METAL CONCENTRATIONS IN MEDITERRANEAN FISH TISSUES: EXPLORING BIOMAGNIFICATION PATTERNS

Teresa Mathews * and Nicholas S. Fisher
Marine Sciences Research Center, Stony Brook University, Stony Brook, NY 11794-5000 USA - teresa.mathews@gmail.com

Abstract
Metal bioaccumulation is highly variable at the upper trophic levels in marine food webs [1], and the dynamics and processes controlling metal uptake and retention remain poorly understood [2]. To explore the behavior of metals in a Mediterranean food web, we collected samples of hake (*Merluccius merluccius*) tissue from different sites (riverine- dominated, marine) in the Gulf of Lions as well as samples of its common prey for metal analysis via ICP-MS. Metal measurements are combined with stable isotope ratios of carbon and nitrogen in an attempt to assess the relative impact of food web pathway in determining metal bioaccumulation. Analyses to date of metal concentrations in hake of different size classes and in two species of its prey indicate that 10 metals (Ag, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sn, Zn) do not display evidence of biomangification but the two metalloids examined, As and Se, do appear to biomagnify. Of these elements, only Se and As speciate predominantly in anionic form in seawater and show negligible uptake by fish from the aqueous phase in laboratory bioaccumulation experiments.
Keywords : Fishes, Food Webs, Metals, Bio-accumulation.

Metal bioaccumulation is of great interest to environmental managers, toxicologists, and public health experts, since risk analyses have shown that the consumption of seafood is a major route in human exposure to environmental contaminants. The biomagnification of metals in marine food chains remains largely understudied. There is increasing recognition of the importance of dietary exposure as a source of metals for marine animals [1], but studies linking trophic level with contaminant level are rare in marine systems.

In ecological studies, the fractionation of the stable isotopes of nitrogen (δ^{15}N) and carbon(δ^{13}C) provide powerful tools to elucidate trophic transfer processes. ^{15}N enrichment allows for the assessment of relative trophic position of an organism within a given system, while δ^{13}C is a good tracer of carbon source [3]. Thus, δ^{15}N and δ^{13}C can provide an integrated (and therefore more realistic) measure of trophic position which represents the energy-weighted mean path length leading to a consumer, and they have the potential to capture complex trophic interactions (e.g., omnivory) [4], [5]. Several studies have used stable isotopes to investigate contaminant bioaccumulation in aquatic systems, primarily organic contaminants and primarily in freshwater ecosystems, but for metals only Hg has been investigated in this way extensively.

Our laboratory studies have shown that while there are great differences among metals in terms of metal assimilation and retention in marine fish, the differences between fish species are relatively small for the same metal. For this reason, our field study focused on the trophic dynamics and metal transfer in a common species representative of the Mediterranean, the Mediterranean hake (*Merluccius merluccius*). The hake ranks among the most important commercial fishes of the world and is the most heavily fished species in the Gulf of Lions [6]. The major factors affecting interannual recruitment and population variability of this key species, including details about its life cycle, food web, and exposure to contaminants are currently under study as part of the integrative MEDECIS (chemical contamination in the Mediterranean) program.

Under this comprehensive sampling campaign, trawling cruises were conducted in November 2005 at four sites distinguished by their differing riverine inputs in order to sample across gradients of contaminant concentration and to include different size structures in fish populations. Samples of hake from different size classes were taken from each site, as well as samples of the prey species for each size class of hake. Samples from the same individual fish were taken for analysis of metal concentration as well as for stable isotope ratios of carbon and nitrogen. Precautions were taken to dissect and store samples as cleanly as possible. Samples were transported frozen on dry ice and kept frozen until analysis. Sample manipulations were done using trace metal clean techniques and digestion followed established protocols for trace metal analysis via ICP-MS.

Metal concentrations in tissues ranged from the very low μg kg^{-1} range for Ag and Cd to the mid mg kg^{-1} range for Zn in hake liver. Without exception, metal concentrations in liver tissue were higher than in muscle tissue of the same fish, sometimes by about an order of magnitude (e.g., Ag, Cu). Also, for all metals except Se and As, metal concentration in smaller or prey fish was generally higher than for larger fish. Generally, the tissue metal concentration data are consistent with experimental results in laboratory studies examining patterns of metal bioaccumulation in marine animals. Thus, laboratory bioaccumulation studies indicate that Zn is typically regulated to within a fairly narrow range in animal tissue, similar to these first field measurements. Further the experimental uptake rates of the two metalloids being considered, Se and As, are negligible in marine animals following aqueous exposure; these elements only accumulate through dietary pathways, and they are the only elements that display evidence of biomagnification in field samples. In this way, these elements behave similarly to methyl mercury, which also accumulates in fish almost exclusively from diet.

Currently, patterns of metal concentrations in food web tissue samples are being compared to those of stable isotopes (C, N) to determine the relative importance of food web pathways in metal bioaccumulation in upper level carnivores in the Mediterranean.

Tab. 1. Mean metal concentrations (μg kg^{-1}) in the muscle and liver tissue of large hake (*Merluccius merluccius*), length >25 cm; the muscle tissue of small hake, length 15-19 cm; the muscle tissue of squid *(Allo-teuthis* sp.); and the muscle tissue of mackerel (*Trachurus trachurus*), length 15-19 cm.

Tissue type	Pb	Ag	Co	Ni	Cu	Zn	Mn	Cr	Sn	Cd	Se	As
large hake muscle	55	1	4	50	412	5939	256	45	1525	3	5059	4831
large hake liver	239	9	12	285	5720	24701	1181	173	8157	7	15443	10563
small hake muscle	154	2	9	1007	227	5231	383	1969	2227	3	900	3439
squid	73	7	6	387	2193	10763	265	733	1500	6	628	11812
small mackerel muscle	131	1	9	64	510	6346	147	48	5009	3	12485	5666

Acknowledgements: We thank Capucine Mellon, Herve Thebault, and Daniel Cossa for providing some samples and stable isotope data.

References

1 - Luoma, S.N., Rainbow, P.S. 2005. Why is metal bioaccumulation so variable? Biodynamics as a unifying concept. *Environ. Sci. Technol.* 39: 1921-1931.
2 - Stewart, A.R., et al. 2004. Food web pathway determines how selenium affects aquatic ecosystems: A San Francisco Bay case study. *Environ. Sci. Technol.* 38: 4519-4526.
3 - Cabana, G., Rasmussen, J.B. 1994. Modeling food-chain structure and contaminant bioaccumulation using stable nitrogen isotopes. *Nature* 372. 255-257.
4 - Vander Zanden, M.J., Rasmussen, J.B. 1999. Primary consumer delta C-13 and delta N-15 and the trophic position of aquatic consumers. *Ecology* 80: 1395-1404.
5 - Post, D.M. 2002. The long and short of food-chain length. *Trends Ecol. Evol.* 17: 269-277.
6 - Recasens, L., et al. 1998. Spatiotemporal variation in the population structure of the European hake in the NW Mediterranean. *J.Fish Biol.* 53: 387-401.