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ASSESSMENT OF TOXIC SUBSTANCES IN FRESHWATER FISH FROM THE TAJO RIVER BASIN (SPAIN)

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Abstract: *Having taken in account the information obtained from the previous results obtained in the study of dangerous substances in water and fish from eight stretches of the Tajo river basin [1], the bioaccumulation of the most relevant pollutants is observed, in liver and muscle of fish. In that study, eight streams where studied in different locations of the Tajo river basin, suspected to be, in higher or lower degree, affected by chemical pollution, as well as one reference stream of clean, non-impacted water, the Lozoya stream. Water and fishes from these streams are analysed for hazardous substances. The presence levels of these pollutants, considered as acceptable for non polluted streams, are defined. The substances which trend to accumulate in fish are tissues copper, zinc, DDT, dieldrin, endrin. HCH, HCB, lindane and PCBs, mostly in hepatic tissue.*

Key words: *bioaccumulation; chlorinated organic compounds; freshwater fish; metals; dangerous substances; toxicity.*

1. Introduction

A very important process by which chemical substances may affect organisms is bioaccumulation, which produces an increase of the concentration of a substance in the organism with time, compared to the substance concentration in the aquatic environment. Substances accumulate whenever the assimilation rate is higher than its metabolism or elimination. This term includes two kinds of processes which mean an increase of the substance content in the organism. On one side, the process of bioconcentration defines the specific bioaccumulation process, by which the substance content in the organism results higher than in its environment. Besides, the term biomagnification describes the process which deals to the accumulation of a substance in the organism to a higher level than what is found in its food.

The substances bioaccumulation degree may be determined in several ways. According to the U.S.EPA [6], it must be measured in bioassays longer than 27 days. But, even if environmental behaviour of toxic substances seems to depend upon their physical – chemical properties more than on ecological and biological factors [7], it is certain as well that data obtained

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in such way are difficult to apply to real environmental conditions, being also extremely expensive to practice each bioassay necessary for every substance and species [2]. General principles ruling the relationship between bioaccumulation and physical – chemical properties of substances are lipophylity measured as partition coefficient between octanol and water, K_{ow}, and bioconcentration factor, BCF. These parameters may be related to accumulation in organisms through regression equations such as $log\ BCF = a \cdot logK_{ow} - b$. Bioconcentration Factor, BCF, with a value between 1 and 1.000.000, indicates the degree in which a substance accumulates in aquatic organisms. BCF is determined by a coefficient like $BCF = C_o/C_a$, where C_o is the concentration of the substance in the organism and C_a its concentration in water [4].

2. Methods

The degree of bioaccumulation shown by fishes in this study has been defined as Bioaccumulation Coefficient, C_B. It has been calculated for every pollutant in two ways. In first place, average C_B has been estimated for all simples of water and fish taken. In order to do so, average values of concentration for every pollutant have been determined in water, V_w, fish liver, V_L and fish muscle, V_M. Those values have been estimated as follows.

Average concentration value in Water

$$(V_W) = \sum V_j / N$$

Average concentration value in fish liver

$$(V_L) = \sum Vi_{j(L)} / \sum N_{ij}$$

Average concentration value in fish muscle

$$(V_M) = \sum_{Vij(M)} / \sum N_{ij}$$

where V is concentration of the pollutant,

j = stream;
i = specie;
N = number of samples.

After that, the correspondent Bioconcentration Coefficients were determined as a rate such as $C_B = C_0 / C_w$, where C_0 is the pollutant concentration in the organism (µg/g), and C_w is the pollutant concentration in the aquatic environment. C_B is expressed in L/Kg. C_{BL} represents the average coefficient of bioaccumulation in liver, C_{BM} in muscle and *y* $C_{B\ 1/2}$, is average C_B. So, respective C_B have been calculated as follows,

$$C_{BL} = V_H / V_w;$$
$$C_{BM} = V_M / V_w;$$
$$C_{B\frac{1}{2}} = V \tfrac{1}{2} / V_w$$

3. Results

Table 1 shows calculated C_B from the average value in all the analysis taken in water, liver and muscle. From those first estimations, we can restrict the number of parameters of study in terms off bioaccumulation, for, as Kristensen P. and H. Tyle [5] establish in their works for the Organisation for Economic Cooperation and Development, OECD, the limit value from which a pollutant is included in bioaccumulation studies is BCF>100. So, metals As, Cd, Cr and Pb have been excluded of further calculations, for their respective C_B values are less than 100. The other two metals studied. Cu and Zn. show much higher values, which is not anomalous knowing that both of them are present in organisms as micronutrients. It is observed anyway that their value is much higher in liver than in muscle, in a 20 times higher proportion.

Table 1

Calculated Average C_B. V_w is expressed in $\mu g/l$, V_L and V_M in $\mu g/g$. C_B in L/Kg

Pollutant	V_w	V_L	V_M	$C_{B\,L}$	$C_{B\,M}$	$C_{B\,1/2}$
As	10.00	0.08	0.06	8.00	6.00	7.00
Cd	10.00	0.03	0.01	3.00	1.00	2.00
Cu	10.00	12.10	2.05	1210.00	205.00	607.50
Cr	10.00	0.09	0.04	9.00	4.00	6.50
Hg	0.09	0.10	0.08	1100.00	880.00	990.00
Pb	50.00	0.32	0.24	6.40	4.80	5.60
Zn	20.00	39.270	14.010	1963.50	700.50	1332.00
DDT	0.05	$47.49\ 10^{-3}$	$27.73\ 10^{-3}$	949.48	554.60	752.04
Dieldrin	0.01	$5.86\ 10^{-3}$	$3.46\ 10^{-3}$	586.00	346.00	466.00
Endrin	0.01	$2.07\ 10^{-3}$	$1.50\ 10^{-3}$	207.00	150.00	178.50
HCB	0.01	$1.73\ 10^{-3}$	$1.20\ 10^{-3}$	173.00	120.00	146.50
HCH	0.01	$1.87\ 10^{-3}$	$1.64\ 10^{-3}$	187.00	164.00	175.50
Lindane	0.02	$2.30\ 10^{-3}$	$2.05\ 10^{-3}$	115.00	102.50	108.75
PCBs	0.05	$233.25\ 10^{-3}$	$136.45\ 10^{-3}$	4665.00	2729.80	3697.40

Reference C_B values calculated for the Lozoya Stream are shown in Table 2. V_w is expressed in en µg/l, V_L and V_M in µg/g and C_B in L/Kg.

C_B (L/kg) calculated for LOZOYA (reference stream) Table 2

Pollutant	V_w	V_L	V_M	$C_{B\,L}$	$C_{B\,M}$	$C_{B\,1/2}$
Cu	10.00	14.68	0.58	1468.00	57.88	762.94
Hg	0.05	0.05	0.05	1000.00	900.00	950.00
Zn	10.00	32.18	13.06	3218.00	1306.00	2262.00
DDT	0.05	$7.50\cdot10^{-3}$	$3.88\cdot10^{-3}$	150.00	77.50	113.75
Dieldrin	0.01	$2.63\cdot10^{-3}$	$1.75\cdot10^{-3}$	262.50	175.00	218.75
Endrin	0.01	$0.50\cdot10^{-3}$	$0.50\cdot10^{-3}$	50.00	50.00	50.00
HCB	0.01	$0.50\cdot10^{-3}$	$0.50\cdot10^{-3}$	50.00	50.00	50.00
HCH	0.01	$2.50\cdot10^{-3}$	$2.50\cdot10^{-3}$	250.00	250.00	250.00
Lindane	0.01	$0.50\cdot10^{-3}$	$0.50\cdot10^{-3}$	50.00	50.00	50.00
PCBs	0.05	$13.50\cdot10^{-3}$	$7.25\cdot10^{-3}$	270.00	145.00	207.50

Following the same procedures, C_B correspondent to every pollutant have been calculated en every stream (Table 3) in order to observe possible differences due to the pollution degree in each one and to be able to compare them with the data obtained for the reference stream. V_W is expressed in en µg/l, V_L and V_M in µg/g and C_B in L/Kg.

Table 3

C_B (L/kg) calculated for every stream

Stream	HENARES	TAJO 1	CUERPO DE HOMBRE	JARAMA	TAJO 2	GUADA-RRAMA	JERTE
Cu	546.00	706.50	1011.00	336.00	461.50	485.00	863.50
Hg	400.00	300.00	580.00	1450.00	650.00	3900.00	1130.00
Zn	742.00	65.50	2143.50	588.00	3739.00	2026.75	1594.00
DDT	262.00	843.40	942.60	593.80	625.00	1382.10	1255.40
Dieldrin	320.00	385.50	128.50	619.00	928.50	791.00	337.00
Endrin	110.00	137.50	50.00	213.00	241.00	574.50	50.00
HCB	145.00	154.50	50.00	256.50	188.00	123.50	80.50
HCH	50.00	150.00	469.00	228.50	156.50	50.00	50.00
Lindane	50.00	50.00	334.50	170.50	97.00	164.25	59.50
PCBs	1736.00	4521.30	1252.60	5372.50	4056.30	11230.40	1199.20

Chlorinated compounds results show that the most susceptible of accumulation are PCBs. with C_B > 1000 L/Kg in every case and higher even than 10000 L/Kg in the GUADARRAMA stream with a value of 13350 L/Kg. Reference value is 3500 L/Kg. Other chlorinated compounds susceptible of accumulation are DDT. dieldrin and endrin. The rest of them, HCH, HCB and lindane, present lower C_B values. Anyhow, they are hazardous substances, considered as potentially toxic and bioaccumulative in organisms, so their harmful potential must be taken in account in further studies.

Pollutants have been arranged as shown in Table 10 attending to their bioaccumulation potential in this study.

Pollutants arranged by C_B (L/Kg.) in decreasing order Table 4

Pollutant	$C_{B\,0}$	C_B	Range	
PCBs	207.5	3.697.4	145	13.350
Zn	2.262.0	1.332.0	665	8.707
Hg	1.000.0	990.0	200	4.400
DDT	113.7	752.0	156	1.745
Cu	762.9	607.5	48	1.969
Dieldrin	75.0	466.0	84	1.088
Endrin	50.0	178.0	50	590
HCH	50.0	175.5	50	750
HCB	50.0	146.5	50	250
Lindane	50.0	108.7	50	469

$C_{B\,0}$ = reference C_B. in LOZOYA stream.

Finally, most affected species where determined. Values have been calculated from the average values for every species in hepatic tissue, for this is the tissue that shows a higher concentration of the studied pollutants. Only those pollutants that showed significant C_B values in the previous results have been studied.

Figure 1 shows calculated C_B in metals for every fish species of study. Values indicate that Zn is the most accumulative metal. The most affected species is *Cyprinus carpio* for Zn. *Barbus bocagei* for Hg and *Chondrostoma polylepis*, for Cu.

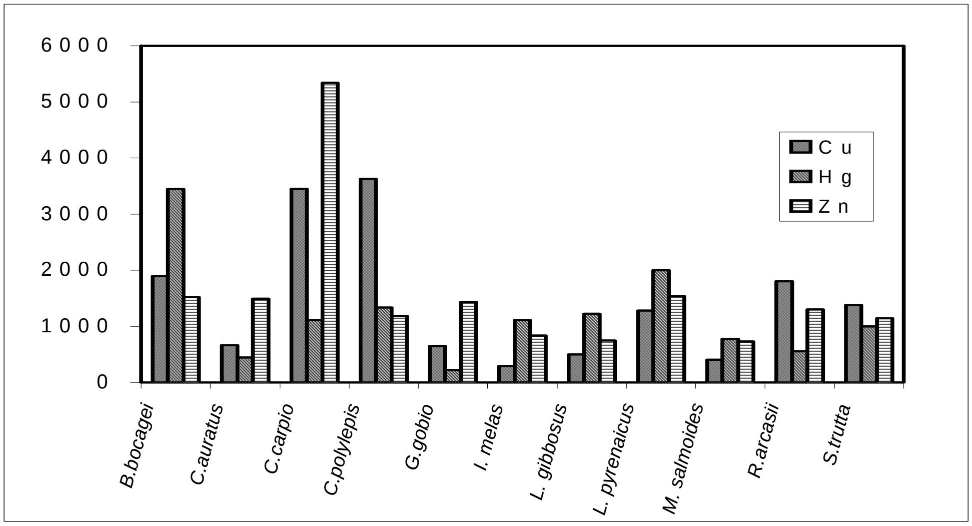

Fig. 1**.** *Average C_B (L/Kg) for metals in every species of study in liver tissue*

The same calculations have been made for POPs y PCBs. Results are shown in Figure 2. PCBs and DDT are, with difference, the most accumulative compounds. The most affected species are again. *Cyprinus carpio* and *Barbus bocagei*.

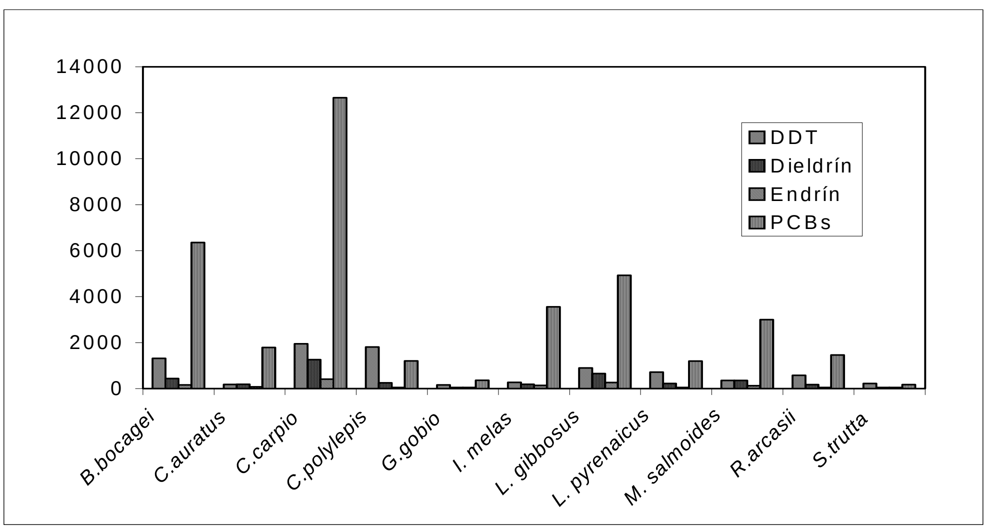

Fig. 2. *Average C_B (L/Kg) for POPs y PCBs in every species of study in liver tissue*

4. Conclussions

The Spanish normative limits established for fish fresh water and the reduced number of pollutants it includes do not prevent bioaccumulation processes, which may reach high toxic levels in fish. In this study, Cu, Hg, Zn, DDT, dieldrin, endrin, HCH, HCB, lindane and PCBs are recognized as priority pollutants to be studied in fish tissues. Taking as reference the values obtained in LOZOYA stream, which show a Bioaccumulation Coefficient lower than 100 L/Kg. concentration levels for every pollutant accepted for clean freshwater are determined. Hg is the metal with the highest Bioconcentration Coefficient in fish, Cu and Zn high values are not so anomalous knowing that both of them are present in organisms as micronutrients. Chlorinated compounds most susceptible of accumulation are PCBs followed by DDT, Dieldrin and Endrin. *Cyprinus carpio* and *Barbus bocagei* are the most affected species in terms of bioaccumulation.

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