Trace metal concentrations in the offshore surficial sediments of Heraklion Gulf (Crete Island, East Mediterranean Sea)

Ioli-Nikoleta KOUKOUNARI1, Vasiliki PARASKEVOPOULOU2, Alkateri KARDITSA3, Panayota KOULOURI4, Serafeim E. Poulos4, Costas G. DOUNAS3 and Manos DASSENAKIS2

1Section of Geography & Climatology, Department of Geology & Geoenvironment, National & Kapodistrian University of Athens, Panepistimioupoli-Zografou, 15784, Attiki, Greece
2Laboratory of Environmental Chemistry, Department of Chemistry, National & Kapodistrian University of Athens, Panepistimioupoli-Zografou, GR-15784, Attiki, Greece
3HCMR, Biology & Genetics Institute, Gournes Pediados, Heraklio, 71003, Kriti, Greece

Corresponding author: vparask@chem.uoa.gr

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Abstract

The present study investigates the distribution of trace metals (Fe, Mn, Cr, Zn, Pb, Cu and Al) as pollution indicators in the surficial inner shelf sediments along the northern coast of Heraklion Gulf (Crete Island). Despite the fact that Heraklion Gulf is an industrialized urban area, hosting the third most important commercial harbour in Greece, the levels of trace metals in sediments are not considerably high. According to Sediment Quality Guidelines (SQGs), the sediments are considered unpolluted with low probability of adverse effects on biota in the case of Cu, Zn and Pb, and moderately to heavily polluted in the case of Cr. Moreover, Zn, Cu and Pb concentrations are lower than those measured in a previous study (1989). This improvement in the environmental status of the study area is a response to more efficient control of terrestrial pollution sources, following the enforcement of Directive 91/271/EEC (as amended by Directive 98/15/EU) on urban wastewater treatment and disposal.

Keywords: Geochemistry; pollution; ecosystem health; SQG; human impact; South Aegean.

Introduction

Coastal margins, especially those influenced by riverine inputs, are active interfaces between terrestrial and oceanic environments (Dagg et al., 2004; Bianchi & Allison, 2009) where terrestrial fluxes, complex biogeochemical processes and anthropogenic inputs are present. Since ancient times humans have set their activities and civil-cultural foundations near the coast. Nowadays, more than 50% of the European population is gathered in coastal areas (EEA, 2008; Eurostat, 2013), with most of the terrestrial and coastal usage waste discharged into the marine environment.

Trace metal content in coastal sediments may derive from natural processes such as weathering, erosion and volcanic activity but is mostly considered as a pollution indicator related to anthropogenic activities such as mining, metallurgical and other (various) industrial wastewater, fossil fuel combustion and other atmospheric emissions, treated and untreated municipal sewage, urban and agricultural runoff, harbour activities and aquaculture (e.g., Morillo et al., 2004; Luo et al., 2006; Squadrone et al., 2016).

Once trace metals enter the aquatic environment, they generally exhibit a preferential tendency to bind to suspended matter, and thus, through sedimentation, to accumulate in sediments. In addition, trace metals participate in various biogeochemical mechanisms, have significant mobility and can affect ecosystems through bioaccumulation and bio-magnification processes (GESAMP/UNE-SCO, 1994; Salomons & Förstner, 1984). Hence, trace metal concentrations could be regarded as environmental indicators, for both spatial and temporal trend monitoring of marine pollution, contributing to pollution control, as well.

For the assessment of sediment quality, Sediment Quality Guidelines (SQGs) have been developed by the U.S. Environmental Protection Agency (EPA), the U.S. National Oceanic and Atmospheric Administration (NOAA) and the Canadian Council of Ministers for the Environment (CCME, 1995). They include sediment quality classification categories, concentration ranges and thresholds that have been set after taking into account large series of chemical and biological field data collected from North American coastal regions. These concen-
tration ranges and thresholds have been widely used in monitoring studies as guidelines or screening tools for the possible hazards and biological effects incurred by sediments on local aquatic biota (e.g. Long et al., 1995; Long & Wilson, 1997; MacDonald et al., 2000; Buchman, 2008). Since the beginning of the 21st century, several studies have been published on Mediterranean and Black Sea regions such as those concerning the Marmara Sea (Balkis & Çağatay, 2001), Evoikos Gulf in Central Aegean Sea (Dassenakis et al., 2003), the Spanish coast (Morillo et al., 2004), the NW Aegean Sea (Karageorgis et al., 2005), the south-central Black Sea shelf (Duman et al., 2006), Saronikos Gulf in the Aegean Sea (Scoullos et al., 2006), Thermaikos Gulf in the NW Aegean Sea (Christophoridis et al., 2009), the Gulf of Corinth adjacent to the Ionian Sea (Iatrou et al., 2010), offshore the NE Sicilian Coast (Sacca et al., 2011), the northern Cyprus shelf (Duman et al., 2012), the Egyptian shelf (El Nemr et al., 2007), the Adriatic coast of Italy (Goudeau et al., 2013), the Alexandroupolis Gulf in the NE Aegean Sea (Karditsa et al., 2014) and Ierissos Gulf in the North Aegean Sea (Pappa et al., 2016).

The present study, investigates the distribution of certain trace metal (Fe, Zn, Mn, Cu, Cr and Pb) concentrations, as indicators of pollution, utilising a data set collected in June 2010, in the surficial inner-shelf sediments along the northern coast of Heraklion (region) (north coast of Crete Island), which hosts several potential sources of pollution (urban, industrial). The results of this study are then compared to those published by Poulos et al. (2009) for the same area during a sampling campaign that took place in September 1989. This comparison becomes more interesting as the first data set (in 1989) was collected prior to the transposition of Directive 91/271/EEC on urban wastewater treatment and disposal (as amended by Directive 98/15/EU) into Greek national legislation (Government Gazette 192B/14-3-1997).

The study area

Marine geomorphology and sedimentology

The coastal area under investigation is located in the Heraklion Prefecture of Crete Island (Greece), lying between Cape Panagia to the west and Malia Bay to the east and extending to depths between 10 and 70 m (Fig. 1). The area belongs to the southern continental margin of the central Cretan Sea which is narrow (<10 km) and relatively steep (1.5° slope gradient) becoming wider eastwards. The shelf break is found at depths ranging between 100 m and 150 m, followed by relatively steep slope (2°-4°) and variable morphology (Chronis et al., 2000). The nearshore zone consists of sands, while the outer part of the continental shelf by fine material, mainly terrigenous (silt and clay) (Poulos et al., 2002 and 2009; Dounas and Papadopoulou, 1993; and Chronis et al., 2000). The hinterland area of this coastal strip (1.67 km²), is drained by ten ephemeral streams and torrents (Fig. 1).

Oceanographic conditions

The average tidal range is <10 cm (Tsimplis, 1994), while the meteorologically induced sea level rise may exceed 1 m (HNHS, 2005). According to the Wind and Wave atlas (Athanasoulis & Skarsoulis, 1992) the study area is influenced, on an annual basis, primarily by NW (23.62%), N (12.43%) and partially E (6.79%) wind-induced waves. The wave characteristics (significant height (H_s), period (T), closure depth (h_c), wave breaking zone (db) and depth of wave propagation in intermediate waters (L/4)) according to Komar (1976), of the most frequent and the highest incoming offshore waves, are presented in Table 1 and graphically in Figure 2. In addition, it is noteworthy that the coastal stretch to the west of Heraklio
city receives reduced wave energy, as the predominant NW waves undergo refraction at the Panagia promontory (Alexandrakis et al., 2013).

**Anthropogenic sources of pollution**

The coastal region under investigation concentrates vast trade, industrial (including tourism) and agricultural activities and a vivid urban area since the city of Heraklio is the administrative capital of Crete. Among the various human infrastructure, the most significant—from west to east—are (see Fig. 1): (i) The Electric Power Station located in the extreme west end of the bay, using the adjacent Almiros River water for its cooling systems and discharging it into the sea; (ii) crude oil storage facilities, which supply tankers through an underwater pipeline; (iii) the port of Heraklion, which is of major importance for Greece and the Eastern Mediterranean; (iv) the city wastewater treatment plant that discharges effluents in Heraklion Bay through a 1000 m long underwater outfall at a depth of 10 m; and (v) the mouths of five small rivers and some other ephemeral streams discharging farming and agricultural waste, urban runoff as well as eroded sediments from the hinterland area.

**Materials and Methods**

The sampling campaign was carried out in June 2010 with the R/V Philia conducting a field survey of 55 stations over 9 transects perpendicular to the coastline of Heraklion Gulf. The water depths ranged from 10 to 70 m except for the reference station sample at 200m in transect D (Fig.1). Positioning was established with FURUNO SFN-70 satellite navigator and depth was measured by SIMRAD K-400 echo sounder. At each station, a single undisturbed sediment sample was taken using a Smith McIntyre box corer (Smith & McIntyre, 1954). The uppermost 2 cm were collected and stored in plastic bags. Samples intended for chemical analysis were immediately stored and frozen at -20°C on board.

The standard sieve analysis technique (Folk, 1980) was used to determine the sand and mud percentages of each of the surficial sediment samples, while the silt and clay percentages were determined by Malvern’s particle size “Mastersizer 2000 Hydro”.

For geochemical analysis, sediment samples were lyophilized (freeze-dried below minus 40°C and 133 mbar under vacuum pressure with a “LABCONCO” apparatus), slightly ground with an agate mortar and pestle and sieved for the estimation and separation of the fractions above and below 63 μm. The percentage of both fractions (sand and silt-clay) was calculated and further analytical procedures were carried out to those fractions with adequate mass (>10% of the total sediment).

The particulate organic carbon (POC) content was

| Table 1. Wave characteristics of most frequent (mf) and highest (max) incoming waves. |
|--------------------------------------------------|
|                                | NW | N | NE |
|----------------------------------|----|---|----|
| Significant wave height (Hs in m) | 1.6| 1.7| 0.5|
| Wave period (T in sec)           | 7.2| 6.5| 4.1|
| Intermediate waters (wave length/4 in m) | 20.1| 16.4| 6.4|
| Water breaking zone (d_b in m)   | 2.5| 2.6| 0.8|
| Closure depth (hc, in m)         | 12.0| 10.9| 6.1|

**Fig. 2:** Determination of the offshore zone (blue zone) by means of L/4 (according to Komar, 1976) for approaching waves of different wave lengths (L). Closure depth limit (hc) is also presented (12 m isobath).
measured using the standard Walkley method (Walkley, 1947) as modified by Jackson (1958) and Loring & Rantala (1992), which is based on the exothermic reaction (oxidation) of the sediment with potassium dichromate (K₂Cr₂O₇) and concentrated sulfuric acid (H₂SO₄), followed by back-titration with ferrous ammonium sulfate (FeSO₄) and ferroine indicator.

The carbonate content was determined by calculating the weight difference of the sample before and after the strong effervescence caused by adding hydrogen chloride (HCl) 6M (exothermic reaction followed by HCl gas and CO₂ emission, method modified from Loring & Rantala (1992).

Non-lattice held metals (nlh) were extracted by shaking the sediment samples overnight with HCl 0.5M. For the extraction of total metals, the samples were digested in Teflon beakers with concentrated acids (HF – HClO₄ – HNO₃). The concentrations of total and non-lattice held metal contents Cu, Zn, Fe, Mn, Cr, Pb, and Al) were determined by Flame Atomic Absorption Spectrophotometry (Varian SpectraAA 200-FAAS) with background correction (Dassenakis et al., 2003). The software SPSS 17 was used for the statistical analysis of data.

The geospatial distribution of trace element contents was performed by Arc GIS desktop software. The Inverse Distance Weighted (IDW) algorithm was used to interpolate the data spatially, as, in a comparison of several different interpolation procedures, it has been found to be most consistent with the original input data (eg. Magesh et al., 2011; Xie et al., 2011; Mathes & Rasmussen, 2006). In order to evaluate the precision and accuracy of the method for total metal analysis certified reference materials (IJE 921, 80MS, PACS-2) from Wepal, Quasimeme and NRC-CNRC were carried through the analytical procedure along with the sediment samples. Accuracy was calculated as % recovery (percentage ratio of the measured to the certified value). The precision was evaluated by replicate analysis (n=3) of the reference materials under reproducibility conditions (different days of digestion and measurement) and the %RSD-Relative Standard Deviation (percent ratio of the standard deviation to the average concentration of the replicates) was calculated for each metal. The quality data for the total metal method, given in Table 2, show that all recoveries are between the recommended US EPA ranges (75-125%).

The extent of sediment pollution was estimated by calculating Ef (enrichment factor) as defined by Salomons & Förstner (1984) using the following formula, with aluminium as the normalization element:

\[
Ef = \frac{Me_{sed}}{Me_{back}} \times \frac{Al_{back}}{Al_{sed}}
\]

where, Me_{sed} and Al_{sed} are the concentrations of each metal and aluminium, respectively, in the analysed sediment sample, while Me_{back} and Al_{back} are accepted background concentrations of the elements.

Two approaches are used in the selection of the background values. The safest approach is to use metal data from deep horizons (>50-100cm, depending on sedimentation rates) of dated core sediments from the same area. These values should prove to refer to metal contents, prior to any type of anthropogenic pollution by earliest or modern activities. When no background sediment core samples are available most researchers use trace metal levels proposed as representative of the average earth crust (Salomons & Förstner, 1984). In this study, both the average earth crust metal values and the values from a subsurface sediment recovered from 200 m of water depth have been used.

Subsequently, enrichment factor (Ef) has been applied to classify sediments into five (5) contamination classes (after Sutherland, 2000), which are:

1. Ef <2: Depletion to minimal enrichment suggestive of no or minimal pollution
2. Ef 2-5: Moderate enrichment, suggestive of moderate pollution
3. Ef 5-20: Significant enrichment, suggestive of a significant pollution signal
4. Ef 20-40: Very highly enriched, indicating a very strong pollution signal
5. Ef >40: Extremely enriched, indicating an extreme pollution signal.

Furthermore, sediment metal contents were compared

Table 2. Quality assurance data (%relative standard deviation and recovery) for total metal determination in sediments.

| Certified Reference Material / Quality Measures | Al | Cr | Cu | Fe | Mn | Pb | Zn |
|-----------------------------------------------|----|----|----|----|----|----|----|
| %RSD                                         | 3.4| 6.5| -  | 1.5| 2.2| 1.8| 4.6|
| %Recovery                                    | 87-92| 87-95| - | 93-95| 87-90| 101-104| 96-104|
| PACS-2                                        | 1.6| -  | -  | 1.1| 3.4| 1.7| 4.1|
| %Recovery                                    | 79-80| -  | -  | 90 | 78-83| 93-96| 98-104|
| IJE 921                                       | -  | 2.9| -  | -  | -  | -  | -  |
| %Recovery                                    | -  | -  | 97-101| -  | -  | -  | -  |
to Sediment Quality Guidelines (SQGs) commonly used, which provide scientific benchmarks, or reference points, for evaluating the potential of sediments to cause toxicity and adverse biological effects in aquatic systems. The SQGs used are given in Table 3, adapted from Buchman (2008). The numerical values of TEL (threshold effects level), ERL (effects range low), PEL (probable effects level) and ERM (effects range median) create the following ranges of biological effects: (1) adverse effects rarely occur (below TEL and ERL); (2) some adverse effects occur occasionally (between TEL - PEL, and ERL - ERM); and (3) adverse effects occur frequently (above PEL and ERM). The values of TEL and PEL are proposed as guidelines in Canada (CCME, 1995) while the values ERL and ERM in the US (Long et al., 1995; Long & Wilson, 1997; Buchman, 2008).

Further characterization of the marine sediments has been enforced by applying the quality classification categories given by US EPA (Nichols, 1991) and presented in Table 4.

Also, it must be mentioned that EU has so far not adopted quality guidelines for metals in marine sediments, with the exception of Hg (the guideline was set at 20μg/kg in Directive 105/2008 EC). However, for the implementation and improvement of the Marine Strategy Framework Directive each Member State has submitted initial proposals for Good Environmental Status (GES) criteria in sediments. The suggested Greek GES thresholds for metals in sediments are 40mg/kg for Cu; 50mg/kg for Pb; and 150 mg/kg for Zn (Anagnopoulos et al. 2012).

Results and Discussion

Grain size distribution and sediment texture

The texture of the seafloor is presented in Figure 3, while the spatial grain size (sand-silt-clay) distribution in Appendix A (Fig. A1). The grain size analysis (see also Table A1 in Appendix A) shows that the nearshore zone is composed mainly of coarse sand (S) (90-100% content), reflecting the high-energy wave regime. It is worth mentioning that the seaward limit of this zone coincides with the closure depth (hc) that lies around 12 m of water depth (Fig. 3). Seawards sediments become finer (silty

![Fig. 3: Texture map based on grain size analysis according to Folk 1974. (gmS: gravelly muddy Sand; S: Sand; zS: silty Sand; sZ: sandy Silt; Z:Silt; C: Clay; M: Mud (=silt+clay) and hc: closure depth in red).](image-url)
sand) following a zonal distribution, almost parallel to the coastline, with the silt content reaching almost 40% (Fig. 3). The sediments of the outer part of the west sub-region, which is partially protected by the NW incoming waves, present a silty zone (Z), which is not present in the east sub-region.

Organic carbon and carbonate content

The POC (particulate organic carbon) content in surface sediments varies between 0.11% and 0.86 % (mg/kg) (see Fig. A1 and Table A1, in Appendix A). The increasing content in POC seawards (see Fig. 4) indicates its association with the shift to finer sediments (i.e. increasing silt+clay content). A statistical difference of POC between the grain size groups is proven at the 95% confidence interval and thus the corresponding median POC values (Fig. 4a) follow the order: 0.17<0.30<0.40<0.63 = 0.67%.

The eastward transects, consisting of coarser material, present lower overall POC values (Fig 4b); while few samples with increased values (>0.40%) are found at the 40 m and 50m isobaths of transect A, at depths above 20m in transect B and above 40m at transect H and with the second highest POC value (0.84%) of the entire dataset located at 20m of transect G. The coarser material of transect C is associated with the lowest POC values (0.14-0.52%). In general, the western transects (E, I, D and F) present increased POC levels (>0.50%) seawards. The maximum observed POC value (0.86%), found in transect F at 50m of water depth, is most likely related to the nearby treated sewage outfall of Heraklion city. However, the detected increased POC value cannot be considered as a definite indicator of pollution since it is well below organic carbon content reported for polluted gulfs of Greece such as Thessaloniki Bay (1.2-3%; after Karageorgis et al., 2005) and Elefsina Bay (2.6-3.0%; after Paraskevopoulou, pers. comm.). In general, the organic carbon content of Heraklion Gulf sediments is similar to values reported for Aegean Sea sediments, as in the case of Sporades basin (0.4-0.6%; after Karageorgis et al., 2005) and Saronikos Gulf (0.33-0.52%; after Paraskevopoulou, pers. comm.). Undoubtedly, the operation of the urban wastewater treatment plant, the increased wave activity and the water circulation conditions contribute to the observed low organic carbon concentrations.

The carbonate content is generally low (<20%).

Fig. 4(a): Particulate Organic Carbon (POC) values box-plot grouped by percent silt+clay; (b): Particulate Organic Carbon (POC) values box-plot per transect (from west to east) [(•) outlier value symbol, numbers refer to the isobaths].

Fig. 5: (a): Carbonate content box plots grouped by percent silt+clay, b) Carbonate content box plots per transect (west to east) [(•) outlier value symbol, (*) extreme value symbol, numbers refer to the isobaths].
fine-grained sediments (silt+clay content >90%) present statistically lower carbonate contents (10-13%), compared to more coarse-grained sediments (with silt+clay content <90%) that have slightly increased carbonate percentages (13-15%). Carbonate contents above 20% are observed only locally (Fig. 5a). Figures 4b and 5b reveal that the trends of POC and carbonate contents are consistent with the established norms that carbonate minerals are mostly found in the coarser sediment particles, while the content of organic carbon increases with decreasing grain size (Salomons & Forstner, 1984).

The carbonate content of the inner shelf of Heraklion Gulf (<20%) is similar to that reported for the coastal areas of the North Aegean, but much lower than those reported for other marine areas of Greece (>40%) such as those of Evoikos and Saronikos gulfs, the Cyclades plateau and Alexandroupolis Gulf (Poulos 2009; Karditsa & Poulos, 2013).

**Trace metals**

The spatial distribution of the total and non-lattice held concentrations of Fe, Mn, Cr, Zn, Pb, Cu trace metals are shown in Figures 6 and 7 respectively, while the ranges of their abundances are given in Table 5. All the analytical results are presented in Table A1 (Appendix A).

Fe and Al present the highest concentrations among
all metals with total values ranging between 5120-26004 mg/kg and 10326-52529 mg/kg, respectively. This is anticipated since Fe and Al are basic constituents in natural minerals (aluminosilicates) and mostly of lithogenic origin. Non-lattice held (nlh) Fe concentrations range between 1010 and 4942 mg/kg and the percentages of nlhFe to the total content varies between 11% and 31%. The values of total Al and Fe increase seawards and in the western transects wherein sediment becomes finer (see Fig 6a and Fig. A2a,b in Appendix A). Moreover, the differentiation between the western transects (more affected by riverine lithogenic contributions) and the eastern transects is more prominent for Al than for Fe. This is even more apparent in the case of nlhFe and %nlhFe, where the absolute difference between western and eastern transects ceases to exist. There is a degree of uniformity in non-lattice held Fe content among transects (Fig. A2c in Appendix A) but with some high values in transects I, D and F (river mouths of Gazanos, Xiropotamos and Giofyros), as expected, and also in transect G (former military base, Gouvianos). However, the percent of nlh Fe, more indicative of non-lithogenic sources is higher in transects C (navigation channel), G and A (former military base, Gouvianos, Aposelemis, Sfakoryako) followed by transect I (rivers Gazanos and Xiropotamos). Surprisingly, the lowest nlhFe percentages are found in transect E, where Almiros and Gazanos streams debouch spring water (Fig. A2d).

The total Mn content ranges from 273 to 494 mg/kg and the non-lattice held Mn content between 176 and 376 mg/kg. In contrast to Fe and Cr, that exhibit low non-lattice held percentages (20% and 14%, on average), the %nlhMn ranges from 58% to 88% (73% on average). Moreover, in the case of Mn, in contrast to Fe and Al, higher values are not observed in the finer sediments or the western transects. The highest values are found at 10m depth in transects I, D, B and H, in some samples of transect D (20m and 150m of water depth) and in all samples of transect F (waste treatment terminal outfall). The lowest values of total nlhMn are observed in transect E (Almiros, Gazanos) and the lowest percent nlhMn in transects E and I (Almiros, Gazanos and Xiropotamos river mouths) (see Fig. 6d, Fig 7c and Fig. A3a,b,c, in Appendix A).

The range of total Cr is 51-234 mg/kg and for nlhCr 6-24 mg/kg (Table 5). Similarly to Fe, Cr also exhibits low %nlh ranging from 4% to 27%. However, Cr presents a different spatial distribution (see Fig. 6f, Fig 7d and A4, a in Appendix A). In this case, higher levels of total Cr (>100mg/kg) are identified not only in transects E, I, D, and F (west of Heraklion harbour), similarly to Al and Fe,

| Metal | Min | Max | Average |
|-------|-----|-----|---------|
| Cr    | 51  | 234 | 108     |
| Fe    | 1010| 4942| 2869    |
| Mn    | 176 | 376 | 258     |
| Zn    | 5   | 16  | 10      |
| Al    | 10326| 52529| 28984   |
| Cu    | 5   | 28  | 13      |
| Pb    | 5   | 23  | 9       |

Note: non-lattice held Cu and Pb are below detection limits and labile Al was not measured.
but also in transects C (navigation channel) and B (former outfall of untreated wastewaters, Krateros and Vathylagkos streams). Higher levels of nlhCr and %nlhCr in transects C (navigation channel) and G (former military base) are apparent in Fig. 7d and Fig. A4c, indicating slightly increased anthropogenic inputs, in contrast to the lower values in transects near the river mouths and ephemeral streams attributed to lithogenic non labile input.

Pb, Cu and Zn (usually considered as pollution indicators) present much lower concentrations 5-23, 5-28 and 12-69 mg/kg, respectively. Concerning the total contents of Cu, Pb and Zn, as well as nlhZn, there is a clear increasing trend with decreasing grain size. The spatial distribution of total Cu resembles to those of the other metals already discussed. Similarly to Al, the lowest levels of total Cu are found in transect C, while similarly to Fe, sediments of the western transects are slightly more enriched in Cu than the eastern ones. Moreover, the increased value of total Cr and total Cu in transect B (at depths of 50m and above) differentiate B from its neighbouring transects H, G and A (see Fig. A5a, in Appendix A). The highest values of total Pb are found in transects E and D (Fig. 6c), while in all other transects Pb presents lower contents. Total Zn is similar to Al and Cu, with transect C exhibiting the lowest total content, with relatively enriched presence in transects B (former outfall of untreated wastewaters), F (waste treatment terminal outfall) and E (Almiros, Gazanos). Non-lattice held Zn levels are quite low (5-16mg/kg) at all transects, with the exception of transect A where it is slightly lower (see Fig. A5c in Appendix A). Finally, the spatial distribution of %nlh Zn is highly comparable to that of %nlh Cr (see Fig. A5d in Appendix A) with the lowest values in transects E, I, D, F and B located seawards to river mouths, while higher values are observed at the navigation channel and along the eastern transects.

**Associations among (i) metals and (ii) metals and grain size, carbonates and total organic carbon**

The associations among metal concentrations and the fine-grained, carbonate and POC percentages are given in Table 6, while Tables 7 and 8 present the correlations of the non-lattice held (nlh) metals and the percentages of the non-lattice held (%nlh) metals, respectively.

On the basis of the findings in Table 6, fine-grained sediments (silt+clay fraction) are strongly associated with organic carbon and all trace metals with the exception of Mn and total Cr, as they present correlation coefficients statistically significant at 99% confidence level. Organic carbon is positively correlated to all metals (total content and nlh content) except Cr and presents a strong negative correlation to total Mn, nlhMn and %nlhMn. Carbonates

### Table 7. Correlation matrix of non-lattice held metals (nlh).

| M (%) | CaCO₃ | POC | nlhMn | nlhZn | nlhFe | nlhCr |
|-------|-------|-----|-------|-------|-------|-------|
| M (%) | 1     |     |       |       |       |       |
| CaCO₃ | -0.21 |     |       |       |       |       |
| POC   | 0.85**| -0.04| 1     |       |       |       |
| nlhMn | -0.50**| -0.05| -0.52**| 1     |       |       |
| nlhZn | 0.87**| -0.28′| 0.73**| -0.39''| 1     |       |
| nlhFe | 0.76**| -0.25′| 0.69**| -0.28′| 0.85**| 1     |
| nlhCr | 0.39**| -0.27′| 0.37**| -0.12 | 0.48**| 0.56**| 1     |

Note. (*) correlations statistically significant at the 95% confidence level; (**) correlations statistically significant at the 99% confidence level.

### Table 8. Correlation matrix of percent non-lattice held metals (nlh).

| M (%) | CaCO₃ | POC | %nlhMn | %nlhZn | %nlhFe | %nlhCr |
|-------|-------|-----|--------|--------|--------|--------|
| M (%) | 1     |     |        |        |        |        |
| CaCO₃ | -0.21 |     |        |        |        |        |
| POC   | 0.85**| -0.04| 1     |        |        |        |
| %nlhMn| -0.61**| 0.40**| -0.52**| 1     |        |        |
| %nlhZn| -0.37**| 0.34’| -0.22 | 0.55**| 1     |        |
| %nlhFe| 0.12 | 0.25’| 0.21 | 0.35’| 0.52**| 1     | **    |
| %nlhCr| 0.03 | 0.17 | 0.04 | 0.23 | 0.49’| 0.37’| 1     |

Note. (*) correlations statistically significant at the 95% confidence level; (**) correlations statistically significant at the 99% confidence level.
have strong negative correlations to all total metals, nlh Zn, Fe and Cr. Also, there are statistically significant positive correlations (99% confidence level) between the percentage of the fine fraction and nlhFe ($r=0.76^{**}$), nlhZn ($r=0.87^{**}$) and nlhCr ($r=0.39^{**}$), and a strong negative correlation for nlhMn ($r=0.50^{**}$). Finally, the percentage of the non-lattice held (%nlh) metal contents have either no correlation with %nlhFe, %nlhCr and organic carbon, or strong negative correlations with %nlhZn and %nlhMn and fine grained sediments. Strong correlations to carbonates exist especially for %nlhZn and %nlhMn and to a lesser degree for %nlhFe.

The clear trend of total Al, Fe, nlhFe, Cu, Pb, Zn, nlhZn and nlhCr to increase in finer sediments is anticipated because when the size of sediment grains decreases their surface area increases, as well as the concentrations of many geochemical phases known to bind trace metals (Fe and Mn oxides and hydroxides, organic carbon, and clay minerals). The existing strong correlation between metals (e.g. Cu, Zn, Fe, Pb, Al) and the organic carbon content results from this primary relation to grain size (Salomons & Förstner 1984; Horowitz & Elrick 1987, Calvert et al. 1985).

The strong association between Fe and Al is reasonable, as they are principal lithogenic constituents of natural minerals (aluminosilicates) in sediments and are present in high concentrations (i.e. one order of magnitude) above the mean value of the other metals.

The different spatial distributions of the main lithogenic metals, Fe and Al on one hand, and Mn on the other, along with the marked difference between the percentages of non-lattice held fractions, support the existence of very different lithogenic phases. Fe, Al, non-lattice held Cr, Zn, Pb and Cu are increased to the west, while seabed sediment is finer and most likely occur in aluminosilicate minerals of terrestrial origin. In contrast, Mn exhibits higher concentrations in coarse-grained sediments, indicating a correlation with other mineral phases. All samples with coarser grain sizes (sand > 50%) exhibit Mn/Al ratios quite above the average $106\times10^{-4}$ shale ratio and an average value of $176\times10^{-4}$. Other researchers have also found similar associations of Mn to coarse-grained sediments and proposed the existence of authigenic manganese carbonate, or Mn oxyhydrates, or Mn enriched mica grains (e.g. Pedersen & Price, 1982; Karageorgis et al., 2005).

### Sediment quality and enrichment evaluation

The US-EPA limits presented in Table 4 are used to evaluate the pollution status of the studied sediments. The average concentrations of Zn, Pb and Cu are low and according to US-EPA limits (90mg/kg for Zn, 40 mg/kg for Pb and 25mg/kg for Cu) indicate non polluted sediments. On the contrary, the average Cr content (108mg/kg) leads to the characterization of possible heavy pollution. In more detail, 11% of the samples could be considered as moderately polluted sediments with the remaining as heavily polluted.

The metal concentrations were also compared to the SQGs proposed by NOAA and CCME (see Table 3). For Cu, Zn and Pb, all samples present concentrations below TEL and ERL limits, which means that adverse effects on benthic biota due to exposure to these metals are unlikely to occur. However, in the case of Cr, the content in 63 out of 65 samples was in the range between TEL and PEL, which means that adverse effects are probable.

Furthermore, in order to examine whether the pollution origin is anthropogenic or not, the Enrichment Factor (Ef) was used. Thus, the enrichment factors of metals in the sediments, after normalisation with respect to Al, were calculated using two sets of metal background levels. The first set refers to metal contents proposed for the earth’s crust (Salomons & Förstner, 1984) and the second set refers to metal levels of a subsurface sediment (approximately 15cm beneath the seafloor) collected at the reference station (D-200m). The metal background values (in mg/kg) are given in Table 9, while the results of the Ef calculations are summarized in Table 10.

Efs based on local background levels (reference area subsurface sediment) are considered to be more reliable compared to those of the average crust metal levels. According to the contamination classes of Sunderland (2000), the so-called anthropogenic metals (Cu, Pb and Zn) - along with Fe present Enrichment Factors below 2, against the background value of the reference station - are characterized as causing minimal pollution. In the case

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**Table 9. Metal background values for Enrichment Factor (Ef) calculations.**

| Background         | Al  | Cr  | Cu  | Fe  | Mn  | Pb  | Zn  |
|--------------------|-----|-----|-----|-----|-----|-----|-----|
| Average Crust      | 82000 | 100 | 50  | 41000 | 950 | 14  | 75  |
| Reference station  | 53761 | 139 | 27  | 25740 | 390 | 20  | 54  |

**Table 10. Enrichment Factors (Ef) based on Al as a normalization element for both the average crust and the reference station background.**

|  | Fe  | Mn  | Cr  | Cu  | Pb  | Zn  |
|---|-----|-----|-----|-----|-----|-----|
|  | Crust | Ref | Crust | Ref | Crust | Ref | Crust | Ref | Crust | Ref | Crust | Ref |
| Min | 0.7  | 0.7  | 0.6  | 0.9  | 1.8  | 0.8  | 0.4  | 0.4  | 1.1  | 0.5  | 0.9  | 0.6  |
| Max | 1.4  | 1.4  | 2.2  | 3.6  | 8.4  | 4.0  | 1.4  | 1.7  | 3.3  | 1.6  | 2.1  | 1.9  |
| Average | 1.0  | 1.0  | 1.1  | 1.7  | 3.2  | 1.5  | 0.8  | 0.9  | 1.8  | 0.9  | 1.3  | 1.1  |

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of Cr, 12 samples (19% of the total number of samples) present Enrichment Factors in the range of 2-5, suggesting moderate pollution. The highest Enrichment Factors for Cr are found near the mouth of Gazanos river (transect I), east of the harbour (transect C), west of the harbour near the outfall of treated waste waters (transect F), near a former site of untreated waste outfall (transect B) and, finally, in some samples of transect A. Unfortunately, the available dataset does not allow to fully identify the reasons (e.g. lithology, human intervention) involved in the occurrence of the aforementioned increased Cr concentrations and Enrichment factors.

Comparison between 1989 and 2010 datasets

A comparison between the 2010 dataset (present study) and the 1989 dataset (Poulos et al. 2009) is presented in Table 11 (locations of both sampling campaigns presented in Figure 8).

The 2010 dataset shows reduction of metal concentrations in bottom sediments, while the POC contents are consistent with those of the previous study, where most samples exhibited values of approximately 0.5% (5 mg/g) with a maximum value of 1.013% (i.e. 10.13 mg/g). This improvement of environmental conditions could be both attributed to the restriction of sources of pollution (e.g. installation and operation of the Heraklion Municipality sewage treatment plant and marine outfall) and to the circulation (renewal) of shelf waters.

Comparisons with other coastal Greek and Mediterranean sediments

From the referenced sediment data presented in Table 12, it is observed that the values of the lithogenic elements Fe, Mn and Cr in the sediments of Heraklion Gulf are similar to most in other Mediterranean areas. In addition, the maximum Cr concentrations in Heraklion are lower than those in other Greek areas characterised by either specific (i.e. the red mud input in the Gulf of Corinth, after Iatrou et al., 2010) or other natural sources (i.e. geologic/ophiolithic -volcanic input in NW Saronikos, after Paraskevopoulos 2009). Fine-grained offshore sediments and sediments affected by mining activities (Pappa et al., 2016), riverine inputs (Karageorgis et al., 2005 and Karditsa et al., 2014), industrial activities (Dasenakis et al., 2003) and the aforementioned red mud industrial discharge in the Gulf of Corinth (Iatrou et al., 2010) are also characterized by higher concentrations of Fe and Mn. The maximum and mean concentrations of Cu, Pb, Zn (the so-called anthropogenic elements) in the sediments of Heraklion Gulf are generally much lower.

Table 11. Minimum, maximum and averaged total values of the common trace metals (Cu, Pb, Zn in mg/kg) and Particulate Organic Carbon (POC in %) for the sampling campaigns of 1989 (Poulos et al., 2009) and 2010 (present study), along with changes expressed in percentages.

|        | 2010    |         | 1989    |         | Change (in %) from 1989 to 2010 |
|--------|---------|---------|---------|---------|-------------------------------|
| Cu     | 5.0     | 28.0    | 13.0    | 2.07    | +43.2 -45.3 -21.6             |
| Pb     | 5.0     | 23.0    | 9.0     | 8.26    | -54.4 -78.1 -50.4             |
| Zn     | 12.0    | 69.0    | 34.0    | 6.89    | +38.9 -63.5 -62.2             |
| POC (%)| 0.11    | 0.86    | 0.5     | 0.002   | +98.2 -15.5 -53.1             |

Fig. 8: Map showing the sampling stations in 1989 (referred by Poulos et al., 2009) (·) and those of the present investigation (x) over the bathymetry.
Table 12. Ranges and mean or median values (in parentheses) of trace metal concentrations in coastal sediments of Greece and the Mediterranean Sea (nd: non detected).

| Area (reference) | Sediment type, metal sources | Cr  | Fe  | Mn  | Cu  | Pb  | Zn  |
|------------------|------------------------------|-----|-----|-----|-----|-----|-----|
|                  |                              | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg | mg/kg |
| Heraklio Gulf (this study) | Sandy, various | 51.3-234 (104) | 5120-17329 (11294) | 273-494 (365) | 4.5-16.0 (8.8) | 5.0-11.9 (7.3) | 12.1-39.2 (23.8) |
|                  | Muddy, various | 83.8-152 (114) | 12558-26004 (18345) | 279-421 (348) | 8.9-27.6 (18.9) | 6.5-23.0 (11.3) | 24.6-68.5 (45.0) |
| Central Evoikos Gulf (Dassenakis et al., 2002) | Sandy, Urban, Cu mining | 9.0-46 | 1800-8400 | 141-1214 | 1.6-74 | 1.6-92 | 5.0-78 |
| Northern Cyprus (Duman et al., 2012) | Sandy, Industrial, urban, | 11.6-110 (58.2) | 124-37852 (9314) | 13.5-1384 (469) | 6.9-192 (41.7) | 39.9-120 (78.7) | 16.6-167 (75.3) |
| Gulf of Alexandria, Egypt (El Nemr et al., 2007) | Mostly coarse sediments, industrial | 1030-4312 (2281) | 30400-36700 (35400) | 800-3501 (2119) | 110-148 (133) | 111-195 (146) | 95-143 (122) |
| Antikyra bay-Gulf of Corinth (Iatrou et al., 2010) | Mostly sandy, Mining | - | - | - | - | - | - |
| NW Aegean Sea (Karageorgis et al., 2005) | Mostly muddy, industrial, urban, riverine input | 39-458 (222) | 47900-28575 (20808) | 286-4336 (1378) | 4-108 (34) | 17-265 (52) | 33-429 (120) |
| Alexandroupolis Gulf, NE Aegean (Karditsa et al., 2014) | Mostly fine and coarser, industrial, urban, agricultural, riverine input | 23-221 (66) | 12800-48400 (30800) | 271-1332 (557) | 3-78 (20) | 9-113 (38) | 37-248 (93) |
| Ierissos gulf, North Aegean (Pappa et al., 2016) | Mostly sandy, Mining | - | - | - | - | - | - |
| NW Saronikos (Paraskevopoulou, 2009) | Mostly coarse grained, few muddy, oil refinery, vacation area, volcanic | 180-5642 | 8108-44069 (10150) | 264-4822 (143) | 5.6-40.4 | 4.5-56.6 | 27.7-120 |
| NE Sicilian coast, SE Tyrrhenian Sea, Italy (Saccà et al., 2011) | Mostly muddy, industrial, urban, riverine, volcanic | 68-205 (137) | 22731-34972 (31124) | 40.9-105 (75.3) | - | 127 | 339 (202) |

The values of CaCO₃ content, ranging from 10% to 24% with an eastward increasing trend, are attributed mostly to biogenic fragments.

The total values of Fe, Zn, Pb, Cu and Al increase with increasing water depth and are associated with the decrease in the size of the sediment granules as confirmed by the SPSS correlations.

On the basis of the spatial distribution of trace metals, POC and the location of potential pollution sources onshore the coastal area under investigation could be divided into two sections relative to the port of Heraklion: (1) the hydrodynamically semi-protected western province, where there are more sources of potential pollution; and (2) the open eastern province with much less potential sources of pollution and more energetic hydrodynamic conditions. This is evidenced by the relatively lower concentrations of most trace metals and POC in the eastern province compared to the western one.

Conclusions

The surficial sediments of the coastal area of Heraklion region present a zonal, textural distribution that generally follows the bathymetry, presenting a decreasing grain size (S→zS→S→Z) trend seawards. This zonal distribution is related to the wave propagation in the intermediate zone, where water depths are smaller than the ¼ of the length of incoming waves. The maximum depth of wave-induced sea-bed mobility is 10-12 m coinciding with the sandy zone.
The relatively lower values of trace metal concentrations, presented by the currently analysed dataset of 2010, compared to that of 1989, indicate an improvement of the coastal environmental status of the examined area; the latter is believed to be the outcome of a better control of terrestrial pollution sources, following the transposition of Directive 91/271/EEC (as amended by Directive 98/15/EU) into Greek national legislation in March 1997 entitled “Measures and Conditions for the Treatment of Urban Wastewater” and its implementation.

Overall, the concentrations of Cu, Zn and Pb in all sediment samples show values below the TEL and ERL limits indicating very low to zero probability for adverse effects on benthic biota due to exposure to these metals. However, in the case of Cr, most samples were in the range between TEL and PEL, increasing the probability of adverse effects on benthic biota; hence, more detailed monitoring of Cr concentrations, including non-latitude levels, is recommended.

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Fig. A1: Schematic presentation of sand, silt, clay distribution and Particulate Organic Carbon (POC) percentages.
Fig. A2: Al and Fe (total, nlh and %nlh) per transect [transects are presented from west to east, (•)the outlier value symbol and numbers refer to the isobaths].
**Fig. A3:** Mn (total, nlh and %nlh) per transect [transects are presented from west to east, (•) the outlier value symbol and numbers refer to the isobaths].
Fig. A4: Cr (total, nlh and %nlh) per transect [transects are presented from west to east, (•) the outlier value symbol and numbers refer to the isobaths].
Fig. A5: Total Cu, Pb and Zn and nlhZn per transect [transects are presented from west to east, (•) the outlier value symbol and numbers refer to the isobaths].
Table A1. Sediment texture (after Folk, 1980), metals in total and non-lattice held values (in mg/kg), CaCO$_3$ and Particulate Organic Carbon (POC) content expressed in percentages [gmS: gravelly muddy Sand; S: Sand; zS: silty Sand; sZ: sandy Silt; Z: Silt; C: Clay; M: Mud (=silt+clay)].

| Transect | Stations | Depth (m) | Texture | Cr | Fe | Mn | Zn | $\text{Al}_{\text{tot}}$ | $\text{Cu}_{\text{tot}}$ | $\text{Pb}_{\text{tot}}$ | CaCO$_3$ (%) | POC (%) |
|----------|----------|-----------|---------|----|----|----|----|----------------|----------------|----------------|--------------|---------|
| A        |          |           |         |    |    |    |    |                 |                 |                 |              |         |
| 1        | 10       | 59        | S       | 5120 | 1010 | 322 | 266 | 12 | 5 | 10326 | 7 | 5 | 17 | 0.22 |
| 2        | 20.6     | mS        | 60      | 6640 | 1259 | 319 | 238 | 15 | 5 | 17887 | 7 | 6 | 15 | 0.27 |
| 3        | 30.6     | zS        | 85      | 7592 | 1561 | 273 | 217 | 16 | 7 | 16913 | 8 | 7 | 18 | 0.40 |
| 4        | 40.5     | sZ        | 104     | 12558 | 2541 | 320 | 231 | 26 | 9 | 25087 | 12 | 11 | 16 | 0.52 |
| 5        | 55       | sZ        | 95      | 13451 | 3419 | 279 | 192 | 27 | 9 | 22604 | 14 | 10 | 23 | 0.80 |
| 6        | 75       | sZ        | 84      | 12636 | 3659 | 298 | 234 | 25 | 10 | 13875 | 12 | 10 | 21 | 0.38 |
| B        |          |           |         |    |    |    |    |                 |                 |                 |              |         |
| 7        | 10       | S         | 158     | 8937 | 1101 | 445 | 305 | 21 | 5 | 19815 | 7 | 6 | 15 | 0.21 |
| 8        | 19.2     | zS        | 89      | 8562 | 1350 | 377 | 298 | 21 | 6 | 21660 | 8 | 6 | 13 | 0.16 |
| 9        | 29.3     | zS        | 129     | 9342 | 1615 | 360 | 264 | 29 | 7 | 22617 | 12 | 6 | 15 | 0.34 |
| 10       | 40       | zS        | 131     | 12966 | 2612 | 310 | 233 | 43 | 11 | 29274 | 19 | 6 | 16 | 0.44 |
| 11       | 49.8     | zS        | 142     | 15633 | 2961 | 330 | 239 | 60 | 11 | 33506 | 23 | 8 | 14 | 0.61 |
| 12       | 75.3     | sZ        | 152     | 18534 | 3557 | 356 | 256 | 64 | 13 | 36691 | 27 | 11 | 14 | 0.75 |
| C        |          |           |         |    |    |    |    |                 |                 |                 |              |         |
| 13       | 12.1     | gmS       | 57      | 7310 | 1441 | 274 | 223 | 19 | 7 | 10529 | 6 | 6 | 20 | 0.13 |
| 14       | 21.5     | zS        | 82      | 9197 | 2112 | 337 | 298 | 21 | 6 | 15728 | 8 | 6 | 21 | 0.17 |
| 15       | 31.5     | zS        | 115     | 11783 | 2709 | 341 | 243 | 25 | 8 | 21654 | 10 | 7 | 13 | 0.36 |
| 16       | 42.4     | zS        | 128     | 15368 | 3848 | 370 | 282 | 31 | 11 | 25735 | 13 | 9 | 12 | 0.52 |
| 17       | 52.1     | zS        | 123     | 13026 | 3117 | 365 | 289 | 26 | 10 | 22528 | 11 | 8 | 12 | 0.34 |
| 18       | 71.1     | zS        | 126     | 14395 | 3611 | 383 | 298 | 28 | 10 | 24362 | 12 | 7 | 15 | 0.44 |
| D        |          |           |         |    |    |    |    |                 |                 |                 |              |         |
| 19       | 10       | S         | 106     | 9930 | 1558 | 392 | 313 | 20 | 6 | 22081 | 7 | 6 | 11 | 0.11 |
| 20       | 19.5     | zS        | 113     | 10469 | 2099 | 392 | 297 | 21 | 7 | 24260 | 8 | 8 | 14 | 0.23 |
| 21       | 30       | zS        | 97      | 12921 | 2449 | 379 | 285 | 24 | 7 | 25548 | 11 | 9 | 15 | 0.54 |
| 22       | 40       | zS        | 102     | 14524 | 2542 | 360 | 262 | 27 | 8 | 29414 | 14 | 10 | 17 | 0.58 |
| 23       | 49.4     | zS        | 130     | 18991 | 3909 | 369 | 238 | 37 | 12 | 40983 | 19 | 14 | 13 | 0.84 |
| 24       | 60       | zS        | 131     | 19302 | 3913 | 380 | 251 | 38 | 12 | 41267 | 18 | 14 | 12 | 0.76 |
| 25       | 75.1     | Z         | 126     | 21067 | 3744 | 366 | 243 | 40 | 12 | 43011 | 19 | 12 | 12 | 0.71 |
| E        |          |           |         |    |    |    |    |                 |                 |                 |              |         |
| 26       | 11.1     | S         | 123     | 15249 | 1662 | 356 | 269 | 29 | 7 | 27401 | 7 | 11 | 13 | 0.18 |
| 27       | 20.1     | zS        | 120     | 14301 | 1783 | 292 | 196 | 28 | 8 | 30227 | 7 | 12 | 13 | 0.32 |
| 28       | 31.5     | zS        | 124     | 17936 | 2607 | 286 | 176 | 41 | 11 | 35013 | 13 | 13 | 13 | 0.50 |
| 29       | 41       | zS        | 115     | 20675 | 3346 | 279 | 178 | 53 | 14 | 37717 | 22 | 15 | 12 | 0.81 |
| 30       | 50.5     | zS        | 112     | 19316 | 3225 | 307 | 193 | 56 | 12 | 39328 | 21 | 16 | 12 | 0.59 |
| 31       | 75.1     | zS        | 112     | 19477 | 3247 | 287 | 189 | 56 | 12 | 39846 | 21 | 15 | 13 | 0.50 |

continued
| Transect | Stations | Depth (m) | Texture | Cr tot | Cr n.l. | Fe tot | Fe n.l. | Mn tot | Mn n.l. | Zn tot | Zn n.l. | Al tot | Cu tot | Pb tot | CaCO₃% | TOC% |
|----------|----------|-----------|---------|--------|---------|--------|---------|--------|---------|--------|---------|--------|--------|--------|--------|------|
| F        | 32       | 9.5       | S       | 137    | 9       | 10183  | 1481    | 468    | 328     | 22     | 7       | 23613  | 6      | 6      | 14     | 0.12 |
|          | 33       | 20.5      | S       | 51     | 11      | 9636   | 1809    | 445    | 376     | 20     | 7       | 23654  | 7      | 5      | 15     | 0.16 |
|          | 34       | 30.3      | zS      | 95     | 11      | 12267  | 2496    | 397    | 314     | 39     | 10      | 28327  | 16     | 8      | 13     | 0.37 |
|          | 35       | 38.7      | sZ      | 102    | 13      | 15373  | 3164    | 369    | 275     | 45     | 11      | 34901  | 19     | 8      | 15     | 0.67 |
|          | 36       | 45.3      | sZ      | 117    | 15      | 21071  | 4174    | 408    | 264     | 45     | 14      | 41045  | 21     | 10     | 14     | 0.86 |
|          | 37       | 73.2      | Z       | 124    | 12      | 20409  | 3856    | 391    | 254     | 59     | 13      | 43632  | 25     | 13     | 13     | 0.69 |
| G        | 38       | 12.4      | S       | 71     | 11      | 8338   | 1307    | 370    | 312     | 17     | 6       | 14488  | 5      | 7      | 14     | 0.13 |
|          | 39       | 19.9      | zS      | 96     | 18      | 12332  | 3240    | 302    | 235     | 27     | 11      | 22024  | 11     | 8      | 15     | 0.84 |
|          | 40       | 31.3      | zS      | 92     | 17      | 11257  | 2645    | 325    | 238     | 26     | 9       | 27188  | 9      | 8      | 16     | 0.40 |
|          | 41       | 40.1      | sZ      | 103    | 19      | 13677  | 3270    | 325    | 240     | 29     | 10      | 30231  | 9      | 8      | 12     | 0.54 |
|          | 42       | 51        | sZ      | 96     | 19      | 15136  | 3975    | 327    | 248     | 33     | 11      | 30994  | 13     | 8      | 13     | 0.63 |
|          | 43       | 73.1      | sZ      | 92     | 18      | 15349  | 4089    | 353    | 277     | 33     | 12      | 28420  | 11     | 9      | 14     | 0.40 |
| H        | 44       | 10.1      | S       | 123    | 14      | 8423   | 1053    | 410    | 305     | 17     | 6       | 19437  | 5      | 5      | 16     | 0.25 |
|          | 45       | 19.3      | S       | 59     | 14      | 7190   | 1224    | 362    | 299     | 16     | 6       | 18909  | 5      | 5      | 15     | 0.25 |
|          | 46       | 30        | zS      | 86     | 15      | 10036  | 1789    | 344    | 265     | 22     | 9       | 24504  | 7      | 5      | 15     | 0.40 |
|          | 47       | 40.5      | sZ      | 87     | 17      | 15082  | 2718    | 348    | 243     | 31     | 11      | 35323  | 13     | 7      | 24     | 0.64 |
|          | 48       | 51.5      | sZ      | 91     | 17      | 17061  | 3182    | 355    | 240     | 35     | 11      | 31904  | 15     | 10     | 16     | 0.72 |
|          | 49       | 75.3      | sZ      | 91     | 17      | 17839  | 3323    | 369    | 260     | 37     | 12      | 33831  | 16     | 11     | 16     | 0.56 |
| I        | 50       | 10.5      | S       | 234    | 10      | 12795  | 1707    | 494    | 305     | 27     | 7       | 22862  | 6      | 6      | 11     | 0.12 |
|          | 51       | 20.5      | zS      | 101    | 11      | 10336  | 2059    | 335    | 259     | 22     | 6       | 22848  | 6      | 6      | 13     | 0.18 |
|          | 52       | 30        | zS      | 129    | 14      | 14622  | 3325    | 339    | 224     | 28     | 9       | 29422  | 11     | 7      | 12     | 0.62 |
|          | 53       | 40.5      | sZ      | 126    | 16      | 18086  | 4234    | 360    | 229     | 36     | 11      | 33701  | 14     | 8      | 11     | 0.67 |
|          | 54       | 50        | Z       | 134    | 20      | 20932  | 4942    | 381    | 253     | 45     | 14      | 38584  | 17     | 8      | 10     | 0.67 |
|          | 55       | 75.5      | sZ      | 114    | 16      | 19821  | 4294    | 377    | 244     | 40     | 12      | 37686  | 15     | 10     | 10     | 0.39 |
| Ref. Stat.| 199      | 132       | 19      | 26004  | 3362    | 354    | 208    | 57     | 16      | 52529  | 27     | 23     | 12     | 0.62 |

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