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Mercury Concentrations in Three Species of Freshwater Fishes from the Lower Gállego and Cinca Rivers, Spain

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Mercury pollution in aquatic ecosystems has received great attention since the discovery of mercury as the cause of Minamata disease in Japan in the 1950s. Large quantities of mercury are released to the environment and are washed into aquatic systems, where it is biologically converted into methylmercury and taken up by aquatic organisms. Fishes accumulate mercury directly from food and the surrounding water (Rainbow 1985) and they can concentrate large amounts of this metal. They are, for instance, the single largest source of mercury to man, often from natural sources (Chovjka and Williams 1980). Investigations of mercury in aquatic ecosystems have been documented in North America and many countries of Europe, but few studies have been concerned with levels of contamination that occur in natural fish populations in Spain. There is, therefore, increasing need for current information on mercury contamination in these aquatic ecosystems.

The objectives of the present study were: (1) to determine mercury concentrations in fishes of the lower Gállego and Cinca Rivers; (2) to determine the distribution of this pollutant within the fish community; and (3) to compare the concentrations of mercury in these fishes with action levels established by the European Union (EU) in order to protect the public health.

MATERIALS AND METHODS

Between July and August 1993, 80 fish were caught by electrofishing from the Gállego and Cinca Rivers, in northeastern Spain. In both rivers the sampling site was located downstream of a

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chlor-alkali plant. Samples were collected immediately above the small towns of Gurrea de Gállego (population 1943) and Ballobar (population 1128), in the lower watercourse of the Gállego and Cinca Rivers, respectively.

The fish species sampled were barbel (*Barbus graellsi*), common carp (*Cyprinus carpio*) and northern pike (*Esox lucius*). The fishes were killed, weighed and the fork length of each fish was measured. Flesh samples were collected from below the dorsal fin, after the skin was removed, and preserved frozen at -20°C in small plastic bags.

Total mercury in samples was measured by the cold vapor method (Hatch and Ott 1968), following digestion with a mixture of nitric and sulphuric acids in combination with vanadium pentoxide (Official Methods of Analysis 1984). The precision and accuracy of the digestion method was tested by comparison against the National Institute of Standards and Technology Research Material 50 Albacore Tuna and proved to be reliable; mean concentrations measured were within 10% of the certified value. The recovery of pre-digestion spikes was 94.9 ± 5.1 %, and the detection limit was 20 µg/kg.

Concentrations of mercury were converted to natural logarithms to correct for the skewed distribution values and geometric means were calculated for all reported concentrations of mercury values in fish.

To determine whether differences in mercury concentration were a factor of fish length, the regression slopes relating mean mercury concentration and corresponding mean fork lengths was tested for the different rivers, using natural logarithms transformed data (Parks et al. 1991). To estimate the effects of the species, the river and their interactions on the mercury concentrations in the fish, a one-way and two-way ANOVA were used. A significance level of $P \leq 0.05$ was used for all statistical tests, unless otherwise specified.

RESULTS AND DISCUSSION

Summary statistics for mercury concentrations quantified in fishes from the sampled areas are shown in Table 1.

None of the fish species gave a significant correlation, with the exception of barbel and northern pike in the Gállego River (Table 2). Mean mercury concentrations of these species can be compared between both rivers without making any adjustment for the difference in the size because the mean lengths for barbel and northern pike in the Gállego and Cinca Rivers were not significantly different. Other studies, too, have shown poor correlations between mercury content and body size of fish (McGregor 1980; Bodoly et al. 1984). Chronic exposure to low levels of mercury may cause fishes to acquire similar tissue concentrations regardless of size.

Fishes of the same size and species, exposed identically, have shown maximum mercury concentrations up to 10 times the minimum (Kent and Johnson 1979).

The barbel is a common species of bottom-feeding fish. It occurs in almost every waterbody in the study area. Although it has been established that during the spring spawning period the barbel migrate up Spanish rivers, to date the migratory movements of *Barbus graellsi* have not been quantified nor have the environmental triggering factors been studied (Rodríguez-Ruiz and Granado-Lorencio 1992). The common carp in Mediterranean aquatic ecosystems are versatile omnivors which utilize whatever food is available (without competition processes). The carp exhibits definitive homing tendencies; except for movements toward shallow water with vegetation associated with spawning, the carp is highly sedentary (Fernández-Delgado 1990). Northern pike is indicated in

Table 1. Geometric mean mercury concentration (mg/kg, wet weight), with ranges, in flesh of barbel (B), common carp (C), and northern pike (P) from the lower Gállego and Cinca Rivers, Spain.

River	Species	n	Fork length (cm)		Total mercury (mg/kg)	
			Mean	Range	Mean	Range
Gállego	B	27	35.6	18-48	2.00	0.25-4.41
	C	5	43.9	40-47	0.74	0.30-1.36
	P	7	46.1	28-67	1.73	1.20-2.61
Cinca	B	23	35.4	18-48	1.96	1.02-3.74
	C	16	26.2	20-39	1.44	1.05-2.59
	P	2	73.0	72-74	2.80	2.74-2.87

Table 2. Relationship between mercury concentration and length for barbel (B), common carp (C), and northern pike (P) from the lower Gállego and Cinca Rivers, Spain.

River	Species	Statistical Analysis					
		n	r	r^2	a	b	p
Gállego	B	27	0.56	0.32	4.01	1.01	0.002
	C	5	0.57	0.33	25.45	-4.98	0.313
	P	7	0.79	0.62	4.69	0.72	0.036
Cinca	B	23	0.26	0.07	9.43	-0.52	0.222
	C	16	0.43	0.19	5.59	0.52	0.092
	P	2	-	-	-	-	-

n: number of samples; r: correlation coefficient: r^2: coefficient of determination; a: intercept; b: regresion coefficient; p: statistical significance

many works (Särkkä et al. 1978; Parks et al. 1991; Rask and Metsala 1991) as a mercury-indicating species for the following reasons: it is a predator at the top of the food chain; pike is territorial and may represent conditions in restricted areas, allowing for the detection of the point sources of pollution; and as an important commercial fish, pike may act as a significant link in the transfer of mercury from the environment to man.

The barbel (1.98 mg/kg) and the northern pike (1.93 mg/kg) exhibited significantly higher mean mercury concentrations than common carp (1.23 mg/kg). This pattern of distribution of mercury within a fish community is generally similar to that reported by Rieder (1993). The results reported in the present study indicate that biomagnification of mercury was evident from common carp, a larger secondary consumer, to northern pike, a tertiary consumer. Särkkä et al. (1978) reached a similar conclusion in the food chain of Lake Päijänne, Finland. However, other large secondary consumers such as barbel accumulate as much or even more mercury as did the northern pike. Different behavioral habits may explain the high mean mercury levels found in barbel.

During summer 1993, water and sediment samples were taken by Ebro Hydrographic Confederation, in an unpublished study, from our sampled areas and analyzed for total mercury. The total

mercury levels in water samples were < 0.1 µg/L. However, the mean mercury concentrations in sediment samples from the lower Gállego and Cinca Rivers were 0.55 and 2.68 mg/kg (dry weight), respectively. Barbel is a benthic species in almost continuous contact with sediments; moreover, it hibernates within these sediments during the colder months of the year. Methylation of mercury by bacteria in the sediment significantly increases the availability of mercury for absorption across the gills of fish. It would therefore seem likely that sediments are a major source of contamination for barbel.

Variations in levels of mercury between rivers were apparent, especially for common carp ($p<0.01$) and northern pike ($p=0.06$). Physicochemical conditions of aquatic systems may modify the bioavailability of mercury to fish, even without high mercury concentrations in sediments and water (Kent and Johnson 1979). Rask and Metsala (1991) reported that mercury concentrations may vary considerably from lake to lake in a small geographical area, and the variation among lakes in the accumulation of mercury in fishes largely depends on lake characteristics and the diet of the fish. In the present study, the variations in levels of mercury for pike can be attributed mainly to size differences between rivers.

Background levels of mercury in noncontaminated fish are generally less than 0.2 mg/kg (D'Itri 1971). Mean values of mercury in the present study exceeded this value. Additionally, 98% of the barbel and 95.24% of the common carp contained more than the EU generic action level (Decision 93/351), 0.5 mg/kg, and the total sample of northern pike exceeded the EU action level for this species, 1 mg/kg. The total sample of fish caught from the lower Cinca River exceeded the EU action levels and only two fishes of the 39 fishes caught from the lower Gállego River were below that level. We conclude that total mercury levels in fishes from the sampled areas of the lower Gállego and Cinca Rivers are very high and may be considered dangerous to human health.

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