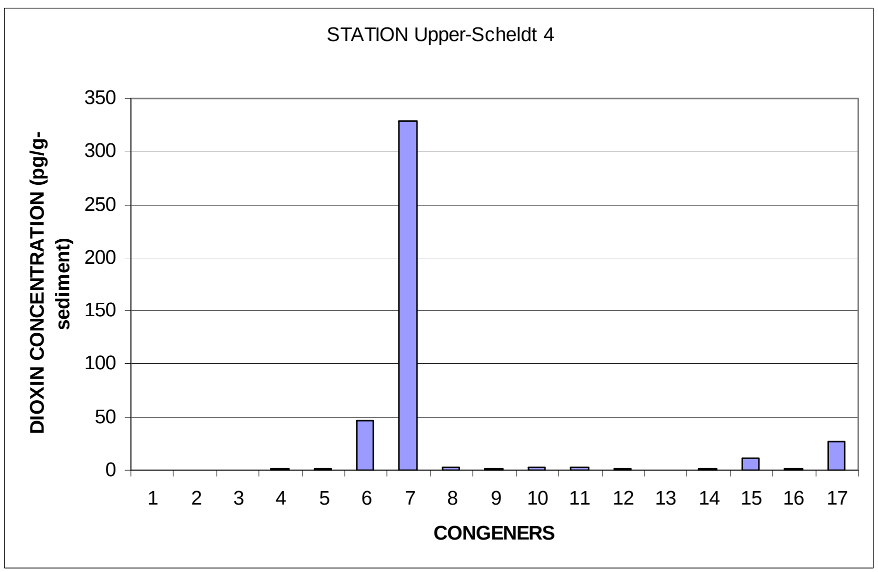


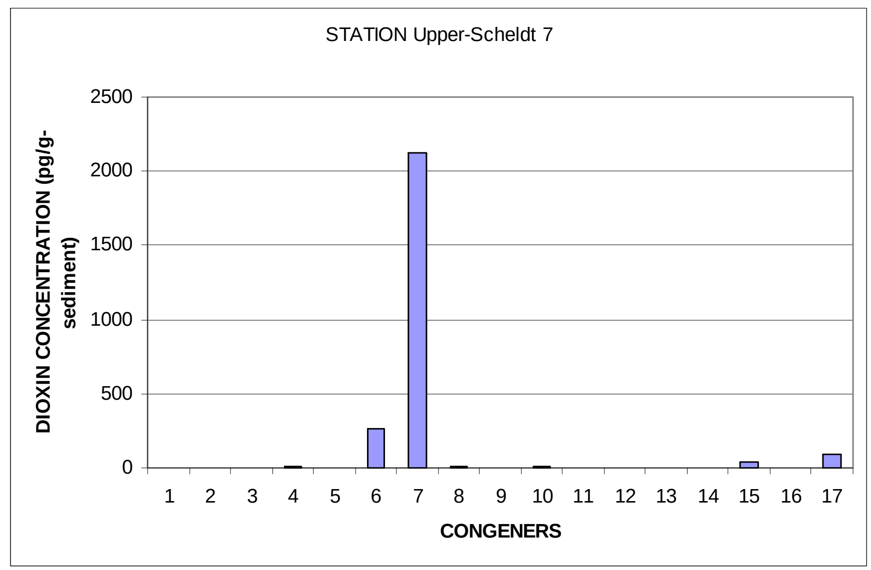
Source : Base de données PEGASE - Ministère de l'Economie, des Finances et de l'Industrie

Dioxin fingerprint in sedimen

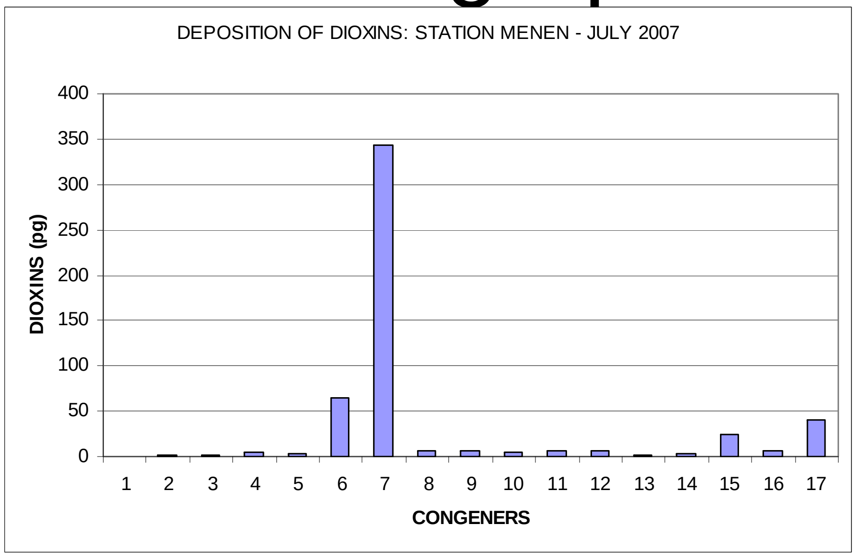


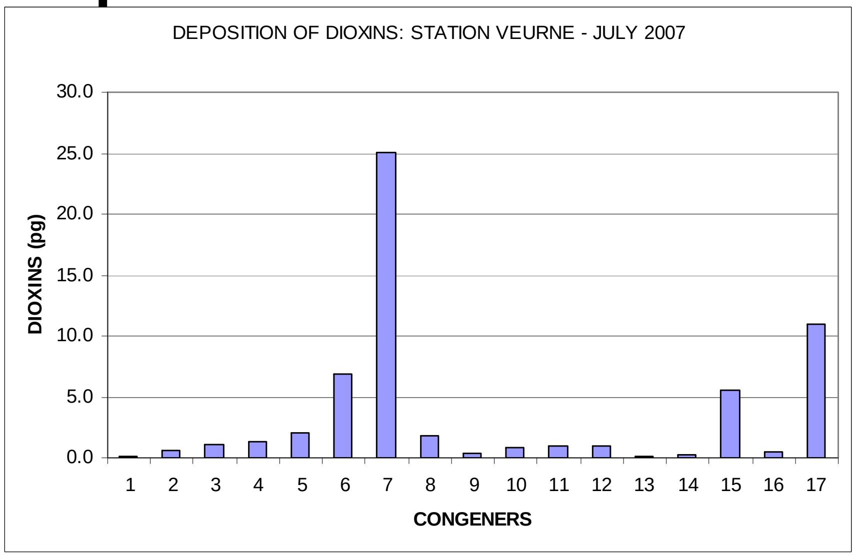


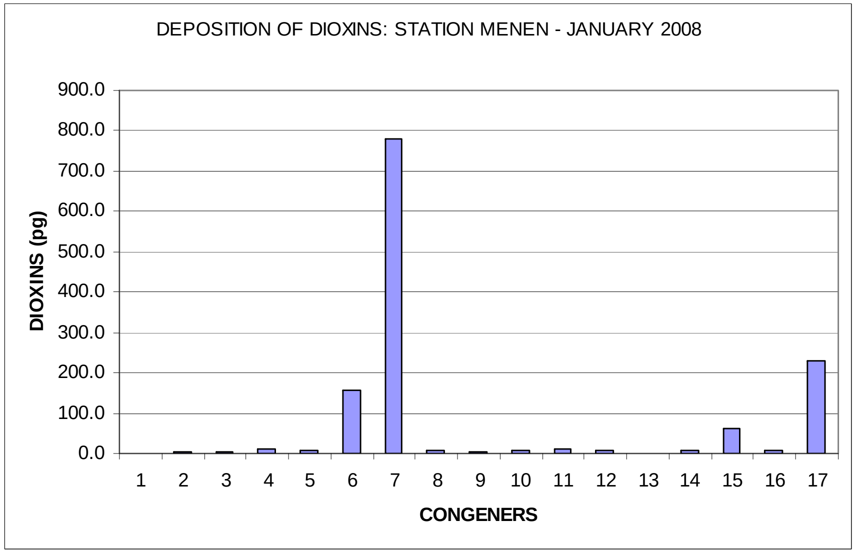


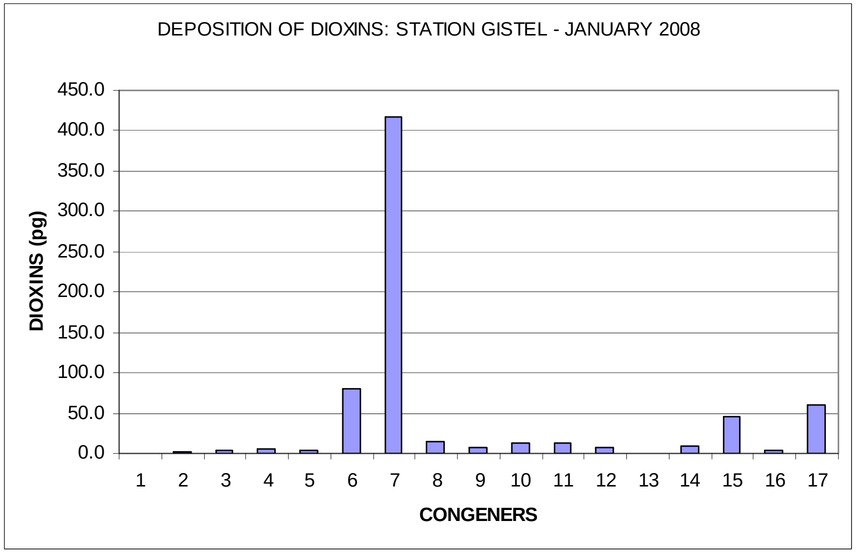


Dioxin fingerprint in deposition material









Most abundant PCDD/F congeners in concentration

Octachloro-dibenzodioxin:

73 to 85 % of the total PCDD/F concentration (pg/g) in sediment.

55 to 66% of the total PCDD/F concentration (pg/g) in deposition.

Next is the Heptachloro-dibenzodioxin.

Pentachlorophenol: direct PCDD/F contribution

Highest concentrations of PCP in Western Europe were found in rivers in Flanders and Northern France.

Atmospheric emissions of PCP in Flanders were estimated at 5 ton y^{-1} while associated dioxin levels at 8 g-TEQ y^{-1} in 1990 and 6.5 g-TEQ y^{-1} in 2000.

Pentachlorophenol: indirect PCDD/F contribution

- Atmospheric conversion of PCP into OCDD. Assuming the same atmospheric rate of conversion as Baker and Hites (2000), the total amount of OCDD in deposition samples comes from PCP.
- This OCDD fraction represents about 8% of the total TEQ-value in our deposition samples.
- The total contribution of dioxins in our deposition samples resulting from the use of PCP will approximate 20%.

Trace metals

The average concentrations of Cd (8.7 mg kg^{-1}), Cu (84 mg kg^{-1}), Pb (192 mg kg^{-1}) and Zn (1,100 mg kg^{-1}) in dredged sediment landfills, mainly from the period 1945-1990 (Vandecasteele et al., 2002) along the stretch Oudenaarde-Antoing, are all above the values observed in the sediments of the Oudenaarde, Spiere-Helkijn (here only slightly) and Antoing stations (see Table results).

Trace metals

Atmospheric trace metal emissions for the whole Flanders Region decreased between 2000 and 2008 with a factor 2 (7 for the period 1996-2008) for Cd, a factor 2.8 (8 for the period 1996-2008) for Pb, a factor 2.1 (2.6 for the period 1996-2008) for Zn and not for Cu (VMM, Flemish Environmental Agency, 2008).

Trace metal and PAH concentrations in sediments (mg/kg d.w.) of the Upper-Scheldt river at Fresnes (km 253) and Eswars (km 284.5).

	FRESNES			ESWARS		
	80-89	90-99	00-07	80-89	90-99	00-07
Cu	50	125	55	65	75	53
Cd	2.0	1.8	0.7	3.0	2.1	1.1
Pb	180	160	95	229	190	105
Zn	1100	560	360	809	657	460
Benzo[a]anthracene		0.95	0.90		1.45	0.77
Benzo[a]pyrene		0.71	0.80		0.83	0.83
Benzo[b]fluoranthene		0.75	1.2		1.39	1.37
Benzo[ghi]perylene		0.50	0.63		0.47	0.79
Benzo[k]fluoranthene		0.46	0.52		0.53	0.65

Conclusions.

Past and present anthropogenic activities heavily contaminated the sediments of the Upper-Scheldt river, much more than those in the Yser river although for most of the pollutants studied in this rural river, Background Concentrations are also several times exceeded.

Conclusions.

A very good correlation between all pollutants in Upper-Scheldt and Yser rivers sediment samples was observed. This may suggest that some common mechanism and/or source(s) are causing that contamination.

Based on diagnostic ratios established for PAH congeners with the same isomeric mass, the PAH contamination in both rivers should be combustion of coal.

Conclusions.

For PCDD/Fs a deposition mechanism can explain the contamination of the sediments. The sources are mainly combustion followed by atmospheric emission and OCDD formation reactions related to the use of pentachlorophenol.

Conclusions.

- For trace metals the contamination sources are more diverse. The high contamination in the Upper-Scheldt sediments is caused via:

  - direct wastewater discharges in the past and nowadays via stock piles of solid waste (Northern France)

  - historical dumping sites of dredged sediments alongside the river border (Flanders)

  - run-off from soils contaminated by atmospheric deposition of trace metals.

Conclusions.

Time trend

For trace metals (except for Cu) a substantial reduction of their sediment concentrations since the 80ies and 90ies is observed, but this is not the case for the PAH sediment concentrations.

For PCDD/Fs this is probably also the case but there are no sediment data available to confirm that.

Acknowledgements.

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- Agence de l’Eau Nord-Pas-de-Calais (Water Protection Agency NPdC)
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