ANNEX 06 : POLLUTION ASSESMENT STUDY

Annex 06.2 Chemical Analysis Pollution Assessment Study

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March 2016

ENERGEAN OIL & GAS

PRINOS OFFSHORE DEVELOPMENT PROJECT

Trace metal determination and pollution assessment in sediments

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PRINOS OFFSHORE DEVELOPMENT PROJECT TRACE METAL DETERMINATION AND POLLUTION ASSESSMENT IN SEDIMENTS				
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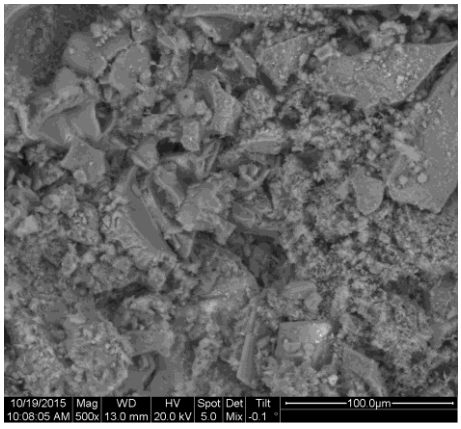
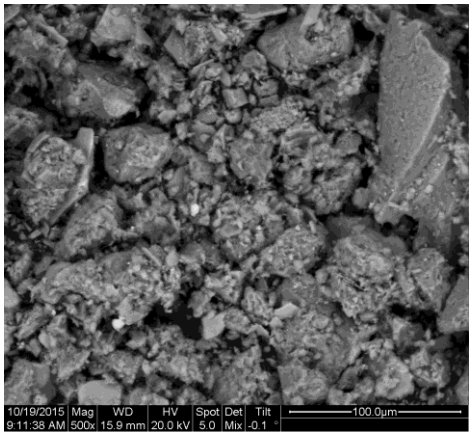
1 MORPHOLOGY OF SEDIMENTS COLLECTED IN PRINOS – KAVALA GULF AREA EXAMINED WITH SCANNING ELECTRON MICROSCOPE (SEM)



Sampling Site 13 (x500)



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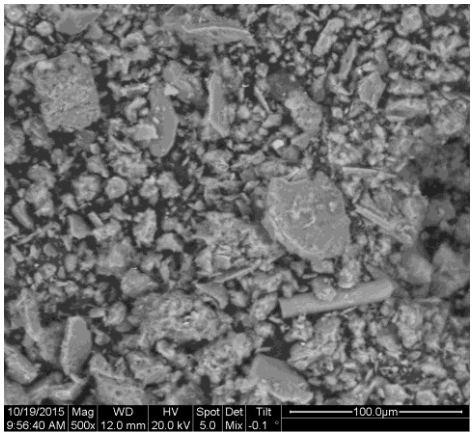
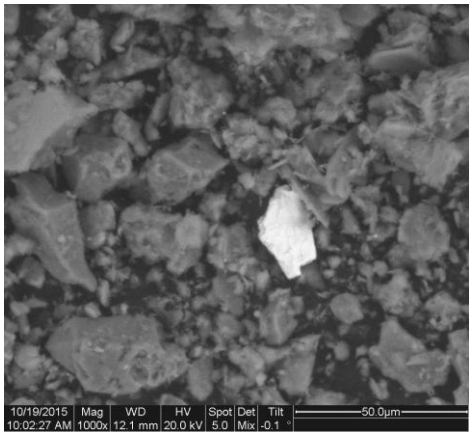


Sampling Site 3 (x500)



Sampling Site 3 (x1000)

1.1. INTRODUCTION

Heavy metals are among the most common environmental pollutants and their occurrence in the aquatic environment has become a major concern worldwide. There are basically three reservoirs of metals: water, sediment and biota. Heavy metals accumulate in sediments, as a result of complex physical and chemical mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds [1]. Adsorption, precipitation, diffusion processes, chemical reactions, biological activity and a combination of all those phenomena, render sediments as a major carrier and source of heavy metals in the aquatic system.

Study of the distribution of trace elements in sediments is of great importance in the context of environmental pollution. Sediments show less variation in time and there for they are preferably used as monitoring tools of contamination assessment. Heavy metals are being continuously introduced to coastal environment from a variety of sources natural or anthropogenic such as discharge of domestic sewage and industrial wastewater. Variations of metal concentrations can reflect the mixing of sediments from different origins and contamination from a variety of pollution sources. Their concentrations are used as fingerprints to locate sites of pollution but due to the wide range of possible contributing factors, care is required in the environmental assessment process [2].

The assessment of sediment enrichment with elements can be carried out in many ways. The different metal assessment indices applied on sediment environments, are mainly classified in three categories: contamination indices, background enrichment indices and ecological risk indices [3]. The most common ones are the index of geo-accumulation (I-geo) and pollution load index (PLI).The I-geo has been widely utilized as a measure of pollution in sediment while the pollution load index (PLI) gives a summative indication of the overall level of heavy metal toxicity in a particular sample.

The aims of this study were to determine the spatial distribution of heavy metals and to evaluate the contamination status of metals using different metal assessment indices such as enrichment factors (EFs), geoaccumulation index (*I*geo) and pollution load index (PLI).

The content of heavy metals in sediments has to be often monitored in order to provide essential information for environmental risk assessment. Monitoring of metal levels in sediments is useful not only for evaluating metal contamination but also for predicting influence on marine ecosystem.

1.2. SAMPLE TREATMENT AND ANALYSIS

Surface sediments were collected from thirteen (13) stations, kept within plastic bags, stored at 5 ^{o}C and were delivered together with five mussels. In addition two seawater samples were delivered separately.

All sediment samples were dried at 65±5 ^{o}C for 48h, after having removed the excess seawater and then sieved through a 1 mm sieve in order to remove coarse material (little rocks, brunches etc) and a 0.25 mm sieve to separate the fine fraction used for analysis. The soft part of two mussels was rinsed with deionised water and was also dried under the same conditions. The samples were ground to powder and homogenized (MNTUA). Two fish samples (F3+F4 and F2) and one mussel sample (MUOA) were delivered already lyophilised and were also ground to powder. The pre-treatment of the samples was according to the Standard Method USEPA 200.2 [1].

Digestion of samples was performed with 9 mL of concentrated HNO_3 and 1 mL of concentrated HCl at 175 ^{o}C for 30 minutes using the Milestone START D microwave digestion system. The temperature programme as well as the whole digestion method was according to the Standard Method USEPA 3051a [2]. The digestion method resulted to partial dissolution of the sediments.

Analyses of resulting solutions were carried out using the Perkin Elmer Optima 7000 DV Inductively Coupled Plasma Emission Spectrometer. The operating parameters and spectral lines were according to the Standard Method USEPA 200.7 [3].

The standard stock solution used was a Scharlau ICP multi element calibration standard solution x 26 element in nitric acid 5%. Analytical blanks were run in the same way as the samples. All measurements were conducted in triplicates with a RSD < 3%. Detection limits as well as quantification limits are presented in Table 1.

Table 1: Detection and quantification limits

Detection and quantification limits		
	Detection limit mg/L	Quantification limit mg/L
As	45	150
Pb	40	130
Cr	10	30
Cu	8	25
Mn	5	20

Detection and quantification limits		
	Detection limit mg/L	Quantification limit mg/L
Ni	15	50
Co	10	30
Zn	5	20
Cd	8	25

The sample from sampling site No 1 was split and treated in duplicate in order to estimate the reproducibility of the overall method. The recovery of the elements was calculated by spiking sample No 13 with standard solution, prior to digestion and measuring all elements in the resulted solution. The % recovery is reported in Table 2. Accuracy of the applied method was checked using the BAUM – U110 certified reference contaminated soil. The % accuracy was calculated as follows:

$$\%\ accuracy = \frac{measured\ value}{certified\ value} \times 100$$

All data are reported in Table 2. The certified values written refer to the extractable with aqua regia [4].

Table 2: Precision and accuracy of analytical method

Precision and accuracy of analytical method											
	Fe	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**	**Mo**
Sample	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
1	1.22	5.1	12.1	8.7	3.8	154.9	5.0	4.7	24.5	0.6	<0.5
1B	1.46	5.2	12.7	10.1	3.2	159.4	6.1	4.6	29.4	0.6	<0.5
Average	1.34	5.2	12.4	9.4	3.5	157.2	5.6	4.7	27.0	0.6	n/a
STD	0.12	0.06	0.3	0.7	0.3	2.3	0.5	0.1	2.5	0.0	n/a
RSTD	9.08	1.1	2.3	7.3	8.5	1.4	9.8	1.0	9.1	0.2	n/a
% recovery	98	83	93	98	103	97	95	92	107	87	84
U110 certified	-	13.0	185	190	262	580	95.6	14.5	990	7.0	-
U110 measured	-	10.9	184	190	267	540	91.4	14.1	946	8.3	-
% accuracy	-	83.8	99.5	100.0	101.9	93.1	95.6	97.2	95.6	118.6	-

1.3. RESULTS AND DISCUSSION

The results obtained from the analyses of all samples are reported in Table 3. All values are expressed in mg/kg of dry sample with the exception of iron Fe in sediments, which is expressed in % w/w. Minimum, maximum and median values determined in the sediments are also reported. The concentrations of all elements determined in the seawater samples were below the quantification limits of the applied method.

Table 3: Metal concentration in sediments, fish and mussels sampled in Kavala Gulf

Metal concentration in sediments, fish and mussels sampled in Kavala Gulf											
Sediments	**% w/w**				**μg/g**						
Sample name	**Fe**	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**	**Mo**
Site 1	1.22	5.1	12.1	8.7	3.8	154.9	5.0	4.7	24.5	0.6	<0.5
Site 3	4.69	12.2	41.6	59.8	24.6	310.3	34.5	11.2	106.4	1.8	<0.5
Site 4	1.82	6.1	22.1	24.9	9.1	226.5	14.8	7.0	51.2	1.1	<0.5
Site 5	1.16	7.1	23.1	17.8	8.1	190.1	9.8	4.4	39.3	0.7	<0.5
Site 6	1.40	6.9	19.7	13.5	4.6	156.5	7.0	4.3	37.2	0.7	<0.5
Site 7	2.85	9.7	34.9	52.5	21.1	283.6	30.3	9.3	89.0	1.4	<0.5
Site 8	1.06	4.3	24.4	16.7	8.0	146.7	9.9	4.0	48.4	0.7	<0.5
Site 10	0.92	7.5	25.7	14.0	6.5	127.1	7.6	3.6	35.4	0.6	<0.5
Site 11	0.61	4.4	31.2	13.6	6.8	97.0	5.8	2.8	33.7	0.4	<0.5
Site 12	0.60	5.8	16.3	9.6	3.7	80.4	5.5	2.6	22.8	0.4	<0.5
Site 13	0.90	3.3	18.8	12.7	5.6	166.4	7.8	3.8	31.6	0.6	<0.5
Site 1E	0.61	7.85	16.13	9.97	25.9	222.2	5.7	4.6	23.5	1.81	<0.5
Site 2E	0.77	6.10	11.46	7.41	30.8	238.3	4.6	2.7	26.8	1.71	<0.5
maximum	4.69	12.2	41.6	59.8	24.6	310.3	34.5	11.2	106.4	1.8	n/a
minimum	0.60	3.3	12.1	8.7	3.7	80.4	5.0	2.6	22.8	0.4	n/a

median	1.16	6.1	23.1	14.0	6.8	156.5	7.8	4.3	37.2	0.7	n/a
STDEV	1.21	2.6	8.5	17.4	7.0	72.1	10.2	2.8	26.7	0.4	n/a
Organisms					**µg/g**						
Sample name	**Fe**	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**	**Mo**
Mussels M_{NTUA}	69.1	5.8	1.7	<0.5	2.3	4.7	1.4	1.1	52.7	0.5	<0.5
Mussels M_{UOA}	81.1	7.1	2.1	<0.5	3.3	3.8	1.7	1.1	74.7	0.6	<0.5
Fish F3+F4	26.5	<0.5	1.2	<0.5	1.4	2.1	0.9	0.7	32.8	0.2	<0.5
Fish F2	35.0	0.3	1.6	<0.5	2.3	1.7	0.9	0.7	26.8	0.1	<0.5

Pearson correlation coefficients were calculated for sediments and organisms (fish and mussels), only for the elements above detection limit and are presented in Tables 4a and 4b.

The strong correlation of most elements reveals a common origin of the examined samples. As it can be seen all elements except copper (Cu) and cadmium (Cd) show strong correlation with iron (Fe), suggesting common lithogenic origin. Cd and Cu on the other hand, show strong correlation between them but not with the rest of the elements thus suggesting a common, most probably, anthropogenic origin. In case of fish and mussels the correlation is strong, as expected, verifying the common origin of the trace elements but it must be underlined that the results should be considered with caution due to the limited number of samples.

Table 4: Pearson's correlation matrices

Table 4a. Pearson's correlation matrix of 10 elements from the 13 sampling sites										
	Fe	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**
Fe	1									
As	0.8060	1								
Pb	0.7499	0.6124	1							
Cr	0.9472	0.7931	0.8525	1						
Cu	0.3795	0.5775	0.1620	0.3970	1					
Mn	0.7506	0.7229	0.3930	0.7334	0.7813	1				
Ni	0.9496	0.7886	0.8230	0.9977	0.4120	0.7559	1			
Co	0.9544	0.7962	0.7117	0.9491	0.4052	0.8126	0.9560	1		
Zn	0.9502	0.7590	0.8643	0.9880	0.3805	0.7204	0.9862	0.9310	1	
Cd	0.4955	0.6670	0.1758	0.4765	0.9582	0.8685	0.4969	0.5550	0.4545	1

Table 4b. Pearson's correlation matrix of 9 elements from the 4 fish and mussels samples									
	Fe	As	Pb	Cu	Mn	Ni	Co	Zn	Cd
Fe	1								
As	0.9941	1							
Pb	0.9008	0.8507	1						
Cu	0.8484	0.7905	0.9932	1					
Mn	0.8699	0.9069	0.5830	0.4863	1				
Ni	0.9833	0.9849	0.8794	0.8349	0.8309	1			
Co	0.9736	0.9890	0.7809	0.7066	0.9588	0.9507	1		
Zn	0.9415	0.9491	0.8383	0.8026	0.7713	0.9871	0.9031	1	
Cd	0.9538	0.9785	0.7576	0.6945	0.9054	0.9755	0.9701	0.9665	1

Estimation of the element distribution among the sampling sites is depicted in graphs Figure 1: Distribution of Cr, Cu, Ni and Cd in the sampling sites (Cd is plotted as ten times the actual concentration for scale reasons)

Figure 2 and Figure 3 revealing peak values for all the examined elements at the sampling sites 3 and 7, although As, Pb and Mn show a broader distribution.

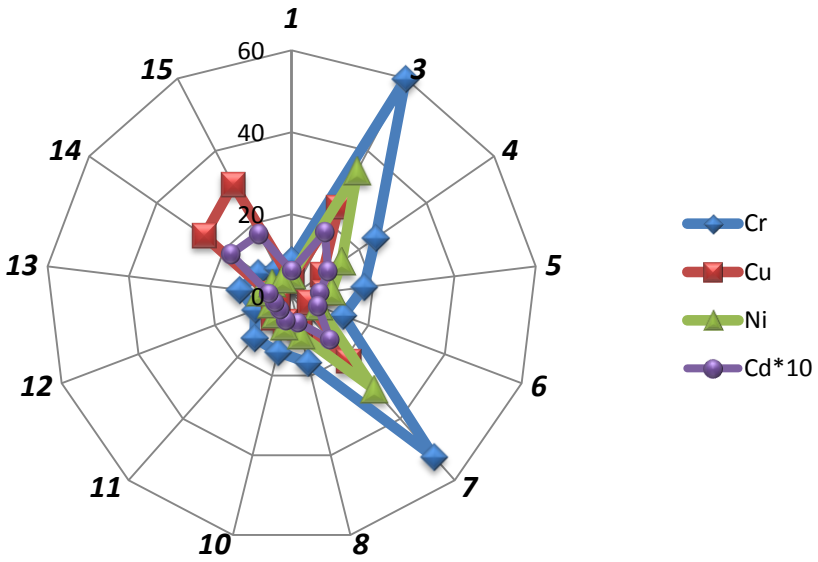


Figure 1: Distribution of Cr, Cu, Ni and Cd in the sampling sites (Cd is plotted as ten times the actual concentration for scale reasons)

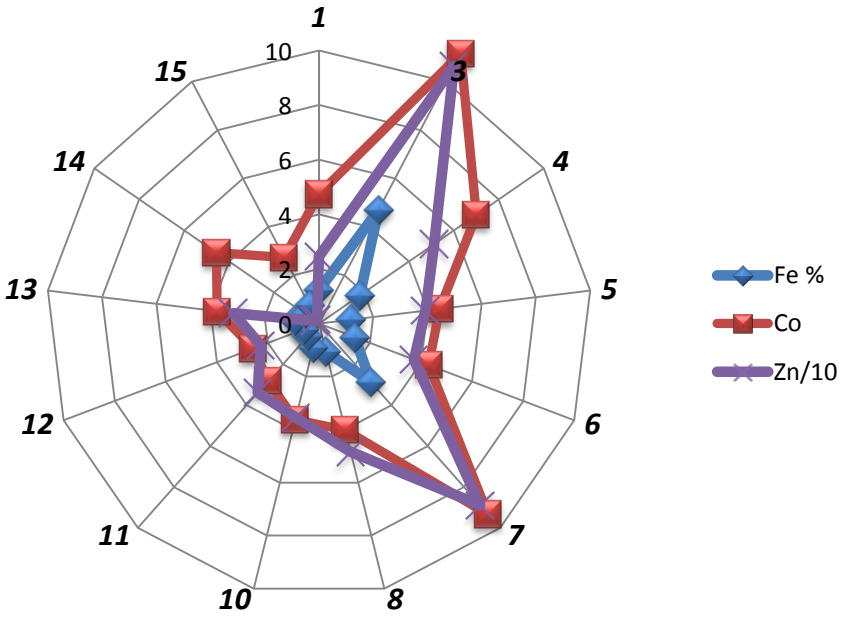


Figure 2: Distribution of Co, Zn and Fe in the sampling sites (Zinc is plotted as 1/10 of the actual concentration for scale reasons)

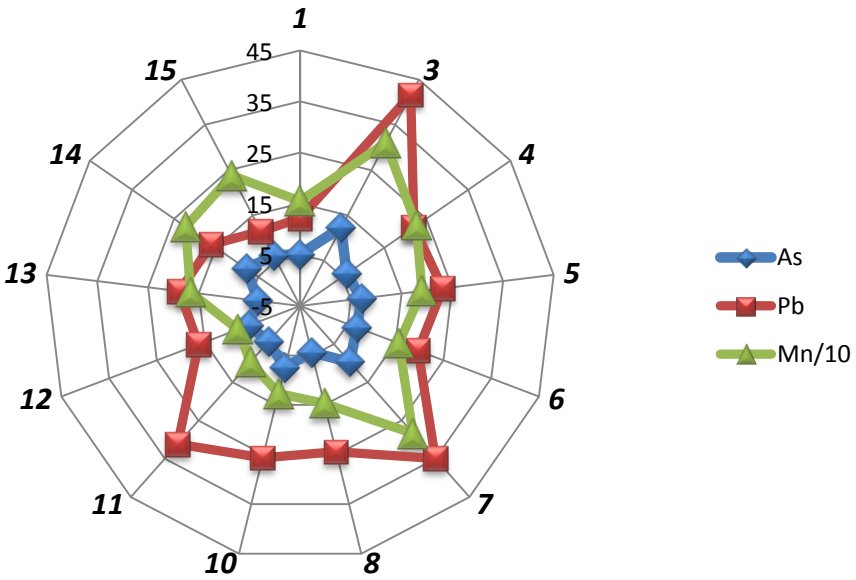


Figure 3: Distribution of Pb, As and Mn in the sampling sites (Manganese is plotted as 1/10 of the actual concentration for scale reasons)

As for the distribution of elements in the organisms analysed, increased values of arsenic and manganese are observed in mussels compared to the fish samples analysed (Figure 4)

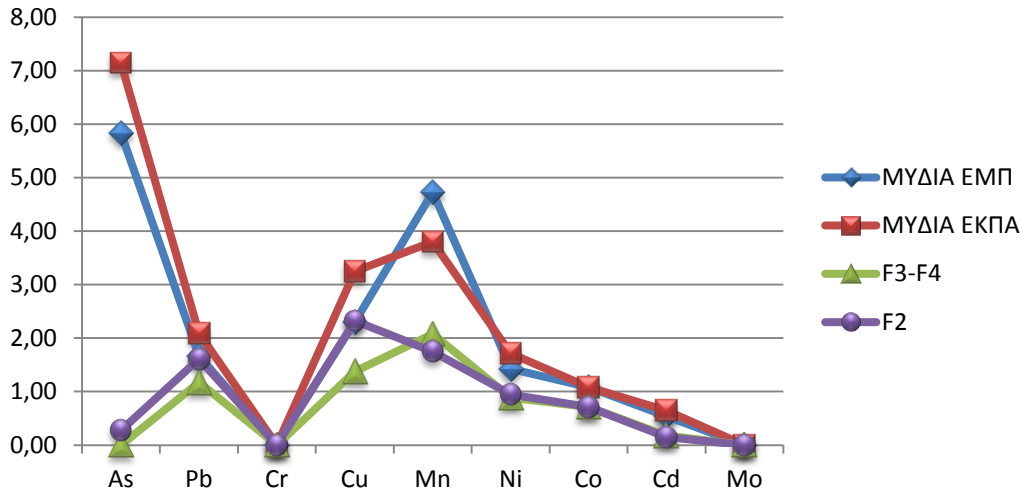


Figure 4: Elemental distribution of fish and mussels samples.

1.4. ASSESSMENT OF METAL CONTAMINATION

Several methods have been proposed for quantifying the metal contamination in soils and sediments by calculating factors and indexes in respect to various reference environments [5].

The methods used in this study are based on the enrichment factors (EF), the contamination factors (CF), the degree of contamination (Cd), the modified degree of contamination (mCd), the geoaccumulation index (Igeo) as well as the pollution load index (PLI).

1.4.1 Enrichment Factor EF

The enrichment factor was calculated using the formula used by Buat-Menard and Chesselet,[6] as shown in (1)

$$EF = \frac{C_n \; C_{ref} \; _{sample}}{B_n \; B_{ref}} \qquad (1)$$

where Cn (sample) is the concentration of the metal element, as determined in the studied environment and Cref (sample) is the concentration of the metal element, as reported in the reference environment. Bn is the concentration of the reference element as determined in the studied environment and Bref is the concentration of the reference element as reported in a reference environment.

The EF method normalizes the examined metal with respect to a reference metal such as Al or Fe. Iron was selected in this study since its distribution is not related to the other metals determined and its natural concentration is relatively high and therefore not expected to be significantly enriched by anthropogenic sources. [7, 8]

The variation of EF highly depends on the selection of reference environment. Average crustal values are widely used although this way, natural geochemical variability is ignored thus often leading to false estimation of anomalies [9]. Using soils originated from the area of interest is proposed as a more realistic approach as long as they can be positively classified as “unpolluted”. The selection of the reference environment is of great importance and in some cases critical. The values available for the area of interest in this study are, besides the average crust, the reported concentrations in Alexandroupolis Gulf [11] and the measured ones at sampling site 13. Alexandroupolis Gulf could be considered of similar lithogenic origin, due to the vicinity and hypothetically unpolluted. Sediment sampled from the sampling site 13 is definitely of the same lithogenic origin and since it is far away from the existing and future platforms, could be considered as non-polluted from the specific activity.

The reference values used in this study were the average crust values[10], for the following reasons: Firstly there are data for all elements showing no significant difference from the values determined in Alexandroupolis Gulf, reported as unpolluted nearby area. Secondly, the goal of this study is not to assess the present pollution load but rather to act as reference for environmental impact assessment of future activities. Choice of site 13 as reference could be justified but since its composition varies with time according to the overall pollution load, it was considered as more accurate to compare always to the standard earth crust values. Never the less, assessment was also performed using sediment from site 13 as reference environment and the results are presented in Appendix I.
The enrichment factors calculated based on average earth crust are presented in Table 5.

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Table 5: Enrichment factors for the sediments at the 13 sampling

Enrichment factors for the sediments at the 13 sampling										
Sample	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**	**median**
1	3.43	2.29	0.30	0.44	0.64	0.34	0.88	1.18	21.41	0.88
3	2.13	2.05	0.54	0.73	0.33	0.61	0.54	1.33	16.72	0.73
4	2.73	2.80	0.58	0.70	0.63	0.68	0.87	1.65	26.34	0.87
5	4.98	4.59	0.65	0.98	0.83	0.71	0.87	1.98	26.24	0.98
6	4.05	3.25	0.41	0.46	0.57	0.42	0.70	1.56	21.81	0.70
7	2.78	2.82	0.78	1.04	0.50	0.89	0.74	1.82	21.37	1.04
8	3.34	5.32	0.67	1.06	0.70	0.78	0.86	2.68	28.81	1.06
10	6.65	6.46	0.65	0.99	0.70	0.70	0.90	2.26	28.50	0.99
11	5.86	11.77	0.95	1.57	0.80	0.80	1.04	3.23	28.52	1.57
12	7.87	6.23	0.68	0.85	0.67	0.76	0.97	2.21	28.90	0.97
13	2.99	4.80	0.60	0.87	0.93	0.72	0.94	2.05	28.93	0.94
14	10.50	6.09	0.70	5.95	1.84	0.78	1.69	2.25	128.80	2.25
15	6.44	3.42	0.41	5.59	1.56	0.50	0.80	2.03	96.34	2.03
median	4.05	4.59	0.65	0.98	0.70	0.71	0.87	2.03	28.50	0.98

Classification of soils relatively to EF [12] used as follows: EF < 2 = deficiently to minimal enrichment, 2 ≤ EF < 5 = moderate enrichment, 5 ≤ EF < 20 = significant enrichment, 20 ≤ EF < 40 = very high enrichment and EF ≥ 40 = extremely high enrichment.

As it is obvious from the results, enrichment factor shows values below 2 for Cr, Cu, Mn, Ni, Co and practically for Zn, depicting not at all to minimum enrichment for these elements. EF values for As vary between 2 to 5 for most sampling sites, suggesting moderate enrichment. Cadmium EF values are within the range of 20 to 40, classified as very high enrichment. The argument of false anomaly due to the choice of average earth crust as reference environment should be taken into consideration. The extreme values for sampling sites 14 and 15 cannot be taken into consideration since they are due rather to low iron content than high Cd values. If the enrichment factors for Cd are calculated using the values reported for Alexandroupolis Gulf, then the sediments fall within the range of 5<EF<20, classified as significant enrichment. In any case the results must be assessed in combination to the other pollution indexes.

1.4.2 Contamination Factor CF, Degree of Contamination Cd and modified Degree of Contamination mCd

The sediments were also assessed for contamination factor CF, degree of contamination and modified degree of contamination. The modified degree of contamination in soil by metals was calculated based on the method presented by Abrahim [9] shown in (2).

$$mC_d = \frac{1}{N}\sum_{i=1}^{N} CF_i \qquad (2)$$

where N is the number of elements analysed and CF is the contamination factor calculated as shown in (3).

$$CF = \frac{C_{m\ Sample}}{C_{m\ Background}} \qquad (3)$$

where Cm Sample is the median concentration of the metal element, as determined in the studied environment and Cm Background is the median concentration of the metal element, as reported in the reference environment. It is worth noting that (2) is a modified and generalized form of the degree of contamination (Cd) formula, in (4), proposed by Håkanson,[13].

$$C_d = \sum_{i=1}^{N} CF_i \qquad (4)$$

The calculated values are given in **Table** 6. Classifications of sediments for the above factors are shown in Table 7.

Table 6: Contamination factors, degree of contamination and modified degree of contamination for the 13 sampling sites

Contamination factors, degree of contamination and modified degree of contamination for the 13 sampling sites.											
	C F									C_d	mC_d
Sample	As	Pb	Cr	Cu	Mn	Ni	Co	Zn	Cd		
1	1.07	0.71	0.09	0.14	0.20	0.11	0.27	0.37	6.67	**9.62**	**1.07**
3	2.55	2.45	0.65	0.88	0.40	0.73	0.65	1.59	20.00	**29.90**	**3.32**
4	1.27	1.30	0.27	0.32	0.29	0.31	0.41	0.76	12.22	**17.16**	**1.91**
5	1.48	1.36	0.19	0.29	0.25	0.21	0.26	0.59	7.78	**12.40**	**1.38**
6	1.44	1.16	0.15	0.16	0.20	0.15	0.25	0.55	7.78	**11.84**	**1.32**
7	2.03	2.05	0.57	0.76	0.37	0.65	0.54	1.33	15.56	**23.84**	**2.65**
8	0.90	1.44	0.18	0.29	0.19	0.21	0.23	0.72	7.78	**11.94**	**1.33**
10	1.55	1.51	0.15	0.23	0.16	0.16	0.21	0.53	6.67	**11.18**	**1.24**
11	0.91	1.83	0.15	0.24	0.13	0.12	0.16	0.50	4.44	**8.50**	**0.94**
12	1.21	0.96	0.10	0.13	0.10	0.12	0.15	0.34	4.44	**7.56**	**0.84**
13	0.69	1.11	0.14	0.20	0.21	0.17	0.22	0.47	6.67	**9.87**	**1.10**
14	1.64	0.95	0.11	0.93	0.29	0.12	0.26	0.35	20.06	**24.70**	**2.74**
15	1.27	0.67	0.08	1.10	0.31	0.10	0.16	0.40	18.99	**23.08**	**2.56**
median	1.27	1.30	0.15	0.29	0.21	0.16	0.25	0.53	7.78	**11.94**	**1.33**

Table 7: Classification of Contamination factors, degree of contamination and modified degree of contamination

Classification of Contamination factors, degree of contamination and modified degree of contamination.				
CF classes	**C_d classes**	**CF and C_d contamination level**	**mC_d classes**	**mC_d contamination level**
			$mC_d < 1.5$	Null to very low degree of contamination
$CF < 1$	**$C_d < 8$**	Low CF indicating low contamination / low C_d	**$1.5 \leq mC_d < 2$**	Low degree of contamination
$1 \leq CF < 3$	**$8 \leq C_d < 16$**	Moderate CF / C_d	**$2 \leq mC_d < 4$**	Moderate degree of contamination
$3 \leq CF < 6$	**$16 \leq C_d < 32$**	Considerable CF / C_d	**$4 \leq mC_d < 8$**	High degree of contamination
$CF \geq 6$	**$C_d \geq 32$**	Very high CF / C_d	**$8 \leq mC_d < 16$**	Very high degree of contamination
			$16 \leq mC_d < 32$	Extremely high degree of contamination
			$mC_d \geq 32$	Ultra-high degree of contamination

The aim of calculating contamination factor is to provide a measure of the degree of overall contamination of surface in the sampled site. The overall contamination of the sediments, based on CF values, indicate very low to moderate degree of contamination with the exception, again, of cadmium which show considerable to very high contamination, especially for the sampling sites 3,7,14 and 15. In case of degree of contamination (Cd), the sediments fall in the category of moderate to considerable contamination. The modified degree of contamination suggests that the studied area shows a low to moderate degree of contamination. Modified degree of contamination (mCd), is an averaging method and should consequently be representative of the studied area although it must be taken into consideration that in this case, the values obtained are due mainly to cadmium.

1.4.3 Geoaccumulation Index, Igeo

The index of geoaccumulation was also calculated using the formula (5), suggested by Müller[14,15].

The Igeo assesses the contamination by comparing the current metal concentrations to the pre-industrial ones. The factor 1.5 introduced in the formula minimises the effect of possible variations in the background values, Cm Background, attributed to lithogenic variations in soils.

$$I_{geo} = \log_2 \left[\frac{C_{m\ sample}}{\left(1.5 \times C_{m\ background}\right)} \right] \quad (5)$$

The geoaccumulation indexes calculated in this study are reported in Table 8, while the classification according to the Igeo is given in Table 9.

Table 8: Geoaccumulation Index (I geo) of the 13 sampling sites

Geoaccumulation Index (I geo) of the 13 sampling sites									
Sample	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**
1	-0,49	-1,07	-3,99	-3,45	-2,91	-3,81	-2,45	-2,04	2,19
3	0,77	0,71	-1,21	-0,77	-1,91	-1,03	-1,22	0,08	3,70
4	-0,24	-0,21	-2,47	-2,21	-2,36	-2,25	-1,89	-0,97	3,00
5	-0,02	-0,14	-2,96	-2,37	-2,61	-2,84	-2,54	-1,36	2,35
6	-0,05	-0,37	-3,36	-3,20	-2,89	-3,33	-2,59	-1,44	2,32
7	0,43	0,45	-1,40	-0,99	-2,04	-1,22	-1,48	-0,18	3,39
8	-0,73	-0,06	-3,05	-2,39	-2,99	-2,83	-2,69	-1,05	2,30
10	0,05	0,01	-3,30	-2,69	-3,19	-3,21	-2,84	-1,50	2,16
11	-0,72	0,29	-3,34	-2,62	-3,58	-3,60	-3,21	-1,57	1,70
12	-0,31	-0,65	-3,85	-3,52	-3,85	-3,69	-3,33	-2,14	1,71
13	-1,12	-0,44	-3,44	-2,90	-2,80	-3,18	-2,79	-1,67	2,05
14	0,12	-0,66	-3,79	-0,70	-2,39	-3,63	-2,51	-2,10	3,74
15	-0,24	-1,15	-4,22	-0,45	-2,29	-3,93	-3,25	-1,91	3,66

Table 9: Classification of geoaccumulation Index

Classification of geoaccumulation Index		
Igeo values	**Class**	**Description**
Igeo > 5	6	Extremely contaminated
4 < Igeo ≤ 5	5	Strongly to extremely contaminated
3 < Igeo ≤ 4	4	Strongly contaminated
2 < Igeo ≤ 3	3	Moderately to strongly contaminated
1 < Igeo ≤ 2	2	Moderately contaminated
0 < Igeo ≤ 1	1	Uncontaminated to moderately contaminated
Igeo = 0	0	Uncontaminated

The geoaccumulation index assessment verifies the conclusion that the studied area is uncontaminated in respect to all elements except cadmium. The values of cadmium lead to the characterisation of the sediments as moderately to strongly contaminated.

1.4.4 Pollution Load index, PLI

Pollution Load index was also calculated according to the formula:

$$PLI = \left(\prod_{i=1}^{N} CF_i\right)^{1/N} \quad (6)$$

where N is the number of metals studied and CF is the contamination factor as calculated above.

The PLI value gives an estimate of the metal contamination status and the relevant actions to be taken. PLI< 1, represents almost perfection, PLI= 1 denotes baseline levels of pollutants while PLI> 1 indicates deterioration of the site and actions should be considered. [16]

PLI values calculated, using the average earth crust as reference (PLI [crust]), are presented in Table 10. PLI values calculated using Alexandroupolis Gulf, as reference environment (PLI [gulf]) [11], are also presented in the Table 10, just for comparison reasons. Sediments classification does not seem to alter significantly according to the different reference environments.

As it is can been seen PLI is less than 1 in all sites except 3 and 7, confirming the status of unpolluted sediments for all sites besides 3 and 7.

Table 10: Pollution Load Index of the 13 sampling sites

Pollution Load Index of the 13 sampling sites		
Sample	**PLI [crust]**	**PLI [gulf]**
1	0.41	0.44
3	1.36	1.70
4	0.74	0.88
5	0.61	0.71
6	0.51	0.58
7	1.17	1.47
8	0.57	0.73
10	0.53	0.63
11	0.45	0.59
12	0.37	0.44
13	0.47	0.57
14	0.63	0.72
15	0.55	0.66

Pollution Load Index of the 13 sampling sites		
Sample	**PLI [crust]**	**PLI [gulf]**
median	0.55	0.66

1.5. CONCLUSION

The overall studied area shows minor enrichment for all elements determined except cadmium (Cd).

Despite this observed anomaly, the quality of the sediments is below baseline pollution with the exception of sites 3 and 7 which show increasing pollution levels and therefore should be monitored and reassessed in near future. The conclusion is drawn based on the average earth crust as reference environment and is considered to be representative of the present situation.

Assessment based on the sample collected at sampling site 13, considered as reference unpolluted environment, was also performed (Appendix I) and can be used for assessing pollution load of future activities.

2 REFERENCES

1. U.S. Environmental Protection Agency Method 200.2, SAMPLE PREPARATION PROCEDURE FOR SPECTROCHEMICAL DETERMINATION OF TOTAL RECOVERABLE ELEMENTS, Revision 2.8 (1994)
2. U.S. Environmental Protection Agency Method 3051a, MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS, SW-846 Ch 3.2, Update IVA (1998)
3. U.S. Environmental Protection Agency Method 200.7, DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY, Revision 4.4 (1994)
4. Certification Report CRM BAM-U110 (2006) BERICHT zur Zertifizierung der Gesamtgehalte und der mit Königswasser extrahierbaren Gehalte der Elemente As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb und Zn in einer Bodenprobe - Zertifiziertes Referenzmaterial BAM - U110), Bundesanstalt für Materialforschung und -prüfung (BAM) (http://www.bam.de/index_en.htm), FG I.1 - Anorganisch-chemische Analytik; Referenzmaterialien, Richard-Willstätter-Str. 11, D - 12489 Berlin.
5. Likuku A.S., Mmolawa K.B., Gaboutloeloe G.K., Environment and Ecology Research 1(2): 32-40 (2013)
6. Buat-Menard P. and Chesselet R., *Earth and Planetary Science Letters,* 42, 399-411 (1979)
7. Deely J.M., Fergusson J.E., The Science of the Total Environment 153, 97-111 (1994)
8. Niencheski L.E., Windom H.L. and Smith R., *Marine Pollution Bulletin,* Vol. 28, No. 2, pp. 96-102 (1994)
9. Abrahim G. M. S. & Parker R. J., Environ Monit Assess 136:227–238 (2008)
10. Rudnick, R., Gao, S., 2003. Composition of the continental crust. In: Rudnick, R.L. (Ed.), The Crust. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry, vol. 3. Elsevier–Pergamon, Oxford, pp. 1–64.
11. Sylaios G., Kamidis N. and Stamatis N., Soil and Sediment Contamination, 21:673-700 (2012)
12. Sutherland R.A., Tolosa C. A., Tack F. M. G., Verloo M. G. , Arch. Environ. Contam. Toxicol. 38, 428–438 (2000)
13. Hakanson L. *Water Research* Vol. 14, pp. 975 to 1001 Pergamon Press Ltd (1980)

14. Muller G Index of geoaccumulation in sediments of the Rhine River. GeoJournal 2:108–118 (1969)
15. U.Forstner and G.Muller, GeoJournal 5.5 417-432 (1981)
16. Iwuoha G.N. , Osuji L.C. and Horsfall M. Jnr. *Research Journal of Chemical Sciences* Vol. 2(8), 1-8, August (2012)

3 APPENDICES

APPENDIX I

Table 11: Enrichment factors for the sediments at the 13 sampling sites using sampling site 13 as reference

Enrichment factors for the sediments at the 13 sampling sites using sampling site 13 as reference										
Sample	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**	**median**
1	1.14	0.47	0.50	0.50	0.69	0.48	0.93	0.57	0.81	0.6
3	0.71	0.42	0.90	0.84	0.36	0.85	0.57	0.65	0.60	0.6
4	0.91	0.58	0.97	0.80	0.67	0.94	0.92	0.80	0.96	0.9
5	1.66	0.95	1.08	1.12	0.88	0.98	0.92	0.96	0.95	1.0
6	1.35	0.67	0.68	0.52	0.61	0.58	0.74	0.76	0.78	0.7
7	0.93	0.58	1.30	1.18	0.54	1.23	0.78	0.89	0.80	0.9
8	1.11	1.10	1.12	1.21	0.75	1.09	0.91	1.30	1.01	1.1
10	2.21	1.34	1.08	1.13	0.75	0.96	0.95	1.10	1.06	1.1
11	1.95	2.44	1.58	1.79	0.86	1.10	1.10	1.57	1.15	1.6
12	2.62	1.29	1.12	0.97	0.72	1.05	1.02	1.07	1.18	1.1
13	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.0
14	3.50	1.26	1.16	6.79	1.97	1.08	1.79	1.10	4.75	1.8
15	2.15	0.71	0.68	6.38	1.67	0.69	0.85	0.99	3.55	1.0
median	1.35	0.95	1.08	1.12	0.75	0.98	0.92	0.99	1.00	

Table 12: Contamination factors, degree of contamination and modified degree of contamination for the 13 sampling sites using sampling site 13 as reference

Contamination factors, degree of contamination and modified degree of contamination for the 13 sampling sites using sampling site 13 as reference											
	C F									**C_d**	**mC_d**
Sample	**As**	**Pb**	**Cr**	**Cu**	**Mn**	**Ni**	**Co**	**Zn**	**Cd**		
1	1.55	0.64	0.68	0.68	0.93	0.65	1.26	0.78	1.10	8.27	0.92
3	3.70	2.21	4.71	4.37	1.87	4.43	2.97	3.37	3.14	30.75	3.42
4	1.84	1.17	1.96	1.62	1.36	1.90	1.86	1.62	1.93	15.26	1.70
5	2.14	1.23	1.40	1.45	1.14	1.26	1.18	1.24	1.23	12.28	1.36
6	2.09	1.05	1.06	0.81	0.94	0.90	1.14	1.18	1.21	10.38	1.15
7	2.94	1.85	4.13	3.76	1.70	3.89	2.48	2.81	2.52	26.09	2.90

Contamination factors, degree of contamination and modified degree of contamination for the 13 sampling sites using sampling site 13 as reference											
	C F									C_d	mC_d
Sample	As	Pb	Cr	Cu	Mn	Ni	Co	Zn	Cd		
8	1.31	1.30	1.31	1.43	0.88	1.28	1.07	1.53	1.18	11.29	1.25
10	2.25	1.36	1.10	1.15	0.76	0.98	0.96	1.12	1.08	10.78	1.20
11	1.32	1.66	1.07	1.21	0.58	0.75	0.75	1.07	0.78	9.20	1.02
12	1.76	0.87	0.75	0.65	0.48	0.70	0.69	0.72	0.79	7.40	0.82
13	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	9.00	1.00
14	2.37	0.86	0.78	4.61	1.34	0.73	1.21	0.74	3.22	15.86	1.76
15	1.84	0.61	0.58	5.48	1.43	0.60	0.73	0.85	3.05	15.16	1.68
median	1.84	1.23	1.10	1.21	0.94	1.00	1.14	1.18	1.18	10.78	1.20

Table 13: Geoaccumulation Index (I geo) of the 13 sampling sites using sampling site 13 as reference

Geoaccumulation Index (I geo) of the 13 sampling sites using sampling site 13 as reference									
Sample	As	Pb	Cr	Cu	Mn	Ni	Co	Zn	Cd
1	0.0	-1.2	-1.1	-1.1	-0.7	-1.2	-0.3	-1.0	-0.4
3	1.3	0.6	1.6	1.5	0.3	1.6	1.0	1.2	1.1
4	0.3	-0.4	0.4	0.1	-0.1	0.3	0.3	0.1	0.4
5	0.5	-0.3	-0.1	-0.1	-0.4	-0.2	-0.3	-0.3	-0.3
6	0.5	-0.5	-0.5	-0.9	-0.7	-0.7	-0.4	-0.4	-0.3
7	1.0	0.3	1.5	1.3	0.2	1.4	0.7	0.9	0.8
8	-0.2	-0.2	-0.2	-0.1	-0.8	-0.2	-0.5	0.0	-0.3
10	0.6	-0.1	-0.4	-0.4	-1.0	-0.6	-0.6	-0.4	-0.5
11	-0.2	0.1	-0.5	-0.3	-1.4	-1.0	-1.0	-0.5	-0.9
12	0.2	-0.8	-1.0	-1.2	-1.6	-1.1	-1.1	-1.1	-0.9
13	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6	-0.6
14	0.7	-0.8	-0.9	1.6	-0.2	-1.0	-0.3	-1.0	1.1
15	0.3	-1.3	-1.4	1.9	-0.1	-1.3	-1.0	-0.8	1.0

Table 14: Pollution Load Index of the 13 sampling sites using sampling site 13 as reference

Pollution Load Index of the 13 sampling sites using sampling site 13 as reference	
Sample	PLI
1	0.89

Pollution Load Index of the 13 sampling sites using sampling site 13 as reference	
3	2.91
4	1.59
5	1.30
6	1.10
7	2.51
8	1.21
10	1.13
11	0.98
12	0.79
13	1.00
14	1.35
15	1.19
median	1.13