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Mercury Distribution in an Ecosystem of the "Parque Nacional de Doñana," Spain

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The movement of mercury and its derivatives and the rates of exchanges in various environmental compartments are important in order to predict the significance of the levels of mercury transfer through a trophic chain. With the aim to contribute to this knowledge in a natural environment not modified by man, a study is being carried out in the "Parque Nacional de Doñana" and its biological reserve. This natural park, with an expanse of about 60,000 Ha, is a very important halting-place and winter habitat for migratory birds which breed in Northern Europe. It is located in the SW of Spain in the delta of the Guadalquivir River on the right bank, in which two main areas can be easily distinguished namely the Marshes and the Dunes.

Part of this study, whose results are reported here, was carried out in the ecosystem formed by two natural lagoons relatively near each other (Lucio de Mary López and Lucio del Cangrejo Grande) and the surrounding area, both located in almost the center of the Marsh where the biotic compartment is very important. It appeared to be necessary to verify if there some influence of a waterborne pollution of the Guadiamar stream coming from the North of the park occurred, where it also receives waters from another northern tributary (Agrio River) that crosses over an area where important mine works (Aznalcollar) for metal extraction exist. In previous publications (HERNANDEZ et al. 1976; BALUJA et al. 1977; BALUJA & HERNANDEZ, 1978; HERNANDEZ et al. in press) some results on the contamination by organochlorine compounds and mercury in the tissues and eggs of resident and wintering birds of the reserve were reported. In this study, water, particulate matter, sediment from the bottom, soil and biological material from trophic chains were sampled according to an ecological criterion in 1979, 80, 81, and 82. Total mercury in the abiotic and biotic samples and methylmercury in most biotic specimens were determined. The distribution of both mercury forms in muscle tissue, liver, and eggs of wild birds was also quantified. A linear relationship in the transference process and bioaccumulation was not found but it is discussed if the mercury levels in the trophic chain can be attributed to either its natural presence or to an over-load of mercury in the environment.

MATERIALS AND METHODS

Sampling and dates. Particulate matter was obtained by centrifuging known volumes of water samples. This matter was composed of clays, inorganic oxydes and an organic component formed by vegetal detritus and microplancton. Soil samples were collected from the shore of the lagoon which was either moist or covered by a thin layer of water. Mercury levels in these substrates are expressed in ppm (µg/g) on dry weight, in ppb (ng/g) on water, and on the other substrates in ppm on fresh weight. Sampling dates are shown in Tables 1 and 2.

Most fish were sampled in the Lucios (lagoons) of Mary López and Cangrejo though some species were also sampled in neighbouring small lagoons. However, the qualitative and quantitative scarcity of faunistic samples in the area did not permit the obtainment of the proposed trophic chain, so it was adapted to the existing species at the time of sampling. All the birds were collected dead from the field and the eggs were randomly picked-up as they appeared abandoned and unhatched in the nests. Biotic species sampled were as follows: Plants: buttercup (*Ranunculus fluitans*), rush (*Scirpus* sp.). Animals: frog (*Rana perezi*), shrimp (*Gammarus* sp.), crawfish (*Procambarus clarkii*), small sand smelt (*Atherina* sp.), (*Valencia hispanica*), carp (*Cyprinus carpio*), lyssa (*Mugil ramada*), eel (*Anguilla anguilla*), spoon duck (*Anas clypeata*), teal (*Anas crecca*), pochard (*Aythya ferina*), mallard (*Anas platyrhynchos*), red-crested pochard (*Netta rufina*), coat (*Fulica atra*), spoon bill (*Platalea leucorodia*), grey lag-goose (*Anser anser*), black-winged stilt (*Himantopus himantopus*), griffon vulture (*Gyps fulvus*). Eggs from: flamingo (*Phoenicopterus ruber*), pochard (*Aythya ferina*), mallard (*Anas platyrhynchos*), white stork (*Ciconia ciconia*).

Analysis. Each sample was cleanly bottled at the time of collection, sent to the laboratory and frozen till the time of analysis. The biotic samples of small size were analyzed whole while those of greater size were dissected to separate the muscle, liver and other tissues for analysis. The particulated matter and soil were previously dried at 50º C till a stable weight. The total mercury was determined by the method of UTHE et al. (1970) and the method of VELGHE et al. (1978) was applied to determine both inorganic and organic forms of mercury in the same tissue. Organic mercury was conventionally attributed to methylmercury. Aliquots of 1 g of either vegetal or animal tissues were previously homogenized and diluted to 10 ml with a 1 % aqueous solution of sodium chloride according to EBBESTAD et al. (1975) and then the method followed. Duplicate analyses were applied and mean recoveries were accounted for in about 95%. A spectrophotometer Perkin-Elmer Mod. 103 was used.

RESULTS AND DISCUSSION

Abiotic support. The main question is to know if the system is over-contaminated by mercury or if the levels found are only concerned with background mercury. In Tables 1 and 2 the mercury levels found are conventionally arranged. It has long been known that the rates of mercury are present everywhere and its natural cicle of circulation is responsible for the occurrence of trace amounts in all substracts, although it is understood that activities of man have considerably altered this natural distribution. There is a need, then, to distinguish between the mercury in the environment from natural sources and those arising from an artificial circulation. It is known that the background mercury in fresh water is in a range of 0.1-0.2 ppb according to various authors (in SAHA 1972). The waters in both the lagoons of Mary López and Cangrejo show analogous mean levels of mercury since the former amounts to 1.97 ppb and the second one to 2.11 ppb. A slightly higher concentration of mercury appears in the rainy months of winter. Comparing these mean levels with those natural mean levels mentioned above, the waters of both lagoons contain a mercury load 10 to 20 times higher, so an unnatural over-contamination appears to occur there. The particulate matter from the Cangrejo Lagoon concentrate about 680 times more mercury than the mean of water.

Various levels of mercury in the soils of the shore around both lagoons were found (Tables 1 and 2), being higher in the soils from Mary López lagoon, but even though those levels increase more significantly during the rainy months of winter around the Cangrejo lagoon, the soil of the former show a mercury load 2.4 times higher than the soil around the latter. However, in spite of these higher levels of mercury it does not appear to be conclusive that there exists an unnatural process of contamination, since the mean level of mercury in the soil of Mary López lagoon amounts to 0.234 ppm and that of the Cangrejo amounts to 0.098 ppm, and it is known that the average of the mercury content of the crust of the earth was calculated at about 0.5 ppm (in SAHA 1972).

Biotic system. The rush that grow on the shore of the Mary López lagoon contain more mercury (0.41 ppm) than the same species sampled around the Cangrejo shore (0.17 ppm) as expected from a more contaminated soil capable of increasing the mercury transfer. On the other hand, since all natural fresh water contains some mercury, fish would be expected to accumulate mercury to some degree that would depend on the level of mercury in the water and the feeding habits as well, among other factors. In fact, fish sampled in the Cangrejo and Mary López lagoons show various levels of mercury that appear to increase according to the feeding habits. Carps, for instance, fished in both lagoons in 1982 show mean levels of total mercury that are not very different from each other, as calculated from the values found for each pool of fish, that is 0.40 ppm for the former and 0.37 ppm for the latter. As the carp is an omnivorous fish with a high dose of carnivorous feeding it seems that food could be an important route of entrance of mercury into its body, while other fish previous in the food chain contain less mercury. On the contrary, the eel, at the top of the food chain in the water environment, show the highest level of mercury as it corresponds to a benthic fish that receives more mercury, mostly methylmercury, transferred from the bottom sediment. Furthermore, organic mercury constitutes the main fraction of mercury in all fish as it is expected, increasing from 73 to 94 per cent according to their position in the food chain. Obviously, these amounts of mercury registered here could signify an important level of mercury contamination but other studies on many fresh water fish from apparently uncontaminated water report levels between 0.2 and 0.4 ppm and even up to 1.4 ppm in pike. However, more studies would be necessary to assess the background levels of mercury in fish from apparently umpolluted waters, otherwise, the current levels in our fish would be only attributed to background mercury.

The data recorded on birds (Tables 1 and 2) indicate a widespread distribution of mercury, but undoubtedly much of this contamination must come from natural mercury. On the basis of muscle content the birds of exclusively vegetal feeding show smaller levels of mercury and slightly higher the birds of omnivorous food habits. Only the spoon bill, mostly carnivorous, sampled in the Mary López area shows a 0.87 ppm of total mercury, the highest level found. But if all the birds of either vegetal or omnivorous food habits are considered, setting

TABLE 1. Total mercury (T-Hg) and methylmercury (Me-Hg) levels in abiotic and biotic samples from the "Lucio del Cangrejo".

Date	Specimen	Sub-sample	T-Hg	Me-Hg	% Me-Hg
7-1980	Water		1.72[a]		
7-1981	"		2.78		
11-1981	"		2.90		
3-1982	"		1.04		
11-1981	Particulate matter[c]		1.440[b]	1.250[b]	87
7-1980	Soil of the shore[c]		0.070		
" "	" "		0.031		
7-1981	" "		0.093		
3-1982	" "		0.155		
5-1982	" "		0.098		
7-1980	Rush[d]	whole	0.170		
5-1982	Frog (22 g)[e]	muscle	0.288	0.175	61
" "	Crawfish	"	0.115	0.073	63
" "	"	carcass	0.207	0.117	56
" "	Shrimp	whole	1.090	0.850	77
7-1980	Lyssa	"	0.150	0.120	80
5-1982	"	"	0.265	0.193	73
7-1980	Valencia hispanica	"	0.168	0.126	75
5-1982	" "	"	0.351	0.260	74
" "	S. sand smelt	"	0.230	0.172	75
" "	" "	"	0.414	0.345	83
" "	Carp (20 g)	muscle	0.408	0.306	75
" "	" (260 g)	"	0.404	0.327	81
" "	Eel (32 g)	"	0.650	0.590	91
" "	" (451 g)	"	1.480	1.390	94
8-1979	Pochard (498 g)	"	0.440	0.080	18
	(M) (R) (O)	liver	0.900	0.160	18
" "	Coat	muscle	0.130	0.050	38
	(M) (W) (O)	liver	0.430	0.057	13
" "	Coat (290 g)	muscle	0.080	0.040	50
	(M) (W) (O)	liver	0.560	0.310	55
" "	Coat (436 g)	muscle	0.030	0.010	33
	(F) (W) (O)	liver	0.590	0.170	29
9-1979	Spoon duck (509 g)	muscle	0.270	0.098	36
	(F) (W) (O)	liver	1.880	0.750	40
2-1981	Griffon vulture	muscle	0.037	na	
	(R) (C)	liver	0.410	"	
5-1979	Pochard	eggs(5)[f]	0.072	"	
6-1979	Flamingo (R) (O)	" (5)	0.227	"	

(a)ppb, (b)ppm and all the other samples, (c) dry weight, (d) fresh weight and all the other samples, (e) grams, (M) male, (F) female, (R) resident, (W) wintering, (O)omnivorous, (C) carnivorous, (f) number, (na) not analysed.

TABLE 2. Total mercury (T-Hg) and methylmercury (Me-Hg) levels in abiotic and biotic samples from the "Lucio Mary López"

Date	Specimen	Sub-sample	T-Hg	Me-Hg	% Me-Hg
7-1980	Water		1.42[a]		
3-1982	"		2.80		
4-1982	"		1.70		
7-1980	Soil of the shore[c]		0.120[b]		
7-1981	" "		0.167		
3-1982	" "		0.370		
4-1982	" "		0.281		
7-1980	Rush[d]	whole	0.410		
7-1982	Buttercup	"	1.210	0.110[b]	9
5-1982	Frog	muscle	0.393	0.150	38
" "	Carp (30 g)[e]	"	0.270	0.200	74
" "	" (103 g)	"	0.470	0.350	85
7-1980	Eel	"	0.580	0.540	93
8-1978	Mallard (998 g)	"	0.120	na	
	(M) (R) (V)	liver	0.310	"	
10-1978	Spoon duck (530 g)	muscle	0.300	0.100	33
	(M) (W) (O)	liver	1.960	0.770	39
" "	Spoon duck (477 g)	muscle	0.620	0.090	14
	(F) (W) (O)	liver	2.730	1.120	41
" "	Teal (308 g)	muscle	0.180	0.070	39
	(M) (W) (O)	liver	1.250	na	
8-1979	Teal (479 g)	muscle	0.640	0.230	35
	(M) (W) (O)	liver	1.540	0.700	45
1979	B.-wing.stilt	muscle	0.460	na	
	(M) (W) (O)	liver	0.780	"	
8-1979	Pochard (341 g)	muscle	0.170	0.050	29
	(F) (R) (V)	liver	0.960	0.260	27
7-1979	Spoon bill (1350 g)	muscle	0.870	na	
	(R) (C)	liver	1.600	0.370	23
1-1981	Grey lag goose	muscle	0.230	na	
	(F) (W) (V)	liver	0.330	"	
8-1978	Mallard (R) (V)	eggs[f]	0.066	"	
5-1979	White stork (W) (C)	"	0.198	"	

(a) ppb, (b) ppm and all the other following samples, (c) dry weight, (d) fresh weight and all the other following samples, (e) grams, (f) without sell, (M) male, (F) female, (R) resident, (W) wintering, (O) omnivorous, (V) vegetarian, (C) carnivorous, (na) not analyzed.

aside other considerations concerned with the randomized movement of birds between both areas to search for food, the specimens from the Mary López area, containing a mean of 0.34 ppm of total mercury, appear two times more contaminated than those specimens collected in the Cangrejo area, which shows a mean content of 0.16 ppm of total mercury. An apparently anomalous case is shown by the griffon vulture from the Cangrejo area, a bird of carrion habits, whose mercury content is 0.037 ppm, but it must be taken into account that it was an old and exhausted bird. No remarkable differences of mercury among resident and migratory birds were found though some slightly high levels appear in wintering species. As a general rule the mercury is concentrated in the liver of the birds in a range between 0.31 and 2.73 ppm, being 0.79 ppm and 1.18 ppm the mean levels for omnivorous birds from the Cangrejo and Mary López areas respectively.

Eggs show two different mercury levels according to food habits, since the duck eggs, a bird of more abundant vegetal nourishment, contain a mean level of 0.07 ppm of mercury while those from more carnivorous birds show a mean of 0.21 ppm, that is three times higher. On the other hand, the average of the methylmercury content in the muscle and the liver of birds increases to 35 per cent with respect to the total mercury, which represents about 50 per cent less that the mean percentage found in fish.

If comparisons are made with other data on total mercury in birds found in analogous estimations carried out in other foreign areas, the levels reported here do not represent an over-load of mercury in our birds. Thus BORG et al. (1966) reported very high levels of mercury, between 6 and 100 ppm in the livers of eagles, buzzards, hawks, and falcons found dead in the Swedish countryside. However, the average of the mercury contents in the tissues of live songbirds and upland game birds sampled in areas of Canada where mercurial seed-treatments had been used were 1.63 and 1.88 ppm respectively, while the levels in similar specimens collected from an untreated area were 0.03 and 0.35 ppm respectively (GURBA 1970; FIMREITE et al. 1970). Concerning the eggs, HASELTINE et al. (1981) reported that the total mercury content in randomly sampled eggs of the mergansers in Door Country, Wisconsin, rose to a mean of 0.62 ppm in 1977 and 0.70 ppm in 1978, but the eggs of the mallard, gadwall, and black duck showed mean levels of 0.08, 0.05, and 0.12 ppm respectively.

It appears to be evident that a widespread existence of mercury occurs in the area of the reserve studied but it seems that most of this mercury has a natural origin. There is evidence to suggest that the Guadiamar River plays a role in the transport of the mercury, either natural or antropogenic, this being originated in the mine works in the far north of the reserve which appears to contribute to the background mercury in the area. Food chains and the direct intake from the environment are implicated in the transference process and bioaccumulation of the mercury.

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