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Study of PCBs in Rain Water, Streams and a Reservoir in a Small Catchment of NW Spain

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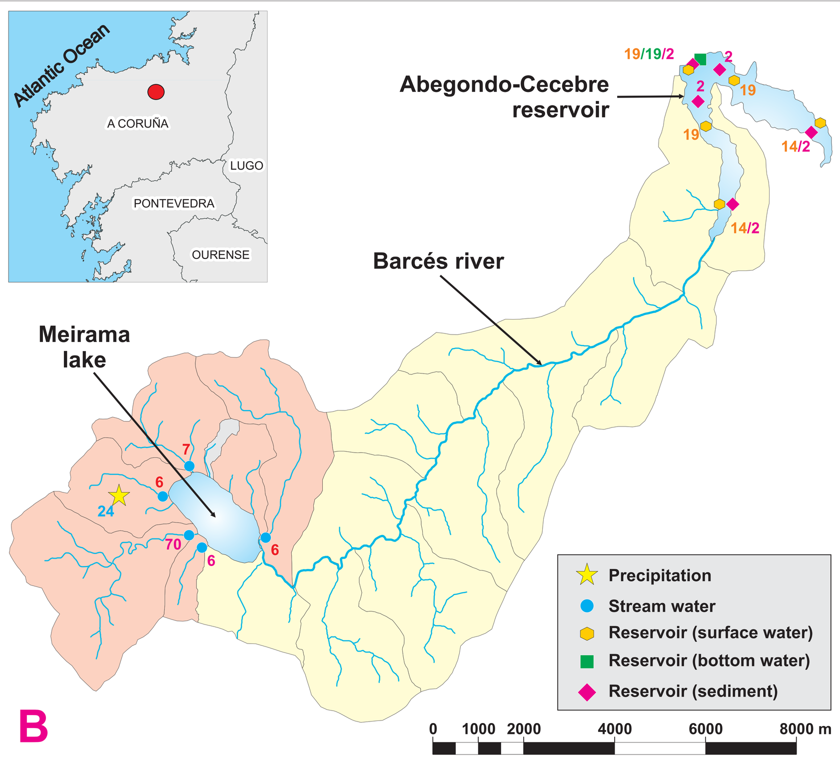
Location & Context of the Study



The context for this study is the flooding of the Meirama pit lake (**A**), a former brown-lignite mine that finished extractions in 2008. Different studies have been perfomed since so far and the data presented here extends the scope of the reclamation monitoring survey to a watershed scale (**B**) inclusive of the Abegondo-Cecebre water supply reservoir (**C**).

The main source for PCBs in local natural waters is expected to be precipitation, whose ultimate loading sources have been described to be worldwide the burning of PCB–containing materials, from air/water and air/soil exchange processes,from sludge and solid waste management, etc.

The study area is rural and relatively low-developed although some potential stationary sources are located in the vicinity (municipal waste incineration plant, coal-fired power plants, etc.).

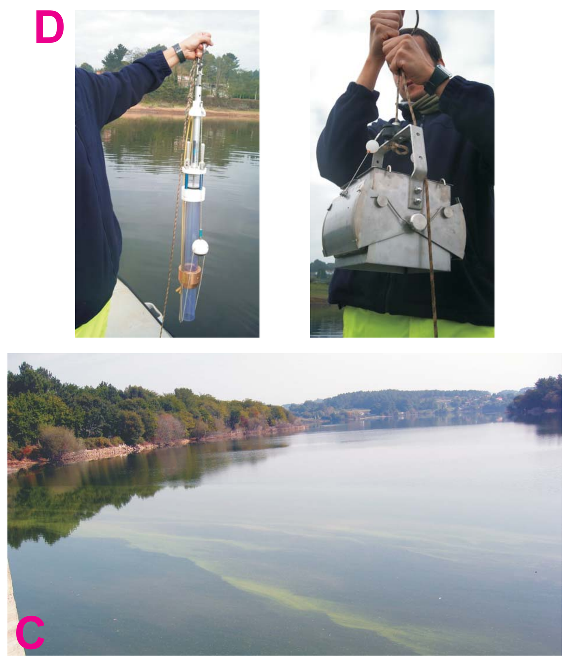
Introduction

PCBs are contaminants of concern due to their environmental persistence, tendency to bio-accumulate, toxicity to living organims and proved ubiquity. Dioxin-like PCBs are in the candidate list of priority substances of the European 2060/60/EC Water Framework Directive (*see the COM(2011)-876 proposal*) for which base line studies are critical to assess the applicability of the environmental quality standards (EQS) and their implementation in the corresponding River Basin Management Plans (RBMP).

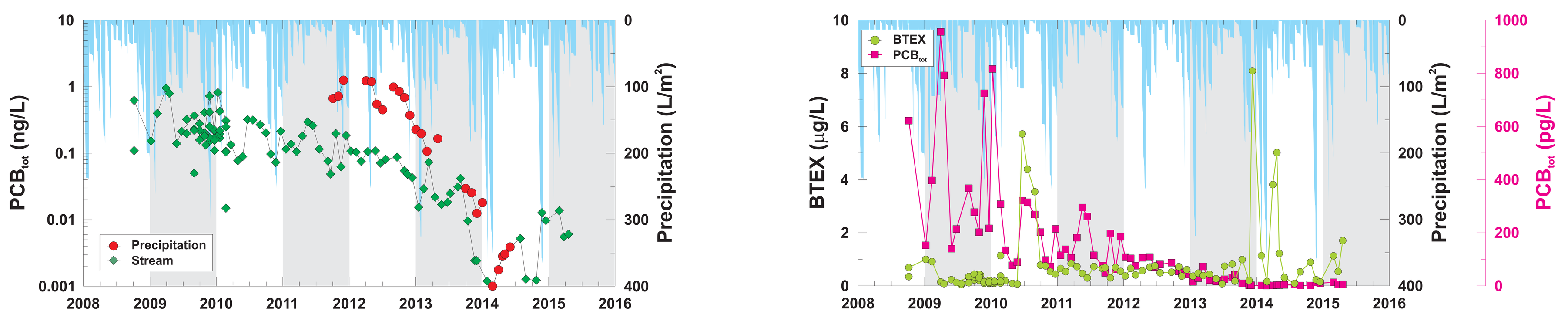
Here we report the results of a surface water monitoring survey which was developed between 2009 and 2014 in the Barcés river catchment (~100 km^2) and the Abegondo-Cecebre water supply reservoir (~23 hm^3). A reduced number of industrial activities potentially contributing PCBs to the local environment are also present in the catchment or in its nearby. That includes a large waste incineration facility, a coal-fired power station, an oil refinery, an aluminum smelter, etc.

The study comprises data from 239 water samples (bulk precipitation; streams; top and bottom reservoir water; and sediment pore water) inclusive of 18 PCB congeners (6 marker and 12 dioxin-like PCBs). Further data on additional parameters (major and trace elements, nutrients, other substances) are not either presented or discussed here.

The survey area has a relatively high pluviometry (~1200 L/m^2-year), temperate climate (mean temperatures in summer and winter of 21.5 and 10.8 ºC, respectively) and rural environment. It has a relatively low industrial development. All this is representative of most of the rest of Atlantic catchments in Galicia and, therefore, our study constitutes a pilot approach with which to test the state of the environment with respect these particular pollutants.



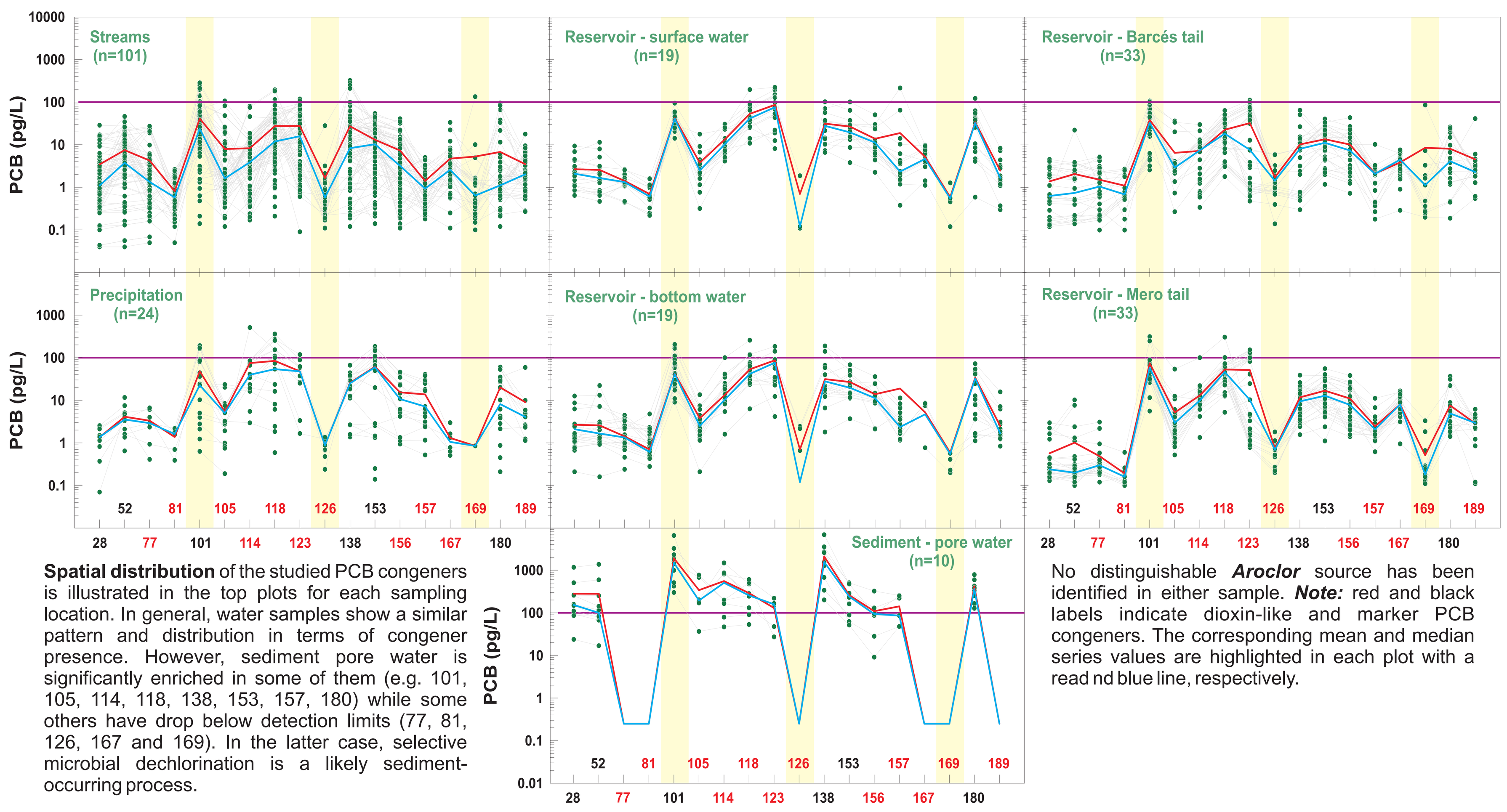
Time evolution



PCBs in bulk precipitation and stream water are illustrated in the top left, figure. We observe that the concentration of total PCB in precipitation was larger than in stream water since the beginning of the survey (november 2011) up to the end of 2014. This is likely due to sorption in the soilor plant uptake. We also observe a significant tendency in stream water to lower the total PCB concentration from 2009 to 2014. The mean and median values of precipitation in the period November 2011- May 2013 are 0.51 and 0.48 ng/L while the same descriptors from May 2013 to June 2014 are 0.01 and 0.004 ng/L.

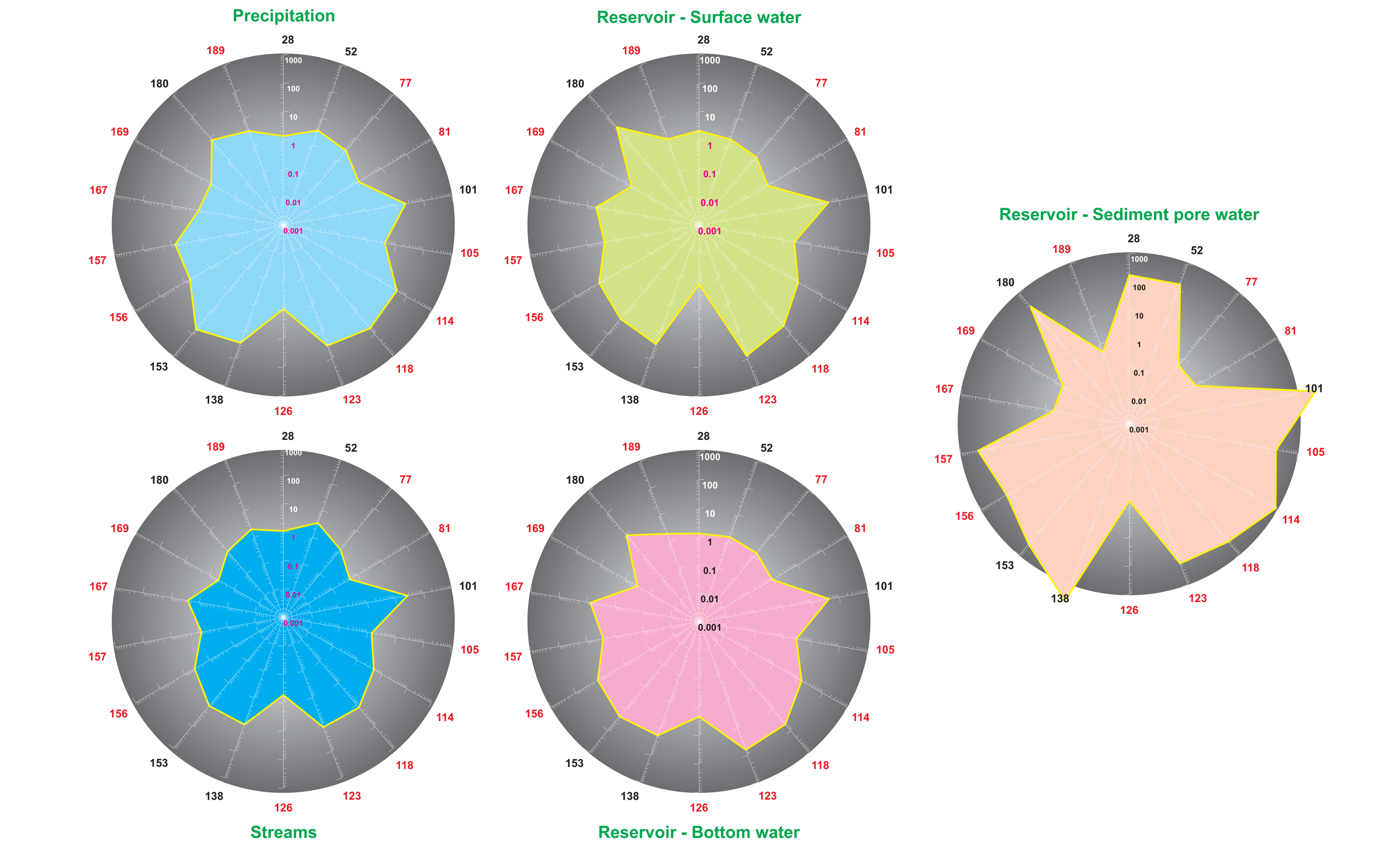
On the top right plot, the compared evolution total PCB and BTEX in stream waters are illustrated. Both aggregated constituents show a disctint tendency to increase concentration during low-rain periods (*i.e.* in the dry season; Observe summer 2010). That points towards significant atmospheric particulate contributions, an observation that has also been performed by other authors. However, the source of PAHs and PCBs compounds do not appear to be the same (observe 2014).

Spatial distribution



Spatial distribution of the studied PCB congeners is illustrated in the top plots for each sampling location. In general, water samples show a similar pattern and distribution in terms of congener presence. However, sediment pore water is significantly enriched in some of them (e.g. 101, 105, 114, 118, 138, 153, 157, 180) while some others have drop below detection limits (77, 81, 126, 167 and 169). In the latter case, selective microbial dechlorination is a likely sediment-occurring process.

No distinguishable ***Aroclor*** source has been identified in either sample. ***Note:*** red and black labels indicate dioxin-like and marker PCB congeners. The corresponding mean and median series values are highlighted in each plot with a read nd blue line, respectively.



The radar plots illustrated above have been constructed by taking the median values of the total PCB concentration for each one of the sample series. Observe that, with the exception of the sediment pore waters, all the groups display a very similar profile, both in terms of total concentration and congener abundance. In the pore water of sediments we observe a significant increase in PCB concentration as well as a selective chemical fractionation. ***Note:*** red and black labels indicate dioxin-like and marker PCB congeners.

Data

		Marker PCBs						Dioxin-like PCBs											
		28	52	101	138	153	180	77	81	105	114	118	123	126	156	157	167	169	189
PRECIPITATION (N=24)	Min	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Max	2.5	11.6	192.0	67.0	184.3	60.1	6.6	2.2	23.5	510.9	358.8	118.4	1.4	45.9	40.7	3.0	0.9	59.0
	X	0.5	3.1	42.2	21.5	56.5	16.7	1.0	0.4	5.2	50.1	80.8	20.1	0.4	9.6	9.8	0.4	0.1	4.2
	P_{50}	<0.1	3.4	22.1	18.4	54.4	4.2	<0.1	<0.1	4.1	21.4	38.8	<0.1	<0.1	2.8	3.6	<0.1	<0.1	<0.1
	GM	0.2	1.2	8.0	5.6	9.7	3.1	0.2	0.1	2.7	4.2	16.6	0.7	0.1	1.2	1.8	0.1	0.1	0.4
STREAMS (N=101)	Min	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Max	28.6	46.1	282.4	323.1	54.1	94.9	27.2	2.6	106.5	79.9	194.4	118.2	28.0	40.7	5.0	33.4	133.8	17.8
	X	2.4	5.8	40.0	24.2	12.6	4.8	2.6	0.4	5.5	6.6	27.2	18.3	0.6	6.1	0.7	2.7	1.8	1.9
	P_{50}	0.5	2.2	24.5	7.5	10.2	0.8	0.5	<0.1	1.0	2.5	12.0	2.9	<0.1	2.2	0.2	1.1	<0.1	0.6
	GM	0.4	1.3	11.9	4.7	4.4	0.5	0.4	0.1	0.7	1.5	8.8	2.0	0.1	1.4	0.2	0.5	0.1	0.4
RESERVOIR (N=104)	Min	<0.1	<0.1	2.58	<0.1	1.1	<0.1	<0.1	<0.1	<0.1	0.34	1.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Max	12.6	22.2	312.0	188.0	101.5	123.2	5.2	4.8	54.0	100.3	304.2	223.7	6.0	50.6	216.2	16.7	86.4	41.3
	X	1.5	2.0	55.6	19.3	19.5	12.0	1.1	0.5	4.2	12.9	46.2	52.0	0.6	11.3	5.1	4.4	1.2	2.5
	P_{50}	0.7	0.8	44.9	12.3	16.2	4.7	0.7	0.2	2.5	9.8	39.1	36.5	<0.1	9.7	2.0	4.4	<0.1	1.9
	GM	0.6	0.7	38.1	9.4	13.7	2.9	0.6	0.2	1.6	8.4	31.1	13.9	0.2	6.4	1.3	1.4	0.1	0.9
SEDIMENTS (N=10)	Min	23.8	16.9	300.7	201.2	51.9	127.6	<0.5	<0.5	<0.5	46.7	53.2	0.3	<0.5	0.3	0.3	<0.5	<0.5	<0.5
	Max	1171.5	1373.1	6533.2	6809.2	507.9	795.1	<0.5	<0.5	768.4	1484.8	607.7	220.8	<0.5	323.4	256.1	<0.5	<0.5	<0.5
	X	281.4	280.9	1917.0	2125.1	260.2	420.3	<0.5	<0.5	204.4	558.6	291.0	78.1	<0.5	76.8	99.6	<0.5	<0.5	<0.5
	P_{50}	153.5	100.4	1501.5	1564.9	242.4	364.2	<0.5	<0.5	103.5	506.8	256.4	37.5	<0.5	57.5	67.0	<0.5	<0.5	<0.5
	GM	169.6	135.9	1293.9	1375.4	197.8	359.5	<0.5	<0.5	14.7	337.0	230.6	9.3	<0.5	12.9	18.1	<0.5	<0.5	<0.5

Water analisys: PCBs were analysed by HRGC-HRMS chromatography (Thermo Finnigan MAT95 XP) with electronic ionization and selected ion recording (SIR) mode. Grab and core sediment samples (**D**) were leached according to the U.S. EPA (1998) method. Sediment data has been corrected according to the S/L ratio and bulk density to represent pore water. Detection limits for surface water and leachates are 0.1 and 0.5 pg/L, respectively. ***Notes:*** X=mean; P_{50}=median; GM=geometric mean

Statistical description

		Marker PCBs						Dioxin-like PCBs											
		28	52	101	138	153	180	77	81	105	114	118	123	126	156	157	167	169	189
PRECIPITATION (N=24)	S-W, p>0.05	2.85E-06	7.86E-03	2.66E-07	2.19E-07	3.09E-05	3.26E-05	2.66E-08	3.20E-04	4.38E-06	8.98E-06	7.19E-03	1.22E-03	1.63E-05	1.36E-04	1.15E-07	2.19E-10	9.54E-05	3.32E-09
	S-W, p>0.05 (log)	3.86E-06	1.18E-04	1.21E-06	3.48E-07	2.22E-02	5.42E-02	2.01E-04	4.37E-02	1.24E-05	5.78E-06	3.38E-04	2.12E-03	7.98E-04	1.32E-03	5.19E-07	2.19E-10	1.14E-02	9.90E-05
	A-D, p>0.05	8.54E-10	3.24E-02	3.10E-12	3.23E-13	1.76E-06	3.19E-05	1.84E-10	1.82E-04	6.61E-09	1.09E-08	1.32E-02	1.01E-03	4.27E-07	1.98E-05	2.77E-12	6.00E-22	6.26E-06	1.59E-14
	A-D, p>0.05 (log)	7.71E-10	3.69E-06	2.69E-11	5.36E-13	4.36E-02	5.61E-02	7.60E-06	3.79E-02	2.11E-08	2.35E-09	8.92E-05	7.60E-04	2.77E-04	7.60E-04	1.23E-12	6.00E-22	2.52E-02	1.08E-06
STREAMS (N=101)	S-W, p>0.05	4.20E-16	1.03E-12	2.32E-17	9.77E-15	1.32E-12	1.27E-18	9.86E-17	2.87E-12	4.01E-13	1.79E-21	9.49E-18	1.52E-07	7.53E-12	2.26E-14	7.08E-17	5.14E-22	2.71E-19	8.35E-15
	S-W, p>0.05 (log)	7.08E-07	3.27E-07	1.23E-07	6.53E-12	4.19E-09	4.58E-06	5.32E-07	1.55E-07	2.13E-08	4.41E-13	8.42E-05	1.55E-08	3.82E-07	3.43E-10	1.33E-09	7.06E-14	2.62E-07	5.44E-10
	A-D, p>0.05	4.25E-40	1.37E-22	7.17E-49	3.82E-35	2.49E-17	1.16E-51	2.95E-30	9.88E-17	4.33E-29	3.05E-79	1.81E-44	3.24E-08	4.63E-21	5.64E-31	8.85E-34	1.69E-89	1.22E-61	1.19E-29
	A-D, p>0.05 (log)	3.04E-09	3.97E-10	1.33E-10	6.75E-28	1.53E-14	9.56E-08	7.31E-10	3.33E-09	1.38E-12	2.46E-32	6.26E-06	2.69E-13	3.24E-09	2.59E-20	1.14E-18	2.65E-34	2.64E-10	8.73E-20
RESERVOIR (N=104)	S-W, p>0.05	6.50E-14	1.35E-16	7.21E-10	9.37E-14	2.45E-12	1.36E-17	7.97E-16	2.37E-13	2.85E-08	3.34E-15	1.67E-15	1.69E-09	8.23E-08	1.29E-21	1.90E-06	3.35E-22	1.15E-14	2.25E-18
	S-W, p>0.05 (log)	1.36E-03	1.04E-02	3.48E-04	7.73E-09	5.38E-05	1.22E-08	1.07E-06	6.61E-05	4.61E-08	1.01E-11	3.14E-06	1.25E-02	1.21E-09	6.20E-09	8.66E-12	5.38E-14	2.77E-07	4.83E-10
	A-D, p>0.05	4.74E-23	5.12E-36	6.06E-15	1.91E-25	7.26E-16	9.31E-40	4.81E-25	3.02E-16	1.19E-11	8.29E-31	9.04E-28	4.48E-09	4.08E-08	1.82E-81	1.17E-06	4.78E-89	2.53E-30	2.24E-46
	A-D, p>0.05 (log)	2.08E-03	7.48E-03	9.31E-04	5.53E-15	5.61E-07	1.14E-15	1.68E-10	3.39E-07	2.18E-12	1.28E-27	2.14E-07	2.83E-03	6.31E-11	1.10E-17	1.81E-26	3.10E-32	2.82E-10	3.52E-21
SEDIMENTS (N=10)	S-W, p>0.05	7.00E-04	1.36E-04	-	-	1.44E-02	2.12E-03	6.42E-02	3.97E-01	1.76E-02	-	5.80E-02	1.68E-01	5.80E-03	2.63E-02	-	-	2.78E-01	-
	S-W, p>0.05 (log)	9.13E-01	5.53E-01	-	-	9.15E-01	7.16E-03	1.75E-01	4.22E-01	3.37E-03	-	7.98E-01	2.21E-01	1.87E-02	2.89E-03	-	-	6.96E-01	-
	A-D, p>0.05	1.20E-03	1.48E-04	-	-	3.22E-02	2.34E-03	4.38E-02	3.30E-01	1.54E-02	-	1.05E-01	2.43E-01	1.55E-02	3.40E-02	-	-	3.28E-01	-
	A-D, p>0.05 (log)	7.18E-01	2.87E-01	-	-	8.83E-01	7.08E-03	1.10E-01	3.69E-01	3.51E-03	-	6.85E-01	3.06E-01	1.75E-02	2.63E-03	-	-	8.15E-01	-

Statistical description: The top table summarizes the results of the Shapiro-Wilk (S-W) and Anderson-Darling (A-D) normality tests. Both tests have also been performed with the log-transformed values (rows indicated with "(log")). We observe that, with the exception of sediments, most of the congeners in samples are not normally or log-normally distributed. In the case of sediments, the small number of samples (n=10) is not fully conclusive with respect their corresponding function distribution. ***Notes:*** green numbers represent congeners for which the corresponding normality test is successful (p>0.05)

Box & Whisker plots: In the box & whisker plots illustrated on the left we present the distribution of the analyzed PCB congeners grouped according with their corresponding origin.

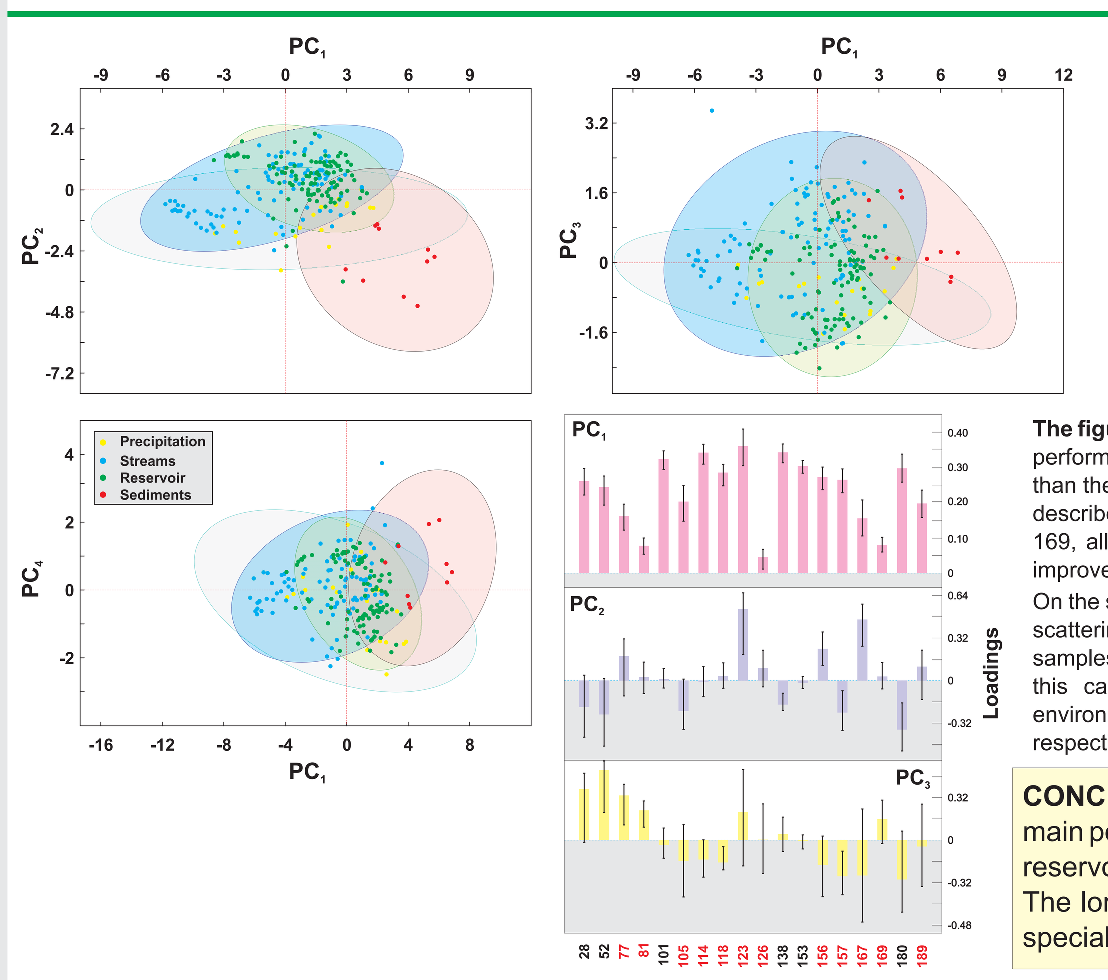
In plots **E**, it is worth to observe the similarity in the distribution of PCBs in bulk precipitation and stream water. Because of the headwaters location of the studied streams, the interaction of precipitation with soil/plants and other related processes do not introduce a major change in the PCB distribution.

Comparing the two tails of the reservoir (**F**) we detect a major dispersion in the results associated with the tail of the Mero river than that of the Barcés river. in order to explain this, more information is still required.

Comparing the two river tails (transition lotic/lentic) with the samples taken next to the dam, in the lentic domain of th reservoir (**G**) we observe an significant homogenization illustrating greater abundances for the intermediate PCB congeners of the analized series. Selective enrichment and chemical fractionation is clearly observed in the pore water of the sediments.

The edges of the box correspond to P_{25} and P_{75} percentiles and the notch in the box represents the mean value. Whiskers extend from the P_5 to the P_{95} percentiles. Red dots are outliers. ***Note:*** red and black labels identify dioxin-like and marker PCB congeners, respectively.

Principal components analysis



		PC_1	PC_2	PC_3	PC_4	PC_5	Sum_{1-3}	Sum_{1-5}
Precipitation	% σ	65.6	25.4	6.5	1.0	0.6	97.5	99.1
	% log (σ)	70.5	7.8	5.7	4.4	3.3	84.1	91.8
Streams	% σ	66.8	13.2	8.4	3.1	3.0	88.4	94.5
	% log (σ)	37.8	15.0	10.4	8.4	6.7	63.1	78.3
Reservoir	% σ	53.9	21.7	10.7	5.0	4.3	86.2	95.5
	% log (σ)	37.8	15.0	10.4	8.4	6.7	63.1	78.3
Sediments	% σ	89.7	5.2	3.5	1.0	0.3	98.4	99.7
	% log (σ)	61.7	26.4	9.3	1.2	0.8	97.3	99.4
All	% σ	93.2	2.6	2.3	0.9	0.4	98.1	99.4
	% log (σ)	48.8	9.6	7.2	6.0	4.9	65.6	76.5

The figures and table illustrated next show the results of a Principal Component Analysis (PCA) performed with the different group samples.We observe that only 1 component explains more than the 50% of group variance and with 3 components, more than 90% of the total variance is described. Those congeners with lower loading in the first principal component are 81, 126 and 169, all of them with concentration close or lower to the detection limit. There is no overall improvement in the scores if we consider the log-transformed concentrations.

On the scatter plots shown on the left we observe a significant tendency to reduce variance (*i.e.* scattering) from bulk precipitation to stream water samples and from the latter to the reservoir samples. The variability of sediments needs to be explained with a different loading scheme and this can be anticipated from the different biogeochemical processes occurring in this environment. ***Note:*** red and black labels identify dioxin-like and marker PCB congeners, respectively.

CONCLUSIONS: Affection of PCBs in the study area is very reduced and the main pollutant load can be tracked to atmospheric inputs. Soil scavenging and reservoir sediment selective enrichment constitute significant sinks for PCBs. The long-term behavior of the reservoir sink needs to be further assessed, specially from the point of view of benthic fluxes and phytoplankton dynamics.

ACKNOWLEDGEMENTS: Funds for this work have been provided by Xunta de Galicia (10MDS008CT), the European Regional Development Funds 2007/2013, Gas Natural Fenosa and EMALCSA