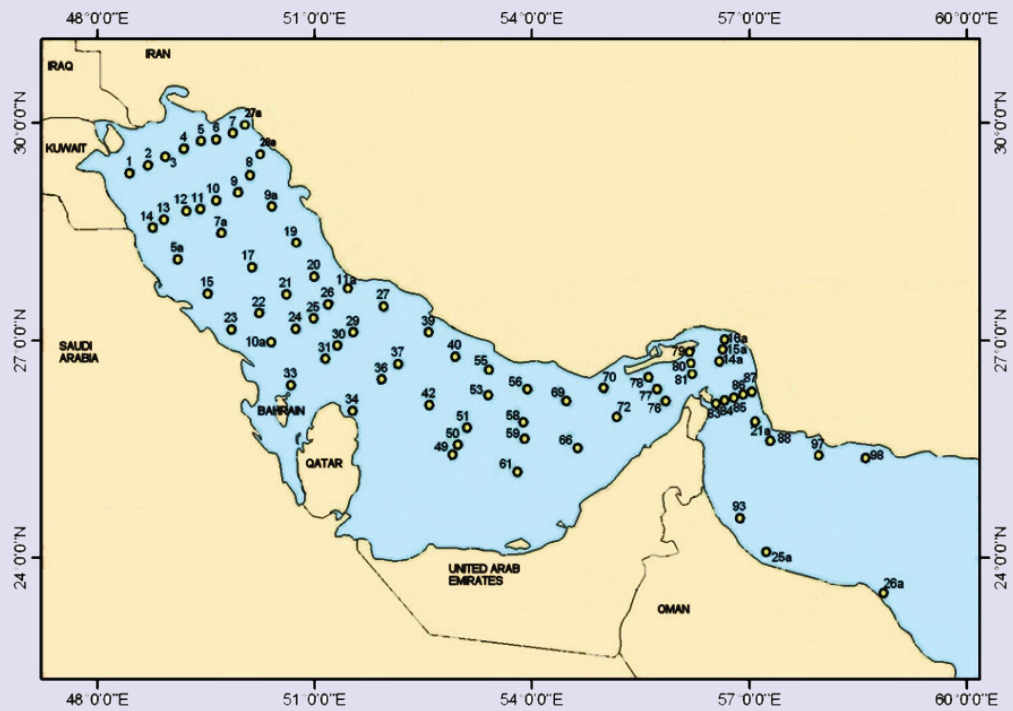


**ROPME/IAEA 2015
NORMALISATION OF TRACE ELEMENTS
CONCENTRATIONS IN SEDIMENTS OF THE
ROPME SEA AREA**



FINAL REPORT

Prepared by:

MESL/IAEA
Monaco, December 2015

For:

REGIONAL ORGANIZATION FOR THE PROTECTION OF THE MARINE ENVIRONMENT





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1. INTRODUCTION

1.1 NORMALISATION OF TRACE ELEMENT CONCENTRATIONS IN SEDIMENTS

Normalization of metal concentrations in sediments to grain-size differences is a common procedure used for the detection and quantification of anomalous metal concentrations, because trace metal concentrations usually increase with decreasing grain size of the sediment. However granulometric approach cannot always successfully compensate for metal variability, because natural trace metal concentrations and their variability in sediments are determined not only by grain size distribution, but also by the composition of minerals and secondary compounds. To overcome this drawback, geochemical normalisation approach is often used. This technique consists in establishing the mathematical relationships between metal concentrations and the concentrations of a conservative element, which represents a certain mineral fraction of the sediment. Elements of natural origin which are structurally combined to one or more of the major fine-grained trace metal carriers are considered conservative and have been used for normalization purposes. Aluminium has been the most widely used element for normalization, because it is a major constituent of fine-grained aluminosilicates with which the bulk of trace metals are associated.

The main assumption for the application of a geochemical normalization to a conservative element is the existence of a linear relationship between the normalizer and other metals. Such a relationship suggests that, in the natural sediments of an area, the concentration of the metal will change proportionally to the concentration of the normalizer. Also a linear relationship must exist between the normalizer's concentration and the percentage of fine-grained (silt and clay) content of the samples. Such a relationship would allow the use of the normalizer concentrations as a proxy for granulometric variability of the sediments, in order to distinguish the pollution-related metal enrichment from the natural enrichment caused by grain size variability (Loring and Rantala, 1992).

1.2 STUDY AREA

Sediment samples have been collected from the ROPME Sea Area during two oceanographic cruises in 2001 and 2006 and during the implementation of the Mussel Watch programme of ROPME in 2011 and 2014. The results of the metal analysis of the samples have been presented in four previous IAEA Reports (IAEA, 2002; IAEA 2008; ROPME, 2013 and ROPME 2016). The purpose of the present study is an attempt to investigate the feasibility of the normalisation of the metal results to a conservative element (Al) in order to assess pollution impact in different areas of the ROPME Sea Area. A similar normalisation attempt was made in the IAEA 2008

Report using metal and grain size results of the sediments collected in the 2006 Oceanographic cruise.

2. METHODS OF GRAIN SIZE ANALYSIS

Sediment samples from all sampling periods were analysed using the same analytical procedure.

Introduction to Particle Size Analysis

The Mastersizer is based on the principle of laser ensemble light scattering. It falls into the category of non-imaging systems due to the fact that sizing is accomplished without forming an image of the particle onto a detector.

The Mastersizer employs two forms of optical configuration to provide its unique specification. The first is the well-known optical method, called “conventional Fourier optics”. The second is called “reverse Fourier optics”, used in order to allow the measurement size range to be extended down to 0.05 μm . There are restrictions placed upon the sample presentation requirements in this configuration which limit its availability to particles dispersed in liquid suspension.

The result of the measurement analysis is a volume distribution characterized over the size limits of the optical configuration used. The results may be presented in a number of ways to suit the user’s needs. For this study, the distribution is listed as a table of results, giving frequency and cumulative forms of distribution. It is also plotted on a log size axis high resolution graph in frequency and oversize form. In addition to this treatment of the fundamental volume measurement it is possible to derive further information using numerical transformations. Finally the standard derived diameters are provided, complete with volume percentiles.

- Preparation of samples

The samples were sieved at 300 μm . Most of the samples have very small portion of material below 300 μm . The portion of material above 300 μm was recorded (by weighing).

Approximately an aliquot of 1 g (or less when not enough material was available), for a large number of samples it was a lot less which implies more uncertainty in the measurements) of sediment was put transferred to in a 10 ml tube. Then, 5 ml of MilliQ water was added and the tube was shaken in order to properly separate the silt particles properly. An equilibration period of about 12 hours was used allowed to insure that the sample was uniformly wet before analysis.

- Particle Size Analysis

The particle size distribution was determined using a Malvern Instrument Mastersizer device. The principle of this device is that small particles cause incident light to be diffracted through a large angle whereas large particles will diffract incident light through a small angle. Particle size information is derived by deconvolution of the diffraction data obtained by the instrument.

- Apparatus used

The MALVERN Mastersizer Micro v2.12 is designed to analyze particle size of silty sediments (<300 μm). The particles need to stay in suspension during the measurement process and therefore the instrument (this device is not suitable for the analysis of coarse sandy material).

- Protocol used

The analysis of the particles is achieved by slurring a sediment sample into a beaker containing 500 ml of water. The mixture is pumped through a cell which is interrogated by the instrument's laser beam. The particle size distribution is determined from the resulting diffraction pattern.

3. RESULTS AND DISCUSSION

The results of the particle size analysis with the analytical method used are translated into percentages of different grain size categories, from 300 μm to <0.364 μm . Fine grained materials (silt and clay), which are the major trace metal carriers in sediments, are defined as the sediment fraction with grain sizes below 63 μm . The part of the sediment above 63 μm is considered as sand.

By studying the grain size analytical results of the coastal sediments collected at the stations of the ROPME Mussel Watch campaigns in 2011 and 2014, it was clear that the samples consisted almost entirely of sand, and in some cases, of shells fragments (Figure 1a and 1b). It was also clear that such samples could not be used for normalising trace element concentrations in sediments, because finer sediments are needed for such a study, including samples with a variety of grain sizes, in order to statistically establish the linear relationship between the grain size and the content in Al.

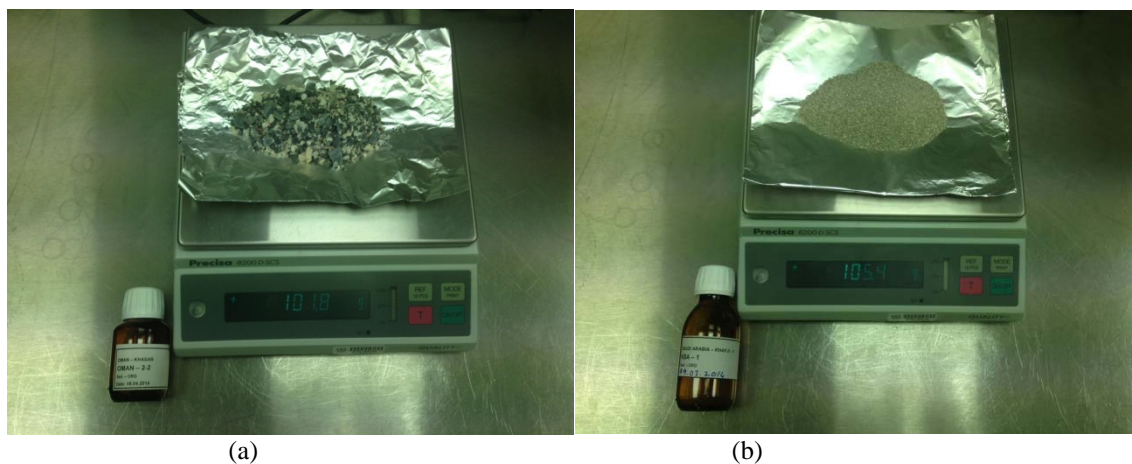


Figure 1. Mussel Watch 2014 sediment samples: a) OMAN-2-2: Shell fragments/gravel, b) KSA-1: 100% Sand

The grain size results of Mussel Watch 2014 indicate that almost all samples consisted mainly of sand, which represented 89.87 - 100% of the sediment, with only one sample (IRAN 2-1) with a substantial percentage (63.01%) of silt and clay. The complete data set of grain size analysis of the samples is presented in the ROPME Technical Report “ROPME Mussel Watch Programme 2014: Trace Metal Screening” (ROPME, 2016). These results indicate that trace element concentrations cannot be normalised to fine grain size (i.e. silt and clay < 63 μm) or to Aluminium content. Comparable results were obtained from the grain size distribution of sediment samples collected during the 2011 ROPME Mussel Watch campaign (ROPME, 2013), with sand content ranging from 66.91% to 100%, and 16 out of 22 samples having sand content above 90%. These results indicate that the coastal sediments collected in the framework of the Mussel Watch Programme in 2011 and 2014 cannot be used for normalisation purposes.

A normalisation attempt of trace elements concentrations was made in the past, using 76 sediment samples collected from the whole ROPME Sea Area during the 2006 ROPME oceanographic cruise (Figure 2). The final Report (IAEA, 2008), which was submitted to ROPME Secretariat, concluded that most of the measured trace elements showed a strong correlation with Al, with decreasing concentrations from northeast to southwest of the RSA. However, it was not possible to normalise the trace element concentrations to grain size, because the percentage of mud (silt and clay with grain size < 63 μm) did not show a strong correlation with Al ($R^2 = 0.485$).

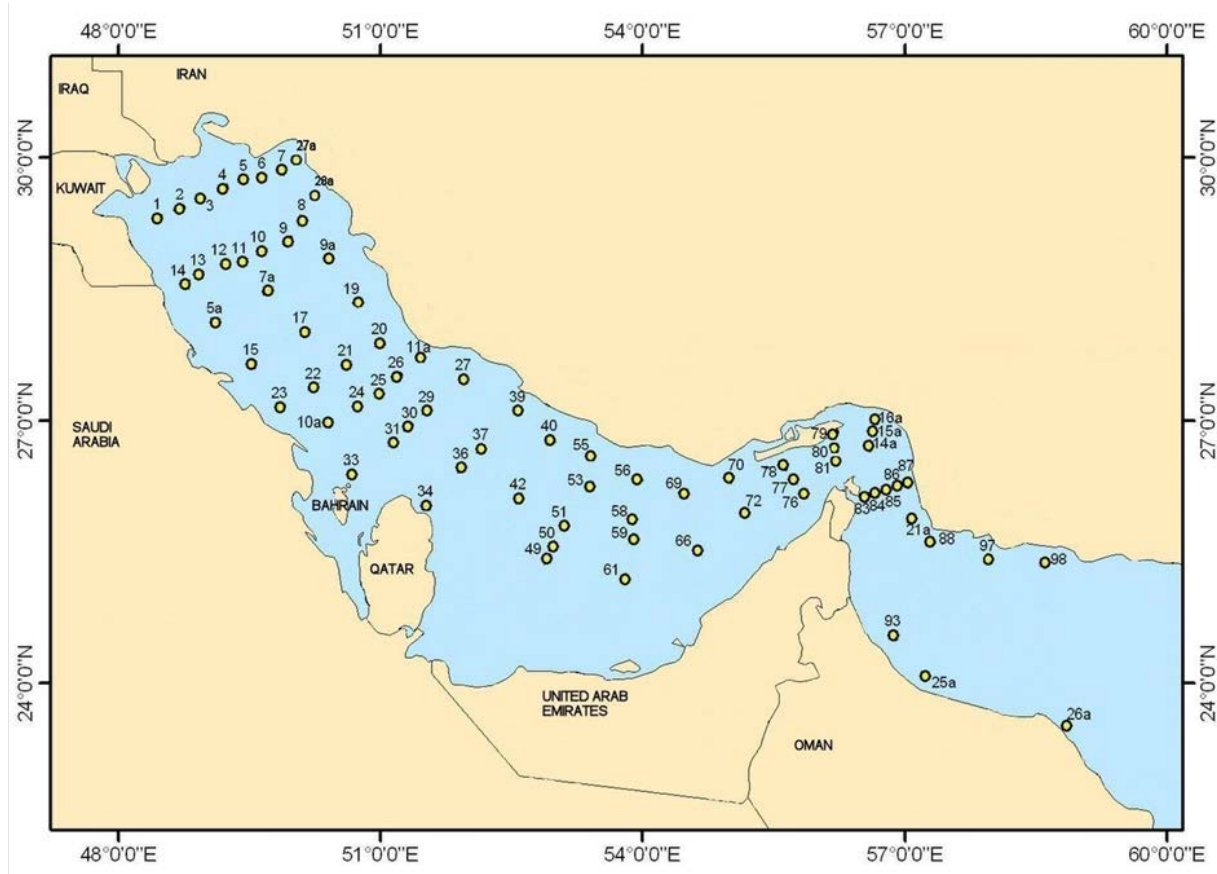


Figure 2. Sampling stations 2001 and 2006 oceanographic cruise

In order to further investigate if a strong correlation may be established between Al concentrations and the content of finer sediments (mud) in the ROPME Sea Area, a new calculation was made using a bigger number of data, combining trace element and grain size data from two sampling campaigns conducted by ROPME in the region in 2001 and in 2006. The 2001 oceanographic cruise collected 35 sediment samples using the similar sampling plan as the 2006 cruise (Figure 2), but collected samples from fewer sampling stations. The detailed results of the grain size and trace element concentrations of the sediment samples collected in the 2001 cruise were presented in detail in the IAEA 2002 Report. The combined data set of both 2001 and 2006 cruises consisted of 111 data points. Although the sampling sites of the 2001 cruise were similar to the 2006 sites, the 2001 data were considered as different data points, because they represent the results of the analysis of independently collected samples from the same location.

As it can be seen in Figure 3, no strong correlation was found between Al concentrations and the percentage of finer material (silt and clay) in the sediments of the RSA ($R^2=0.4388$), which is similar to the conclusion of the IAEA 2008 Report ($R^2 = 0.4859$).

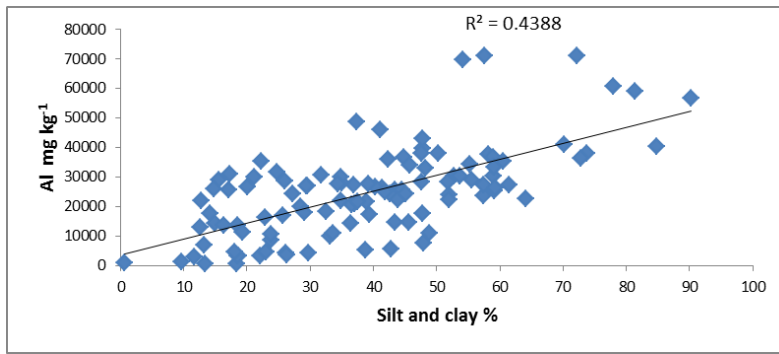


Figure 3. Correlation of Al concentrations with the percentage of finer sediments (silt and clay) (2001 and 2006 combined data)

The lack of strong correlation between Al and the percentage of finer sediments (mud), reaffirms that Al cannot be used as a proxy for finer sediment in the region neither be used as a normalising element to assess metal enrichment in the ROPME region caused by human pollution sources. As it was noted in the IAEA 2008 Report, the sedimentary material in the region appears to be influenced by the differences in mineralogy between the north-eastern and south western land masses. In general, the sediments at the north-eastern part of the RSA had higher Al concentrations that the stations located at the south-western part of the region, while the sediments from the south-western part had higher carbonate contents, which in several cases were above 9% [Stations10a, 15, 31, 33, 34, 49, 50, 59, 61, 66, 69, 72, 76, 93, (IAEA, 2008)]. A negative correlation exists between Al and Ca (Figure 4) supporting the mineralogical differences in the sources for the sedimentary material in different areas of the RSA. These mineralogy differences are contributing to the absence of strong correlation between the grain size of the sediments and Al concentrations, since fine grained sediments cannot solely be attributed to aluminosilicate minerals.

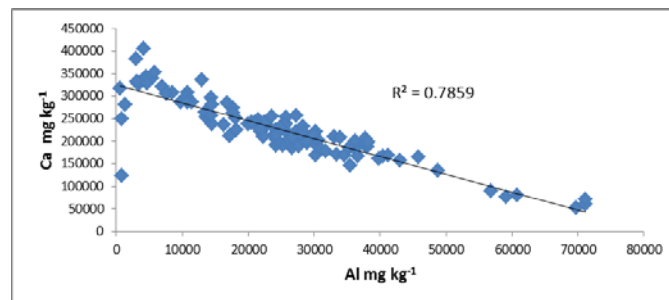


Figure 4. Correlation between Ca and Al

Although Al cannot be used efficiently as a conservative element for normalisation purposes in the ROPME Sea Area, it was plotted against other trace elements in view of detecting relationships between possible metal sources (Figures 5-9).

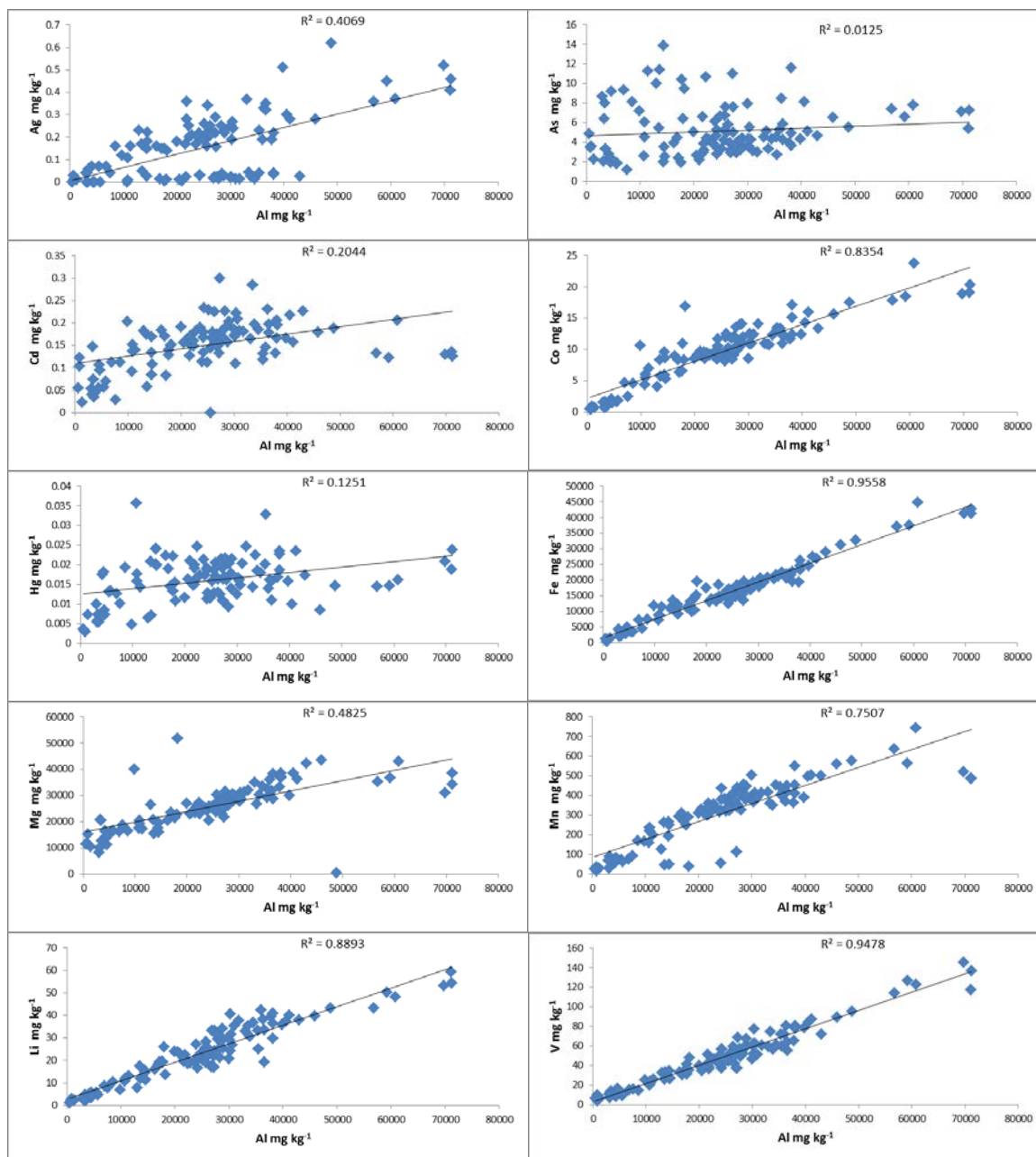


Figure 5. Correlations of trace elements (Ag, As, Cd, Co, Hg, Fe, Mg, Mn, Li, V) with Al

Strong correlations were found between Al and Co ($R^2=0.8354$), Fe ($R^2=0.9558$), Mn ($R^2=0.7507$), Li ($R^2=0.8893$) and V ($R^2=0.9478$), while no strong correlation was found between Al and the elements As, Cd and Hg (Figure 5). Similar results (with small differences) were also found using the 2006 data set alone (IAEA, 2008).

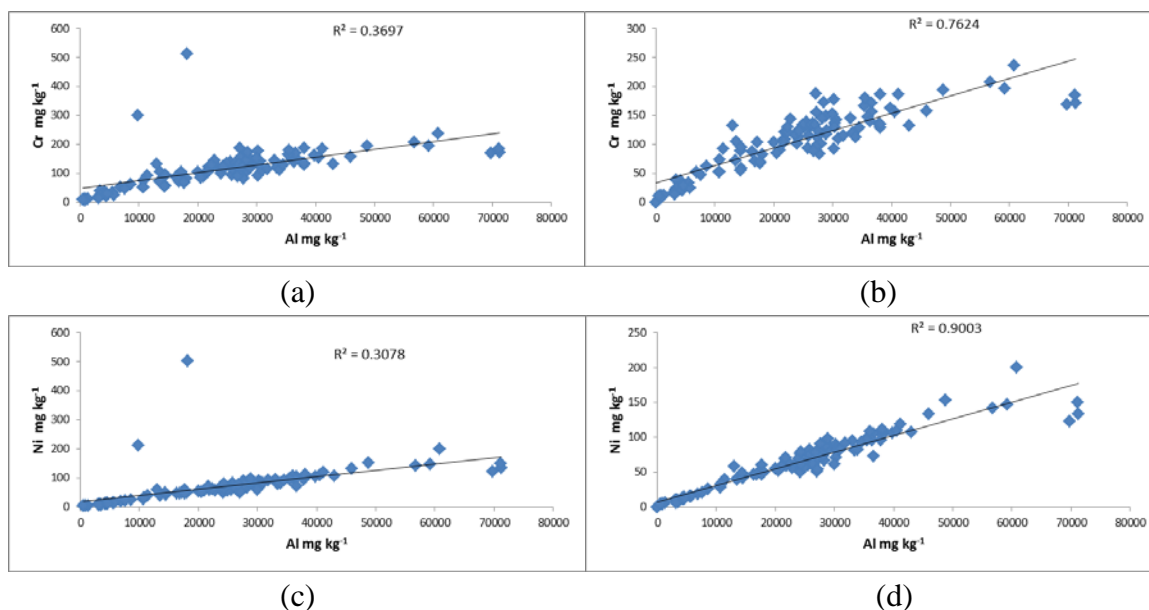


Figure 6. Correlation between Cr and Ni with Al: (a) and (c) all stations, (b) and (d) without stations 25a and 93

Using data from all stations, no strong correlations were found between Cr and Ni with Al (Figure 6a and 6c) as it was also reported in the IAEA 2008 Report. However, if the data points from station 25a and 93 are not included in the calculation, relatively strong correlations are found between the two metals and Al ($R^2=0.7624$ for Cr and $R^2=0.9003$ for Ni). The very high concentrations of Cr and Ni in stations 25a (513 mg kg^{-1} and 505 mg kg^{-1} respectively) and in station 93 (301 mg kg^{-1} and 213 mg kg^{-1} respectively) could be considered as natural enrichment of the sediments at these stations by ultrabasic minerals originating from the coast of Oman. Copper is also an element that has a good correlation with Al, if stations 25a and 37 are excluded from the data set, while no correlation was found using the complete data set (Figure 7). However, no explanation could be provided for the relatively high concentrations of Cu in stations 25a (134 mg kg^{-1}) and 37 (73 mg kg^{-1}) in relation to the other stations in the region.

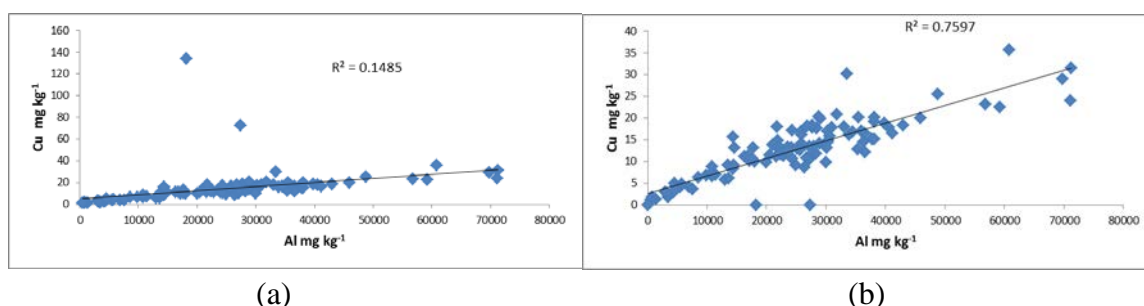


Figure 7. Correlation between Cu and Al: (a) all stations, (b) without stations 25a and 37

In the case of Pb, the correlation of the metal to Al was greatly improved when the high values found in stations 28a and 33 were removed from the data set, but the relation is still not very strong (Figure 8).

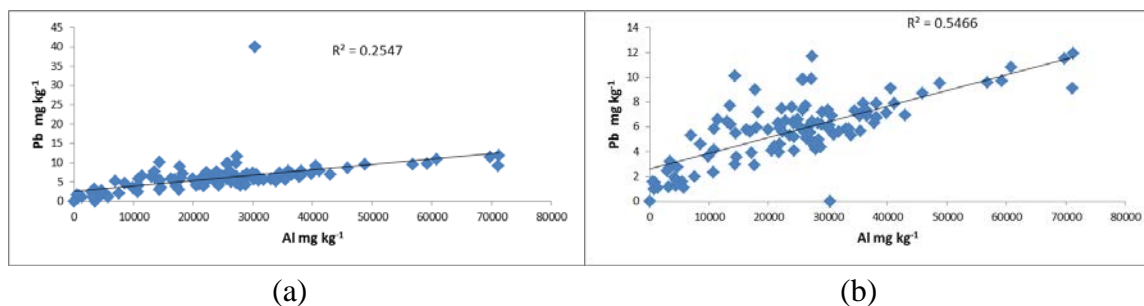


Figure 8. Correlation between Pb and Al: (a) all stations, (b) without stations 33 and 28a

The correlation between Zn and Al can also be greatly improved if the relatively high Zn concentration of station 80 (357 mg kg^{-1}) is removed from the data set (Figure 9).

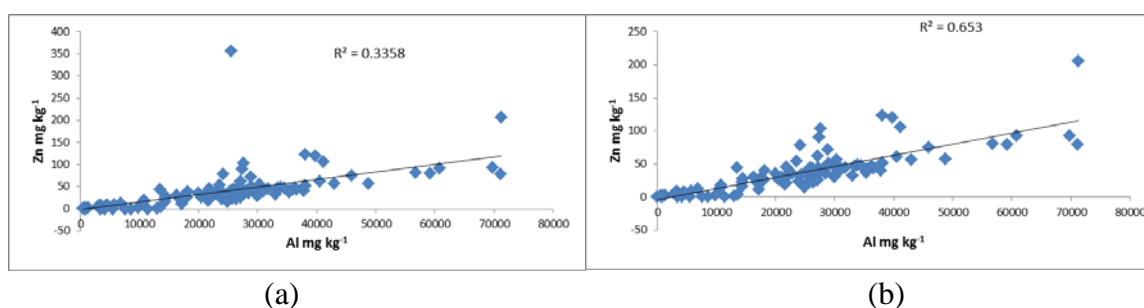


Figure 9. Correlation between Zn and Al: a) all stations, b) without station 80

From the correlations between the trace elements and Al, which were calculated using the combined data set of the 2001 and 2006 oceanographic campaigns, it seems that many trace elements correlate well with Al concentrations in the region, especially if a couple of stations are excluded as outliers. As it was mentioned in the IAEA 2008 Report, there is no clear indication for metal pollution in the broader ROPME Sea Area and the correlations between several elements with Al are probably reflecting their common natural lithogenic provenance.

4. CONCLUSIONS

The absence of substantial amount of fine material (mud) in the sediment samples collected in 2011 and 2014 at the coastal zone of the RSA in the framework of the ROPME Mussel Watch Programme, don't allow the use of this data for studying the relationships between trace elements concentrations and the content of fine material in the sediment, in view of assessing trace element pollution distribution in the region.

To study the relations between trace elements and grain size distributions in the RSA sediments, the data from the 2001 and 2006 ROPME oceanographic cruises was used. Detailed Reports on the results of these cruises have already been submitted to ROPME Secretariat (IAEA, 2002 and IAEA, 2008).

In order to use Al as a geochemical normaliser to assess trace element pollution, a strong correlation has to be established between the concentrations of the conservative element (Al) and the abundance of fine sedimentary material (silt and clay) in the sediment. If such a strong correlation is established between these parameters, Al content could be used as a proxy for the fine aluminosilicate material, which is naturally enriched in trace elements, allowing thus the normalisation of the trace elements to Al in order to compensate for the natural variability of trace elements concentrations due to grain size. The reason to normalise trace elements concentrations to a conservative element (Al) is to distinguish between natural and pollution-related variability of trace elements concentrations, in order to assess pollution impact in sediments.

Using the combined results of the 2001 and 2006 ROPME cruises, no strong correlation was found between Al concentrations and the percentage of fine sedimentary material (silt and clay). The north-eastern parts of the region had substantially higher Al concentrations and lower Ca contents than the south-western area, which probably reflects the diverse mineralogical sedimentary provinces in the ROPME Sea Area. It seems that finer sediments are not only related to aluminosilicates but may also include carbonate-rich sediments, with lower metal concentrations. The lack of strong correlation between Al and mud was also reported in the IAEA 2008 Report, which concluded that normalising trace element concentrations to Al for assessing pollution trends in the region may lead to errors because the fine sediments (mud) do not exclusively represent the trace element-rich fraction. The results of the present study, which are based in a larger data set, reinforce the previous statement. Therefore, normalisation to a conservative element (Al) in the ROPME Sea Area is not meaningful because Al cannot be used as a proxy of fine material in view of establishing the natural trace element variability in the RSA sediments.

Regardless of the unsuitability of the available data for normalisation purposes, several trace elements presented relatively strong correlations with Al (namely Cu, Cr, Co, Fe, Li, Mn, Ni, V), if a few outliers' values were removed from the data set. These correlations may indicate a common natural origin of these trace elements. Other trace elements, which are usually related with anthropogenic sources (such as Ag, As, Cd, Hg) didn't show any correlation with Al. However, in order to study in more detail trace element accumulation in sediments at the vicinity of land-based and sea-based pollution sources, it would be preferable to concentrate the sediment sampling at a more restricted area, which will have more homogeneous sediment mineralogy, allowing for trace element normalisation. Furthermore, to assess the potential impact of toxic trace elements to marine organisms, extraction schemes could be applied to sediments in order to study the bioavailable fraction of trace elements in sediments.

5. ACKNOWLEDGMENTS

This was a collaborative project between the IAEA and ROPME, financially supported by both organizations. The Agency is grateful for the support provided to its Marine Environment Laboratory by the Government of the Principality of Monaco.

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