EFFECTS ON MARINE ENVIRONMENT BY THE NON-RECYCLE BY-PRODUCTS OF FERRONICKEL SMELTING PLANT

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ABSTRACT:

The Euvoikos Gulf is a semi close embayment of the Aegean Sea located between the eastern coast of the Greek mainland and the western coast of Evia Island. A ferronickel smelting plant (founded in 1963) extracts Fe and Ni from laterite ore. During the smelting process it produces enormous quantities of slag as by-product which is dumped in area defined by the Government. Dumping was selected instead of use for sand blasting, asphalt, construction materials or Nickel recovery etc as the more economical solution. The aim of this study is to define the impact of slag on the marine environment where the dumping takes place. Five stations in the Gulf (dumping area) and seven stations around the smelting plant were selected. Water samples were taken in different seasons during two years. Heavy metals concentrations such as Zn, Cu, Mn and Ni both in dissolved and particulate phase were determined by atomic absorption.

Results have been compared with the Greek concentrations of trace metals in seawater and US EPA acute and chronic exposure criteria. Slightly elevated concentrations of some metals were found in the stations that are considered to be more affected.

KEYWORDS: heavy metals, dissolved metals, particulate metals, smelting plant

1-INTRODUCTION:

The pollution of the aquatic environment ecosystem with heavy metals has acknowledged as a worldwide problem during recent years, due to their potential toxic effects and ability to bioaccumulate in aquatic ecosystem (Mac farlane & Burchesett 2002, Miller 2002, C. Fernandes et al 2008).

The Euvoikos Gulf is a semi close embayment of the Aegean Sea located between the eastern coast of Greece and the western coast of Evia island, having a significant and unusual tidal phenomenon. The Gulf receives domestic, industrial and agricultural wastes (Dassenakis et al, 2003). Since 1963 it receives the wastes of an important ferronickel smelting plant. LARCO (G.M.M.S.A) located in Larymna, (South Evoikos Gulf) process nickel ferrous ore (laterite) which is a raw material of the industrial production of stainless steel in Europe. Larco has a total

nickel production capacity of 25000 t/y of nickel (Larco, 2008). The by-product of the smelting plant consists iron oxides, silicon dioxide as well as Fe, Al, Mn, Cr, Ni and Co and has the form of slag (Kozanoglou & Catsiki 1997). The slag could be used for construction material, sand ballast, asphalt etc or even in Nickel recovery processes (World bank Group 1998). Instead slag is deposited in sea at a restricted area, defined by the Greek authorities. The area is about 30km^2 and is located approximately 8 km far from the shore. The slag being dumped at a rate of about 600 tons per day, today has exceed of 2.5 m of thickness .(Simboura et al, 2006. HCMR 2005).

The Hellenic Center for Marine Research (HCMR) has been charged for monitoring the impact of dumping slag on N. Evoikos Gulf, since 1983 (HCMR 2005, Chronis 1985), in addition several other studies have been conducted by other authors (Nicolaidou et al, 1989,).

The slag is not an inert material as the smelting plant authorities' claim, but gradually releases metal ions (Michalopoulos et al 2005). The aim of the present paper was to investigate the impact of dumped slag on the marine environment and especially on sea water.

2-MATERIALS AND METHODS:

Five stations in the Gulf (dumping area) and seven stations around the smelting plant were selected. The stations L8, L10, L12-and L14 are located within the dumping area, while BE1 is selected as reference area (Fig 1a). Additionally the stations LA 2-LA4-LA5-LA7-LA8-LA9 and LA 10 are located on the coastline, station REF located about 14 km east of LA-10 is considered as coastal reference (Fig 1b).

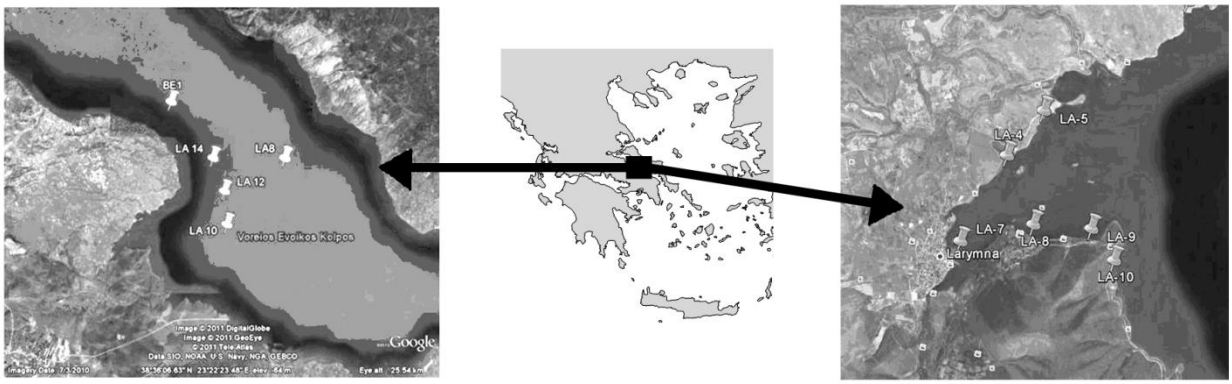


Fig 1: a- Location of sampling stations near the smelting plant (Inshore)
b- Location of sampling stations in dumping area (offshore)

Surface and bottom water samples from the dumping area were taken during two years: June 2009 and March 2010. Sea water was also sampled from the coastline around the smelting plant during four seasons: from October 2009 to October 2010. Heavy metals concentrations such as Zn, Cu, Mn and Ni both in dissolved and particulate phase were measured. Ni and Mn are chosen as two constituents of the by product of smelting plant and Zn and Cu as metals related domestic wastes.

Water samples stored in polyethylene bottles, were filtered through 0.45µm Millipore membrane filters, and left in desiccators for more than a month to be completely dry. The filters were digested with nitric acid in covered Teflon on a hot plate over night. Heavy metals in dissolved phase were pre-concentrated on Chelex -100 resin columns (Dassenakis et al, 1994). Flame atomic absorption Varian spectra AA-200 and Graphite atomic absorption (Varian gta-100 640 Zeeman) was used for measuring the metals.

3-RESULTS AND DISCUSSION:

1-In shore results:

The average metal concentrations in seawater (dissolved and particulate phase) from Larymna bay (N.- Evoikos Gulf) are presented in Table 1 expressed in (µg/l). In the same table, US EPA national recommended water quality criteria are given, in order to be compared with the present results. US EPA values contain chronic (continuous) concentrations (CCC) and maximum ones (CMC).

Table1:
Average metal concentrations in sea water from inshore stations in Larymna Bay (in **µg/l, D**: Dissolved Metal**, P**: particulate metal**, CCC(µg/l):** Criterion Continuous Concentration, **CMC(µg/l):** Criterion Maximum Concentration)

	Cu		**Zn**		**Mn**		**Ni**	
	D	S	D	S	D	S	D	S
Range M **Oct 2009**	0.60-1.53 0.96	0.07-0.24 0.13	2.9-7.8 5.1	0.36-0.58 0.44	1.3-4.7 2.5	0.1-1.9 0.6	1.7-5.0 3±1.1	0.07-4.63 0.83±1.83
Range M **Feb 2010**	0.11-0.86 0.28	0.06-0.13 0.10	0.6-4.7 2.3	0.27-0.68 0.37	0.5-1.7 0.8	0.1-2.7 0.7	0.63-5.2 3.0±1.47	0.11-4.51 0.86±1.62
Range M **May 2010**	0.36-1.1 0.71	0.06-1.2 0.30	6.4-11.6 9.0	0.21-0.33 0.36	0.9-6.1 2.0	0.2-5.9 1.4	2.4-5.1 3.2±0.92	0.11-0.83 0.31±0.24
Range M **Oct 2010**	0.11-2.2 0.72	0.08-0.39 0.27	0.50-4.0 2.9	0.21-2 0.69	0.08-7.1 2.5	0.41-13.31 4.81	0.21-8.0 3.1	0.26-13.60 3.36
Average	0.66	0.2	4.82	0.46	1.95	1.87	3.07	1.34
CCC	3.1		81				74	
CMC	4.8		90				8.2	

Two of four sampling were done in October that permits us to compare the pollution state of two continuously years. The results showed that both dissolved and particulate Zn and Cu were higher in October 2009 than in Oct 2010, while similar levels were detected in dissolved Mn and Ni.

The average concentrations in dissolved phase were higher than in particulate phase during all the samplings except in October 2010. With the exception of Mn the opposite phenomenon occurred, in which the particulate phase were higher than dissolved phase (Table 1).

The average results of metals in May 2010 were slightly higher than the other sampling seasons such as October and February.

In order to evaluate the impact of the slag on the levels of metals in sea water the results of the present study were compared to those from other Greek areas. According to Dassenakis et al. (2005) dissolved Ni in Larymna stations was the highest of the Greek mainland sea water measurements. In addition dissolved Mn was among the highest concentrations determined along Greece. This fact is certainly due to the discharge of the smelting plants' by-products in the sea that contain both Ni & Mn in great amounts. On the contrary, Cu & Zn levels in Larymna bay were similar to those from most Greek areas. Cu concentrations were higher in Larymna than in open sea areas such as in Cretan sea (0.25 μg/l), Ionian sea (0.093 μg/l), North Aegean sea(0.17 μg/l).

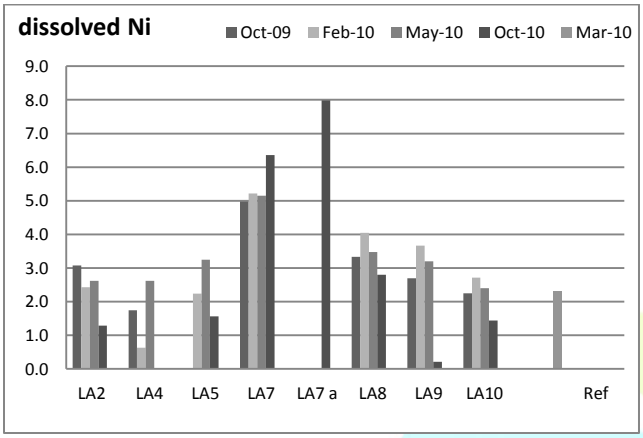
The average concentrations of all metals in dissolved phase were lower than US EPA chronic criteria, while in some individual stations concentrations were slightly higher.

Results are presented graphically per station and season in Figure 2, in order to evaluate the effect of these parameters on metal concentrations.

High values of dissolved and particulate Ni and Mn were recorded at stations near the smelting plant (LA-7 & LA-7a) during all sampling periods (Fig 2a & 2b). This fact is probably due to the fact that these elements are main constituents of the smelting plant by product. The highest levels were measured during the last two samplings which took place in May and October 2010. Dissolved Ni also showed high levels in February sampling in contrast with the other metals which the concentrations were quite low (Fig 2a). The range of dissolved Ni concentration is between 0,21μg/l- 8.0μg/l consequently in some cases the levels were close to the US EPA CCC (Criterion continuous concentration = 8.2μg/l) threshold (Table1).

Concerning Zn & Cu, metals not directly related to slag (Michalopoulos et al 2005), the highest concentrations of Zn in the both dissolved and particulate phase were also detected in stations LA-7 and LA-7a, located in front of smelting plant and on the shore line of Larymna. Dissolved Zn show a relatively high value in all sampling stations in May 2010. On the opposite the dissolved Cu concentrations were higher during all sampling periods in station LA-10, the most faraway station to the smelting plant. Particulate Cu in LA-5 also showed high concentrations in the May sampling. The relatively high values may be due to the vicinity of these stations to fish farms and possibility to the antifouling paints used in aquaculture (Forrest et al, 2007). The range of dissolved Cu concentrations was between 0.11μg/l – 2.2μg/l. In some cases the concentrations of dissolved Cu were close to the EPA CCC (Criterion Continuous Concentration = 3.1μg/l) threshold (Table 1).

a)



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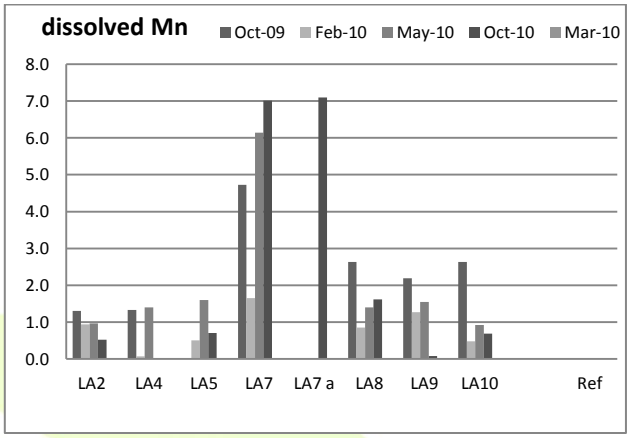

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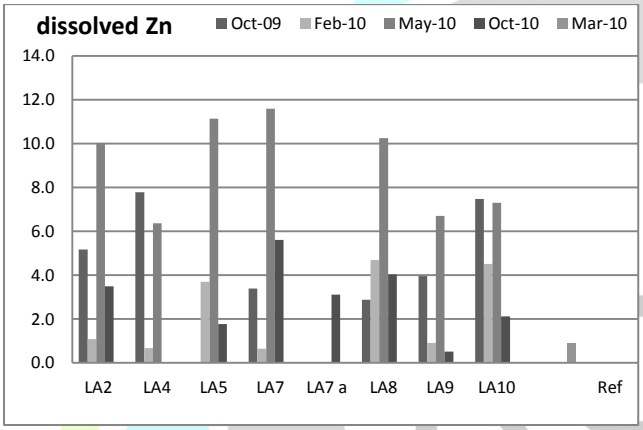

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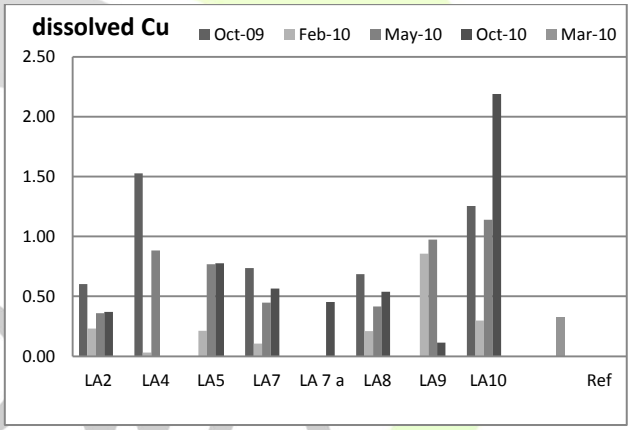

Figure 2 : Dissolved concentrations of Ni, Mn, Zn in(µg/l) and in different sampling seasons around the smelting plants. (Inshore stations)

Zn and Cu are known to be related to direct anthropogenic inputs such as sewages (Dassenakis, 2002). Furthermore atmospheric dry and wet precipitations are also known to have a significant role in metal concentrations (Garcia et al, 2010-Zeri et al, 2009). The sampling of May 2010 was carried out rainy week; therefore the high concentration of Zn may be attributed to both anthropogenic activities and weather conditions.

2- **Offshore results:**

The average offshore metal concentrations in seawater (dissolved and particulate phase) from N.-Evoikos Gulf are presented in Table 2. In the same table, US EPA acute and chronic criteria are given, so as to be compared with the present results. USE PA values contain CCC (Criterion Continuous concentration) and CMC (Criterion Maximum concentration).

Table 2:
Average metal concentrations in sea water from inshore stations in Larymna Bay (in μg/l, D: Dissolved Metal, P: particulate metal, CCC(μg/l): Criterion Continuous Concentration, CMC(μg/l): Criterion Maximum Concentration)

	Cu		Zn		Mn		Ni	
	D	P	D	P	D	P	D	P
Range	0.4-0.9	0.03-0.09	2.6-15.1	0.27-3.88	1.2-4.3	0.32-1.58	3.0-7.4	0.03-0.58
M	0.6	0.06	8.4	0.78	2.2	0.96	4.2	0.13
June 2009								
Range	0.1-0.8	0.02-0.12	1.27-8.7	0.20-0.60	0.56-1.2	0.14-0.66	2.4-4.1	0.02-0.25
M	0.3	0.05	5.3	0.31	0.7	0.28	2.8	0.09
MARCH 2010								
Average	0.45	0.05	6.85	0.54	1.45	0.62	3.5	0.11
CCC	3.1		81				8.2	
CMC	4.8		90				74	

As shown in Table 2, the average concentrations of both dissolved and particulate phase in March 2010 were relatively lower than June 2009.

The results from offshore sampling have been compared again to those from other Greek areas and US EPA recommended water quality criteria. Similar to the inshore findings, dissolved Ni and Mn was significantly higher in Larymna Bay than in other Greek areas (Dassenakis,2005), probably as a consequence of depositing the by- product of smelting plant in this area.

The average concentrations of Zn and Cu were higher than in open seas areas such Cretan sea (0.25 μg/l), Ionian sea (0.093 μg/l), North Aegean sea(0.17 μg/l). Furthermore, the average dissolved Zn, in contrast to the inshore results, was found in greater amount than other contaminated places such as Saronikos Gulf(4.6 μg/l),Patriakos Gulf (4.70 μg/l) and Maliakos Gulf (4.60 μg/l), while dissolved Cu had lower levels.

The results comparison with the US EPA revealed that all the metals concentrations were lower than the both chronic and acute threshold; while in some stations concentrations were slightly higher than CCC (Criterion Continuous concentration).

Both dissolved and particulate concentrations of Ni and Mn decreased in March 2010 (Fig 3). The remarkable rates of Mn and Ni contamination have been found in deep water samples of stations of L-10, L-12 and L-14 in both June 2009 and March 2010, which could be related to the direct slag dumping in these areas. The range of dissolved Ni concentration (2.4 μg/l- 7.4μg/l) was in some stations close to the US EPA (Criterion continuous concentration = 8.2μg/l) threshold (Table2).

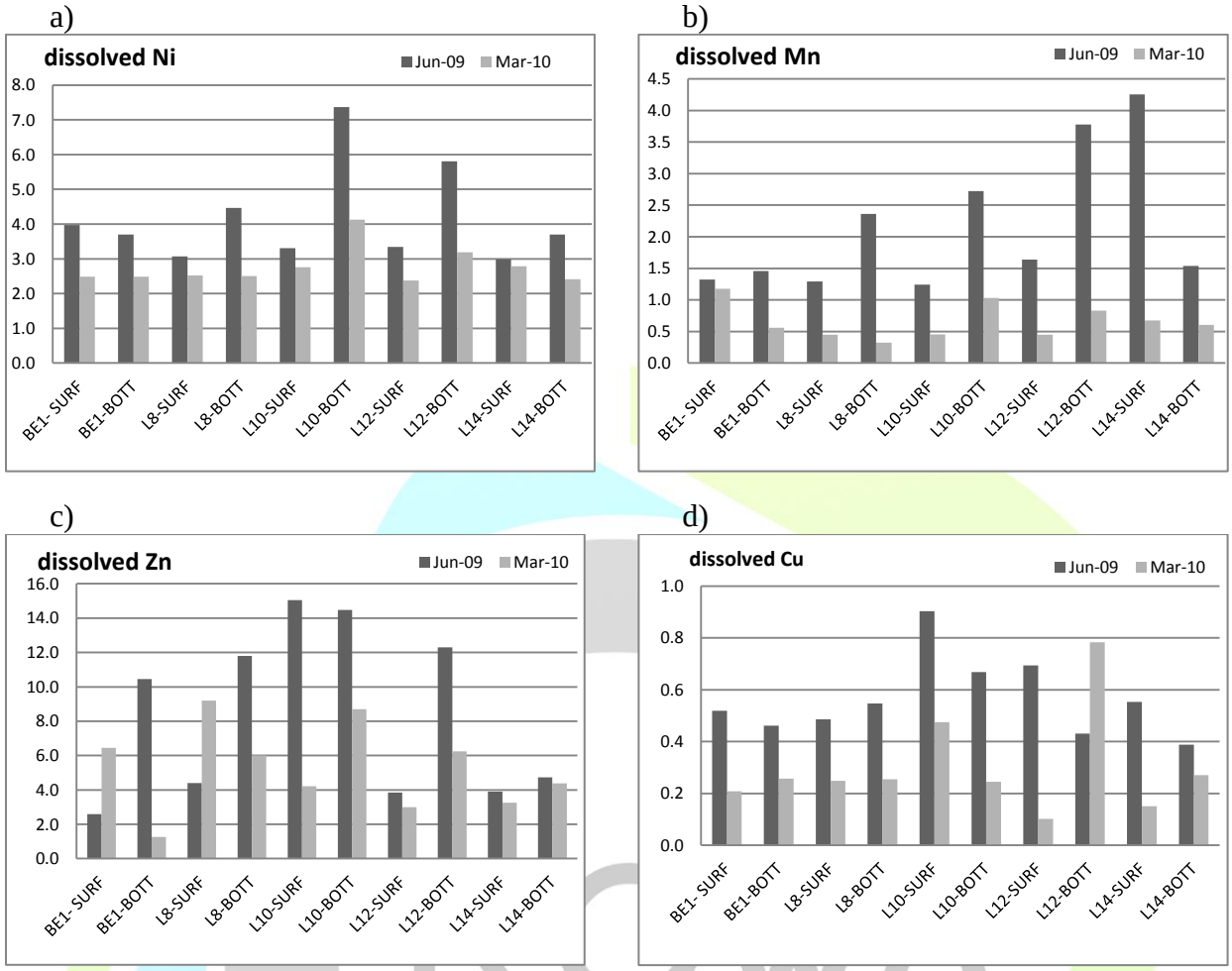

Figure 3: Dissolved concentrations of Ni, Mn, Zn and Cu(µg/l) during different sampling seasons in the dumping area. (Offshore stations)

As Ni & Mn, dissolved Zn and Cu concentrations also decreased during March 2010. There was however some exceptions in stations L-8 and the reference station BE1, where dissolved Zn showed relatively high concentrations in March 2010.

The highest dissolved Zn and Cu levels were determined in stations L-10 and L-12 and mainly in the surface water samples that probably suggests in addition to slag contamination, other sources of anthropogenic activities.

4-CONCLUSION:

Discharging by product of mines and ore processing in sea water makes a major environmental problem in all over the world; the slag by-product of ferronickel smelting plant is a brittle component with considerable amount of toxic heavy metals which is being dumped in N. Euvoikos Gulf instead of being used in various recycling and constructions uses.

Zn and Cu are the two metals mostly affected by anthropogenic sources and their high concentrations in some stations might because of domestic effluent, aquaculture and agriculture activities.

Ni and Mn are the some of the main content of by-product and provided a significantly high quantity in LA- 7 and LA- 7a which are the nearest stations to the smelting plant and the shore line of village. Ni also showed significant concentrations in L-10 station of dumping area.

The results comparison with the US EPA revealed that all the metals concentrations were lower than the both chronic and acute threshold; while in some stations concentrations were slightly higher than CCC (Criterion Continuous concentration).

The comparison of both off shore and In shore results showed that dissolved Ni and Mn was significantly higher to other Greek areas which probably as a consequence of depositing the by-product of smelting plant in Larymna Bay, In addition the average concentration of Zn and Cu detected to be higher than open seas areas and most of the Greek contaminated bay.

The chemical effect of discharging have been discussed in this paper, and research is on-going in order to consider the slag impacts on aquatic animals and their communities, as well as the long term pollution threat posed by the bioaccumulation of heavy metals in sea food tissues, which easily can be transfer to human bodies through food chain.

REFERENCE:

MacFarlane, G. B.,&Burchettt, M. D. Cellular distribution of Cu, Pb, and Zn in the Grey Mangrove Avicemnia marina (Forsk.)., 2000. Vierh Aquatic Botanic, (68), 45–59.

Miller, G. G., Sweet, L. I., Adams, J. V., Omann, G. M., Passino-Reader, D. & Meter, P. G. In vitro toxicity and interactions of environmental contaminants (Arochlor 125 and mercury) and immunomodulatory agents (lipopolysaccharidae and cortisol) on thymocytes from lake trout (Salvelinus namaycus)., 2002, Fish and Shellfish Immunology, (13), 11–26.

Chronis, G. (Ed.). 1985, Study of the environmental impact of dumping metalliferous waste in the southern part of N. Evvoikos gulf. Technical Report IOFR, 254 pp

Dassenakis, M.H, Andrianos.G, Depazi.A, Konstantas. M, Karabela. A,Sakellari. M,Scoullos. The use of various methods for the study of metal pollution in marine sediments, the case of Euvoikos Gulf, Greece., 2003 Applied Geochemistry, (18), 781-794.

Dassenakis, M,. E, Karasakopoulou. B, Matzara. Chemical characteristics of Aetoliko lagoon, Greece, after an ecological shock.,1994, Marine Pollution Bulletin, (28),427-433l.

Fernands, C., A, Fontainhas-Fernandes. D, Cabra. M. A, Salgado. Heavy metals in water, sediments and tissue of *Liaza Salins* from Esmoriz – Paramos lagoon.,2008 Environ Monit Assess, (36), 267-

Forrest, B., N, Keely., P, Gillespic., G, Hopkins., B, Knight. 2007. Review of Ecological Effects of Mrine Finfish Aquaculture, Final report. Cawthorn Institute. New Zealand

Garcia, L.R., L,Tejeda- Valenzuela. E, Martin. G, Agustin. Dissolved and particulate metals in water from Sonora coast: a pristine zone of Gulf of California.,2011 Environ Monit Assess, (176), 109-123

HCMR.2005. In: Simboura, N. (Ed.), Study of the environmental impact of dumping coarse metalliferous waste in N. Euvoikos gulf. Final Technical Report HCMR, 145 pp

HCMR 1992. In: Papathanassiou, E. (Ed.), Environmental study of the Northern Evvoikos gulf. Technical Report HCMR, 243 pp.

Kozanoglou, C., Catsiki, V.A., 1997. Impact of a ferro-nickel smelting plant to the marine benthiclife. Chemosphere, 34 (12), 2673–2982

Michalopoulos, P., A, Karageoris. T, Kanelopoulos., X, Anagnostou, X, Zeri.2005 Environmental study of the Northern Evvoikos gulf. Technical Report HCMR, p 22-39

Nicolaidou, A., Nott, J.A., 1998. Metals in sediment, sea grass and gastropods near a nickel smelter in Greece: possible interactions. Mar. Pollut. Bull. 36 (5), 360–365.

Pollution Prevention & Abatement Handbook,World Bank Group, 1998. Nickel Smelting and Refining

Simboura, M., E,Papathanassiou. D, Sakelariou. The use of biotic index(Bentix) in assessing long term- effect of dumping coarse metalliferous waste on soft bottom benthic communities.2006. Ecological Indicators.

State of the Hellenic Marine Environment. Chapter IV,heavy metals in the marine environment. M, Dassenakis.,H, Kabari. Helenic Center for Marine Research.Institute of Oceanography.Athens 2005.

U.S Environmental Protection Agency (2009). National Recommended Water Quality Criteria. http://www.epa.gov/ost/criteria/wqctable/.

Zeri, C., F, Voutsinou-Taliadouri. Process affecting the distribution of dissolved trace metals in north Aegean Sea (Eater Mediterranean), 2009, Continental Shelf research, 23. 919-934

www. Larco.gr.