Selenium Health Benefit Value (SEHBV) in Selected Fish from Persian Gulf (Khuzestan Shores)

M. Rezayi[*1], A. S. Esmaeli[1], T. Valinasab[2], J. Alavi[3]

[1]Faculty Of Natural Resource & marine science, Tarbiat Modares University, Tehran, Iran

[2]IRAN Fishery Research Center, Tehran, Iran

[3]Department of Civil-Environmental Engineering, Sharif University of Technology, Tehran, Iran

rezayi77@gmail.com

Abstract- **This research was carried out to compute the total mercury and selenium determined in tow commercial fish from Persian Gulf and Selenium Health Benefit Value (SEHBV) of each species. The average ±SD concentration of Hg and Se in edible part of Pesttodes Erumei were 0.077±0.062 and 0.044±0.018 µg/gww, respectively and their values in liver correspondingly were 0.127±0.122 and 0.132±0.061 µg/gww. The average concentration of Hg and Se in edible and liver part of Otolithes Ruber were 0.348±0.27, 0.060±0.021, 0.176±0.174 and 0.093±0.022 µg/gww, respectively. Selenium Health Benefit Value (SEHBV) was positive (1.0) in Pesttodes erumei and negative (-6.2) in Otolithes Ruber. It reveals the fact that Selenium Health Benefit is negligible in both species to reduce mercury bioavailability.**

Keywords- Selenium; Mercury; Selenium Health Benefit Value (SEHBV); Persian Gulf

I. INTRODUCTION

Selenium was first recognized as an essential micronutrient in 1970. This provides the basis of research on its representation in food stuff (Satovic et al., 2003). Selenium is best known for the role it plays in the Glutathion Peroxide (GSH-PX) and enzyme system (Plessi et al., 2001; Mozaffarian, 2009). The first evidence of human response to selenium deficiency was reported from China; Chinese scientists showed that children who are living in selenium deficient area were suffering from a Cardiomyopathy known as Keshan disease. The symptoms of disease were reversed when selenium was added to the diet (Parkman and Hultberg, 2002). Selenium is extremely required for activity of 25-30 genetic enzymes (selenoenzymes). All forms of life that have nervous systems possess selenoenzymes to protect their brains from oxidative damage. Homeostatic mechanisms usually maintain optimal selenoenzyme activities in brain tissues, but high methylmercury (MeHg) causes sequester Se and permanently inhibits selenoenzyme activities. However, nutritionally relevant amounts of Se can replace the Se sequestered by MeHg and maintain normal selenoenzyme activities (Ralston, 2008).

Mercury is a well-known environmental toxicant, particularly in its most common organic form, Methyl Mercury. Consumption of fish and shellfish that contain Methyl Mercury is a dominant source of Mercury exposure in humans and carnivorous wildlife (Burger and Gochfeld, 2005; Inzunza, et al., 2007). Considerable efforts have been focused on assessment of Mercury and its attendant risks in the environment and food sources, including the studies reported in this issue. However, studies of Mercury intoxication have frequently failed to consider the protective effects of the essential trace element, Selenium. Mercury binds to Selenium with extraordinarily high affinity, and high maternal exposures to Mercury inhibit Selenium-dependent enzyme activities in fatal brains. However, increased maternal dietary Selenium intakes preserve these enzyme activities, thereby preventing the pathological effects that would otherwise arise in their absence. Recent evidence indicates that assessments of mercury exposure and tissue levels need to consider selenium intakes and tissue distributions in order to provide meaningful risk evaluations (Berry and Ralston, 2008; Raymond and Ralston, 2004).

Under some conditions, Selenium has interaction with Arsenic, Cadmium, Cooper, Lead and Mercury. Furthermore, Selenium has much interaction with Sulphur compound. This affinity for Sulphur compound may account many synergistic and antagonistic relations between Mercury and Selenium (Irwin, 1997; Cappon and Smith, 1981; Cabanero et al., 2004; Dietz et al., 2000; Plessi et al., 2001; Burger et al., 2001). Role of Selenium in the prevention of Hg toxicity has been recognized for 40 years. Because of Selenium protective effect, it was suggested that the Selenium content is important to define safe Mercury levels in fish (Cappon Smith, 1981). There are some hypothesises to describe protective mechanism of Selenium against Mercury (Belzile, et al., 2005; Branko et al., 2007):

1- formation of a native complex of the Thiol-Hg-Se (Gamberg et al., 2005);
2- redistribution or excretion of Hg in the presence of Se;
3- prevention of Oxidative damage from Hg by Se, through an increase activity of Glutathione Proxidease;
4- conversion of toxic forms to less toxic forms of Hg and formation of Mercury Selenid (Cardellicchio, 2002; Belzile et al., 2005; Yang et al., 2007); and;
5- formation of a complex between a specific plasma protein and the two elements, which are bound to the protein at an equimolar ratio (Yoneda and Suzuki, 2002).

It is reasonable that not only the Selenium has an effect on mercury's bioavailability, but also, Mercury may inhibit formation of essential Se–dependent proteins: Selenoproteins (Raymond, Ralstone; 2004). Likewise, Mercury level in fish is interesting because of the potential effect on fish and fish consumers. Fish consumption is the only significant source of Methyl Mercury entrance to human body (Burger and Guchfeld, 2005; Brookensa et al., 2007). Even low dose of Mercury can damage the nervous and cardiovascular systems in human. The greatest likelihood of risk of MeHg exposed to population will occur in Se-poor areas whose diets originate from fish (McClain et al., 2006). Therefore, there is a cost and benefit analysis in fish consumption and requires constant monitoring of fish safety.

Since marine fish is among the richest nutritional sources of Selenium, it is essential to develop a broader understanding of interactions between Mercury and Selenium and how this correlation might impact on fish advisories based on EPA's reference dose level for Methyl Mercury exposure.

The objective of this study was investigation of total Mercury and Selenium concentration in two commercial fish from Persian Gulf: one predator specie, Otolithes Ruber, that has high fishery and national-local consumption and the other, Pesttodes Erumei, the bottom feeding specie that has high consumption rate in local area. Despite of wide rang investigations about mercury level, the fish Selenium content has not been evaluated in any marine fish in Iran, since measuring the amount of Mercury present in the environment or food sources may provide an inadequate reflection of the health risks without considering the protective effect of Selenium against Mercury (Raymond and Ralston, 2004). Moreover, because of the importance of Selenium supply in diet to maintain sufficient free Selenium to support normal Selenium-dependent enzyme synthesis and activity, it is necessary to set up a comprehensive plan to determinate the Selenium content of common foods in mentioned regions. This research is the first report in the field of health risk assessment of Mercury by taking into account the Selenium content in stated area.

II. MATERIAL AND METHODS

Otolithes Ruber (22) and Pesttodes Erumei (40) were caught in Khuzestan province shore (west of Persian Gulf) by trawl net. Samples were kept on the ice and moved to laboratory and their weights, standards and total lengths were measured. Liver and edible part were removed and placed in polyethylene bags and labeled with unique sample number and stored in -20°C.

Homogenous mass was obtained and wet weight of each sample was recorded. Sample was freeze-dried (OPER-FDU-7012) for 24 hours to attain stable weight, then the dry weight of samples was measured and specimen's powder was kept in Poly-ethylene bottle until analysis.

All container and laboratory tools were washed with detergent, pure water and kept on 20% Nitric acid.

Total mercury was determined by Atomic Absorption Spectrometry using a silicon UV diode detector Leco AMA-254. After pyrolysis of each sample in combustion tube at 750°C under an oxygen atmosphere and collection on a gold amalgamator, Hg concentration was determined. Accuracy of total Hg analysis was checked by running three samples of Standard Reference Materials (SRM), National Institute of Standards and Technology (NIST), SRM 1633b, SRM 2709, and SRM 2711 Recovery varied between 94.8 and 105%. The detection limit of the method used was 0.001 mg/kg in dry weight. Data was obtained as follows (Table 1).

TABLE I RECOVERY TEST FOR MERCURY ANALYSIS

Recovery	Standard Deviation	Mean	Reference Material
94.8	0.042	0.134	ST: 1633 B
105	0.131	1.470	ST: 2709
103	0.197	6.438	ST: 2711

For AAS measurement, approximately 1.0 g of each homogenized dry sample were digested with 9 ml 65% HNO3 regent grade (Sharlau) and 3ml 30% H2O2 extra pure (Merck) in closed digestion vessels and digestion procedure was based on EPA 3052 update method by using Microwave digester (Milestone START D). Every digested sample batch included one blank sample to minimize possible contamination from reagents and containers. After cooling vessels digested content was diluted to 25 ml with ultra pure (0.05 µmc) water, Se concentration was assayed by using Graphic Furnace Atomic Absorption Spectrophotometer (Perkin Elmer 3030) with background correction. All specimens were run in batches that include blanks, spiked specimens and standard calibration cure. The average accepted recoveries for spike were 96%. Also 20% of samples were analyzed twice.

All statistic analyses carry out by using SPSS software (version 11.5, Chicago, 11, USA). After normality test due to the result, we choose Non-Parametric correlation and the existence of correlation between elements concentration and fish size and between elements in different tissue were verified by applying the Spearman correlation coefficient.

III. RESULT AND DISCUSSION

The result of analysis summarized in Table 2. Average Selenium content in edible part and liver of Otolithes Ruber respectively was (0.060±0.021µg/g ww) and (0.093±0.023µg/g ww).

The average of mercury in liver and edible part of Otolithes Ruber was (0. 176±0.174µg/g ww) and (0.348±0.27µg/g ww).

In Pesttodes erumei, average mercury concentration ranged from (0.127±0.122µg/g ww) in liver to (0.077±0.062 µg/g ww) in edible part.

Selenium content in edible and liver part of Pesttodes erumei respectively was (0.044±0.018µg/g ww) and (0.132±0.061µg/g ww).

Selenium-Mercury molar ratio shows that Mercury concentration exceeds Selenium only in edible part of Otolithes Ruber but in Pesttodes erumei Selenium-Mercury molar ratio (liver: 2.5, edible part: 1.47) is greater than Otolithes ruber (liver: 1.34, edible part: 0.43). Se increases with mercury in liver and edible part of two species but correlation coefficient indicates no significant correlation between elements. The results were in agreement with published data by Cappon and Smith in 1981 and Plessi et al., 2001. Correlation between elements in edible part of Otolithes ruber is more significant that suggests probability of selenium bond with mercury in this organ is stronger. The correlation between two elements in total specimens shows significant relation. Better correlation between two elements reported when using Hg instead of total Hg. Because MeHg concentration more closely reflects biological assimilation, whereas total Hg concentration can reflect contribution from non-bio available forms (Belzile et al., 2005).

TABLE II HG AND SE CONCENTRATION µG/G WW (MIN, MAX, MEAN ±SD) IN SELECTED SPECIES

Species	Tissue	Hg			Se		
		Min	Max	Mean±SD	Min	Max	Mean±SD
Pesttodes Erumei	liver	0.007	0.510	0.127±0.122	0.043	0.341	0.132±0.061
	tissue	0.005	0.248	0.077±0.062	0.006	0.117	0.044±0.018
Otolithes ruber	liver	0.003	0.942	0.176±0.174	0.039	0.125	0.093±0.022
	tissue	0.106	1.414	0.348±0.270	0.028	0.118	0.060±0.021

We did not find significant correlation between sizes, weights and elements in Otolithes ruber which is because of the samples uniform size. But in Pesttodes erumei significant relation was found between weight, length and elements. Likewise, there are significant differences between two elements in different organs within and between species ($p<0.05$). That it may be related to different diet and habitat conditions. Pesttodes erumei is bottom feeding and predator that has preference feeding on nektons and bony fish. These species spend time near sediment. Otolithes ruber mainly feeds on shrimp and zoo benthos and is completely movement species.

A. Selenium Health Benefits Value

To better understand and integrate Se-specific nutritional benefits in relation to Hg exposure risk, Selenium health benefit value can be calculated (Kaneko and Ralston; 2007). To do so, all data concentration should convert to molar concentration. To obtain elements molar concentration, data at first were modified to wet weight by using dry weight/wet weight ratio and then mol concentration was calculated by using fallowing formula:

1000*ppm ww/atomic weight

And selenium health benefit value SEHBV is calculated as follows:

$$[Se\ HBV = Hg/Se\ molar\ ratio \times \text{total Hg} - Se/Hg\ molar\ ratio \times \text{total Se}]$$

In Pesttodes erumei, SEHBV was ranged (-2.4 to 6.6) and 32.5% of data have negative values. In Otolithes ruber, SEHBV was ranged (-80 to 0.6) and 95% of the data have negative values (Table 3). To sum up, Selenium Health Benefit is positive (see Figure 1) in Pesttodes erumei and negative in Otolithes Ruber.

TABLE III MOLAR RATIO OF MERCURY AND SELENIUM AND SELENIUM HEALTH BENEFIT VALUE (SEHBV)

	Hg nmol/g		Se nmol/g		Se/Hg Molar Ratio		SEHBV	Percent Negative SEHBV
	Liver	Edible Part	Liver	Edible Part	Liver	Muscle		
Pesttodes erumei	0.64	0.38	1.63	0.56	2.5	1.47	1.00	32.5
Otolithes ruber	0.88	1.73	1.18	0.76	1.34	0.43	-6.2	95.5

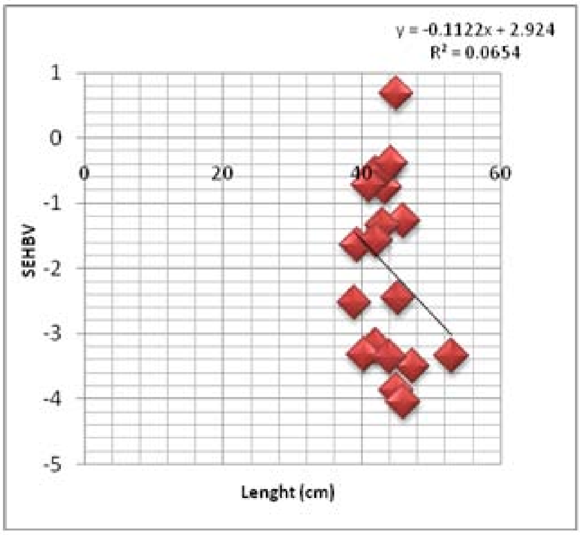

Figure 1 Correlation between SEHBV & length in Otolithes ruber

Statistical analyses between SEHBV and total length show simultaneous diminish of SEHBV with increase of length in both species (Figures 1 and 2), which refers to difference dietary strategy in matures and immature and increase of mercury proportionally with fish's size.

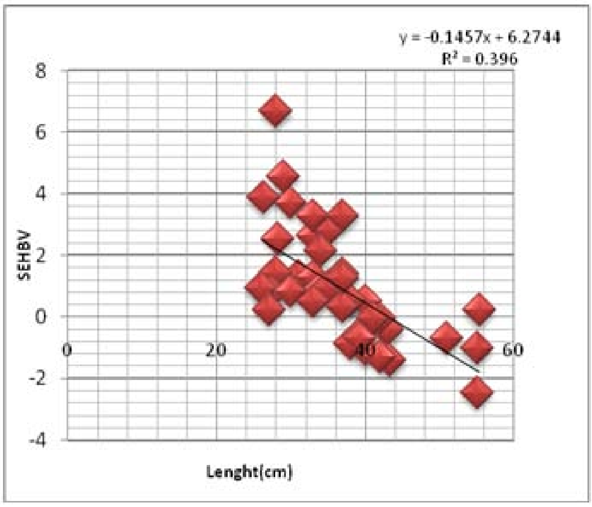

Figure 2 Correlation between SEHBV & length in Pesttodes Erumei

Calculation of Se/Hg ratio shows that selenium is exceeded of mercury in Pesttodes erumei; 70% of data in edible part and 90% in liver have molar ratio in excess of 1 value. In Otolithes ruber Hg concentration is over Se content and 100% of specimens in edible part have molar ratio less than 1. Conversely in liver part 90.9% molar ratio is over 1. It is well known that higher ratio of Se/Hg is contributed to the binding of 1-Hg to MT_s and the existence of M-Hg (Endo et al., 2002; Campos et al., 2002).

The formation of the Hg-Se complex is the last step of the detoxification process through the Dymethylation of M-Hg. On the other hand, Mercury distribution in tissue can be affected by timing of Hg exposure. Edible parts are indicator of a recent exposure. Conversely liver is indicator of the past exposure but other factor as metabolic transformation may change this pattern (Inzunza et al., 2007). According to theses hypothesis, the highest mercury concentration and low Se/Hg molar ratio in edible part of Otolithes ruber may be related to the newly exposure to pollutant. Subsequently detoxification process and $[(Hg-Se)n]m-$ Selenoprotein P formation is under progress in this species.

As it can be observed in the linear regression of Hg and Se presented in Figure 3, there is a positive relation between two elements which is in agreement with a recent work published by Lima et al., 2005 identifying the start of detoxification process which is affected by species, tissue specificity, chemical form of mercury and selenium molecule (Chen et al., 2002).

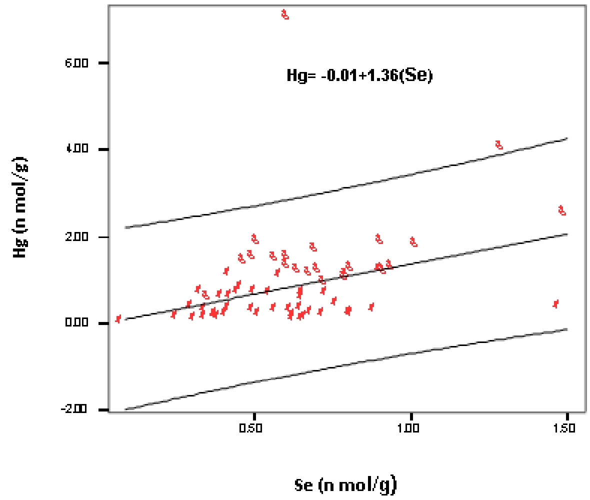

Figure 3 linear regression with 95% individual prediction interval: all data convert to molar concentration

According to USEPA's (2000) recommendation based on the analysis of multiple size classes of fish, within each size class (McClain et al., 2006) samples classifications were carried out. First we identified the largest individuals and then combined it with all individuals within 75% of its total length. After the "large" size class was identified, we repeated the procedure with all the remaining individuals. Using this approach, we divided Pesttodes erumi into three size classes. Due to size uniform in Otolithes ruber it could not be divided into multiple size classes. Data summarize in Table 4. Result has been shown with increase of length Health Benefit Value related to Selenium decrease.

TABLE IV VARIATION OF SELENIUM HEALTH BENEFIT VALUE IN MULTIPLE SIZE CLASSES OF PESTTODES ERUMI AND OTOLITHES RUBER

	Length	Mol Hg	Mol Se	Hg/Se	SEHBV
Pesttodes Erumei	47.5	0.78	0.45	1.72	-1.09
	35.9	0.32	0.59	0.54	0.91
	27.9	0.19	0.55	0.35	1.48
Otolithes Ruber	48	1.73	0.76	2.27	-6.2

B. *Geography Comparison of Selenium-Mercury Ratio*

Due to increase in anthropogenic source of metal because of erosion, and fuel consumption negative impact can occur over short period of time and the ability of biological adoption can-not keep up with these rapid changes in the environment (Jeweet et al., 2007).

Thus, rapid increase in contaminants can threaten the physical health of consumers that fed on them both fish and human. Therefore, the level of Mercury and Selenium in fish is of considerable interest because of potential risk of fish consumption. The range of Hg and Se concentration in selected fish is different compare with another study carried out (Table 5**)** but Hg/S molar ratio is corresponding.

TABLE V GEOGRAPHY COMPARISON OF SELENIUM/MERCURY RATIO

Species	Diets	Sampling Area	Hg/Se Molar Ratio	References
Pestodes Erumei	Carnivora	Persian gulf	0.60	
Otolithes Ruber	Shrimp and Benthoz	Persian gulf	0.42	
Hoplias alabaricus	Carnivora	Berezil	0.65	Lima, 2005
Pseudoplatystoma sp	Carnivora	Berezil	0.63	Lima, 2005
Thresher Shark	Carnivora	Hawaii	0.75	Kaneko and Ralston ,2007
Swordfish	carnivora	Hawaii	0.99	Kaneko and Ralston, 2007
Sardine		Italy	0.09	Plessi,2001
Salmon		Italy	0.17	Plessi,2001

IV. CONCLUSIONS

Sporadic researches had been carried out in the field of mercury concentration in Persian Gulf and Caspian Sea. The population in 6 provinces of Iran is fish based on diet and there are some documents about health risk of mercury in newborns in south of Iran. Due to necessity of Selenium supply in diet, it is required to conduct all-inclusive study to determinate the Selenium content of common foods in these regions. RDA (Recommended Daily Allowance) for Selenium was set at 70 µg for men and 55 µg for women. These levels would be very hard to reach for those people living in a country with Selenium poor soil. Therefore, it is important to evaluate Se content in wide range of foodstuff for further planning, like Selenium additive to soil, foliar spray and seed treatment. According to the research of Burger et al., 2007; Jewett et al., 2007 and results of this study, there is a need for a general strategy to minimize health risk of mercury by maximizing Selenium Health Benefit. Selection of variety of marine species and small fish is advisable to public. Furthermore, for better understanding, other researchers are under taken for another species.

REFERENCES

[1] I. Cabanero, Y. Madrid, C. Cmara, Selenium and mercury bioaccessibility in fish samples an in vitro digestion method, Analytica Chimica Acta, Vol. 526: 51–61, 2004.

[2] P. S. Lima, J. E. S. Sarkis, H. M. Shihomatsu, R. C. S. M. Muler, Mercury and selenium concentration in fish sample from Cachoeria do PiriaMunicipality, ParaState, Brazil,Environ res, Vol. 97: 236-244, 2005.

[3] J. Cappon, J. C. Smith, Mercury and Selenium Content and Chemical Form in Fish Edible part, Environ. Contam Toxicol, Vol. 10: 305-319, 1981.

[4] Mozaffarian, Fish, Mercury, Selenium and Cardiovascular Risk: Current Evidence and Unanswered Questions, Environ. Res. Public Health, Vol. 6: 1894-1916, 2009.

[5] H. Parkman, B. H. Hultberg, Occurence and effect of selenium in the environment (a literature review), Swedish Environmental research institute, 2002.

[6] J. Burger, Gochfeld, Heavy metals in commercial fish in New Jersey, Environ Res, Vol. 99: 403-412, 2005.

[7] J. Burger, K. F. Gaines, C. S. Boring, W. L. Stephens, J. Snodgrass, M. Gochfeld, Mercury and selenium in fish from the Savannah River:species,trophic level and locational difference , Environmental research, Vol. A 87: 108-118, 2001.

[8] J. Burger, M. Gochfeld, K. Sullivan, D. Irons, Mercury, arsenic, cadmium, chromium lead, and selenium in feathers of pigeon guillemots (Cepphus columba) from Prince William Sound and the Aleutian Islands of AlaskaScience of the Total Environ, Vol. 387: 175–184, 2007.

[9] J. J. Kaneko, N. V. C. Ralston, Selenium and Mercury in Pelagic Fish in the Central North Pacific Near Hawaii, Biol Trace Elem Res, Vol. 119: 242–54, 2007.

[10] J. Ruelas-Inzunza, G. Meza-Lopez, F. Paez-Osuna, Mercury in fish that are of dietary importance from the coasts of Sinaloa (SE Gulf of California), J. Food Compos Anal, 21: 211-218, 2008.

[11] J. Yang, T. Kunito, S. Tanabe, N. Miyazaki, Mercury and relation with selenium in the liver of dalls porpoise's ohocoenoides dalli off the sanriku coast of Japan, Environmental Pollution, Vol. 8: 669-673, 2007.

[12] L. J. Raymond, N. V. C. Ralston, Mercury: selenium interactions and health implications, Medical and Dental Journal, Vol. 7, No. 1, 2004.

[13] M. Gamberg, G. Bolia, G. Stern, R. Patrick, Cadmium mercury and selenium concentration in mink Mustela vison from Yukon, Canda, Sience of environment, Vol. 351-352: 523-529, 2005.

[14] M. H. Chen, C. C. Shih, C. L. Chou, L. S. Chou, Mercury organic-mercury and selenium in small cetaceans in Taiwanese waters Marine Pollution Bulletin, Vol. 45: 237-245, 2002.

[15] M. J. Berry, N. V. Ralston, Mercury toxicity and the mitigating role of selenium, Ecohealth; 5(4): 456-9, 2008.

[16] M. Plessi, D. Bertelli, A. Monzani, Mercury and Selenium Content in Selected Seafood, Journal of Food Composition and Analyses, Vol. 14: 461-467, 2001.

[17] M. S. Campos, J. E. S. Sarkis, R. C. S. Muller, E. D. S. Brabo, E. D. O. Santos, Correlation between mercury and selenium concentration in Indian hair from Rondonia state Amazon

region , Brazile, the science of the total environ, Vol. 287: 155-161, 2002.

[18] N. Belzile, Y. Chen, J. M. Gunn, J. Tong, Y. Alarie, T. Delonchamp, C. Y. Lang, The effect of selenium on mercury assimilation by freshwater organisms, http://cjz.nrc.ca on 17 November 2005, 18546.

[19] N. Cardellicchio, A. Decataldo, A. D. Leo, A. Misino, Accumulation and tissue Distribution of mercury and selenium in striped dolphins (Stenella coeruleoalba) from the Mediterranean Sea (southern Italy), Environ Pollut, Vol. 116: 265-271, 2002.

[20] N. V. Ralston, Selenium health benefit values as seafood safety criteria. Ecohealth, 5(4): 442-55, 2004.

[21] R. Dietz, F. Riget, E. W. Born, An assessment of selenium to mercury in Greenland marine animals, The Science of the Total Environment, Vol. 245: 15-24, 2000.

[22] R. J. Irwin, M. Vanmouwerikk, L. Stevens, M. D. Seese, W. Basham, Environmental Contaminant enclopedia. National park service, water resource Division, fort Collins CO, 1979.

[23] S. C. Jewett, L. K. Duffy, Mercury in fishes of Alaska with emphasis on subsistence species, Science of the Total Environment, Vol. 387: 3–27, 2007.

[24] S. Yoneda, K. T. Suzuki, Detoxification of Mercury by Selenium by Binding of Equimolar Hg–Se Complex to a Specific Plasma Protein. Pharmacology, Vol. 274-280, 2002.

[25] T. Endo, K. Haraguchi, M. Sakata, Mercury and selenium concentrations in the internal organs of toothed whales and dolphins marketd for human consumption in Japan, The Science of Total Environment, Vol. 300: 15-22, 2002.

[26] T. J. Brookensa, T. M. O. Hara, R. J. Taylor, G. Bratton, J. Hrvey, Total mercury body burden in Pacific harbor seal, Phoca vitulina richardii, pups from central California, Marine Pollut Bulletin, 2007.

[27] V. Branko, C. Vale, J. Canario, M. Neves dos santos, Mercury and selenium in blue shark (Prionace glauca,L.1758) and swordfish (Xiphias gladius.L.1758) from two are of Atlantic Ocean, 2007.

[28] V. Satovic, D. Beker, K. L. Gumhalter, Selenium content in the pilchard of the Adriatic Sea, Euro Food Res Techno, Vol. 217: 154 –156, 2003.

[29] W. C. McClain, M. M. Chunchal, R. W. Drenner, L. W. Newland, Mercury Concentration in Fish from Lake Meredith, Texas, Implication for the Issuance of Fish Consumption Advisors, Environ monitoring and assess, Vol. 123: 249-258, 2006.