

POLLUTION ASSESSMENT OF THE DRAPETSONA-KERATSINI COASTAL SEABED

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Abstract

The pollution status of the Drapetsona-Keratsini coastal environment is assessed through sedimentological and geochemical analyses of surface sediments. The results show that the sedimentary seabed consists of sandy silts and silty sands with relatively high moisture content (up to 114%) and carbonate concentration (24-86%), whilst the levels (measured in µg/g) of some harmful heavy metals, i.e., As=8-2677, Cd=0.2-15.4, Cr=82-428, Cu=18-567, Fe=5700-289,000, Hg=0.05-0.71, Mn=101-1477, Ni=25-122, Pb=18-1394, Sn=1-18, and Zn=118-4821, are particularly high. The implementation of various pollution indices, such as Geoaccumulation Index (Igeo), Potential Ecological Risk Index (RI), Pollution Load Index (PLI), Combined Contamination Index (W), and Modified Contamination Degree (mCd), together with the evaluation of biological risk using the Sediment Quality Guidelines (ERL/ERM and TEL/PEL) of NOAA indicate a very high degree of pollution with great possibility for serious and irreversible impairments for aquatic communities. The most polluted sector, probably the most heavily contaminated marine environment in Greece, is located in front of the Drapetsona rocky coast (and particularly in the Sfageion Bay), where the synergistic action of urban untreated sewage deposited in the past (before the operation of the sewage treatment plant in Psytalia) and wastes from local industries or facilities has caused significant degradation of the marine system.

Key words: Heavy metals, sediments, pollution indices, urban coast.

Περίληψη

Ο βαθμός ρύπανσης του ιζηματογενούς πυθμένα στο αστικό παράκτιο περιβάλλον της Δραπετσώνας-Κερατσινίου διερευνάται μέσω ιζηματολογικής και γεωχημικής ανάλυσης. Τα αποτελέσματα δείχνουν ότι τα επιφανειακά ιζήματα αποτελούνται από αμμώδεις ιλύες και ιλυώδεις άμμους με σχετικά υψηλή περιεκτικότητα σε υγρασία (έως 114%) και ανθρακικά άλατα (24-86%), ενώ παρουσιάζουν ιδιαίτερα υψηλά επίπεδα συγκεντρώσεων (οι τιμές σε µg/g) σε κάποια επικίνδυνα μέταλλα όπως As=8-2677, Cd=0,2-15,4, Cr=82-428, Cu=18-567, Fe=570-28.900, Hg=0,05-0,71, Mn=101-1477, Ni=25-122, Pb=18-1394, Sn=1-18 και Zn=118-4821. Η εφαρμογή διάφορων δεικτών ρύπανσης, όπως του Δείκτη Γεωσυσσώρευσης (Igeo), Δείκτη Δυνητικής Οικολογικής Επικινδυνότητας (RI), Δείκτη Ρυπαντικού Φορτίου (PLI), Συνδυασμένου

Δείκτη Ρύπανσης (W) και Τροποποιημένου Βαθμού Ρύπανσης (mCd), καθώς και η αξιολόγηση της βιολογικής επικινδυνότητας των υφιστάμενων ιζημάτων με βάση τις Κατευθυντήριες Οδηγίες Ποιότητας Ιζημάτων της NOAA (ERL/ERM και TEL/PEL) δείχνουν ένα πολύ υψηλό βαθμό ρύπανσης με μεγάλη πιθανότητα για σοβαρές και μη αναστρέψιμες βλάβες στους θαλάσσιους οργανισμούς. Η πιο ρυπασμένη περιοχή, ίσως το πιο βαριά ρυπασμένο θαλάσσιο περιβάλλον στην Ελλάδα, βρίσκεται μπροστά από τη βραχώδη ακτή της Δραπετσώνας (και ιδιαίτερα στον Όρμο των Σφαγείων), όπου η συνεργιστική δράση των αστικών ανεπεξέργαστων λυμάτων, που είχαν αποτεθεί πριν από τη λειτουργία της μονάδας επεξεργασίας λυμάτων στην Ψυττάλεια, και των αποβλήτων από τις τοπικές βιομηχανίες έχουν προκαλέσει σημαντική υποβάθμιση του θαλάσσιου περιβάλλοντος.

Λέξεις κλειδιά: βαρέα μέταλλα, ιζήματα, δείκτες ρύπανσης, παράκτιο αστικό μέτωπο.

1. Introduction

Heavy metal pollution of marine ecosystems is a global problem resulting from numerous human activities, such as uncontrolled disposal of urban or industrial wastes, deliberate operational discharge or accidental spills of oil from ships, mining and smelting of metalliferous ores, and draining of intensively cultivated agricultural soils. Many metals, when they exceed a certain concentration, have toxic (e.g., Cr, Ni, Pb, Cd, and As), carcinogenic (e.g., Cr (VI), Ni and Cd) and teratogenic (As and Cd) effects on the health of aquatic organisms (Forstner, 1990). Although some other metals, such as Fe, Mn, Co, Cu, and Zn, are essential micronutrients for fauna and flora, they are harmful at high concentrations (Berkowitz et al., 2008). Contaminants may eventually pass through the food chain to humans and result in a wide range of adverse effects.

Marine sediments are a major “storehouse” of heavy metals and, therefore, they are used for assessing the environmental quality of aquatic areas (Solomons and Förstner, 1984). One of the approaches to estimate the degree of pollution in coastal sediments is based on combining geochemical and statistical methods (Wu et al., 2007), which distinguish the natural from anthropogenic inputs and determine the concentration of the excess heavy metal load and the potential impact of pollutants on the marine life.

This paper aims: (1) to investigate the spatial distribution of heavy metals in the surface sediments of the coastal urban stretch in front of Drapetsona and Keratsini; (2) to define the relationship between the chemical contamination of the sediment and the toxic biological effects on aquatic organisms through widely adopted Sediment Quality Guidelines (SQGs) and quantitative pollution indices for heavy metals.

2. The Study Area

The area under investigation is the coastal region that extends from the Krakaris jetty, at the exit of the Piraeus Port, to the western part of the Keratsini Port (Figure 1). It includes the rocky coast of Drapetsona, the bays of Sfageion and Foron (or Drapetsona), the Akrokeramos Harbour, the Drapetsona quay wall, and the Keratsini Port. Until the mid-1990s, the study area was receiving untreated domestic and industrial wastes from the Attica Basin (Figure 1 shows the location of the sewage outfall). The total daily discharge of sewage was about 600,000 m³ according to Theodorou and Perissoratis (1991). The operation of the waste treatment plant in Psyttalia has resulted in the gradual improvement of the environmental status of the Drapetsona-Keratsini coastal area and Saronikos Gulf (Krasakopoulou and Karageorgis, 2005). However, there are still many medium- to small-scale industries and facilities, such as a fertilizer plant (see FP in Figure 1), factories of plaster and cement, units of storage of petroleum and shipyards, as well as intense shipping activities (including transport of fuel, chemicals and other harmful compounds) that continue to degrade the quality of the marine environment.

Recently, Gkaragkouni (2005) studied the distribution of heavy metals and natural radionuclides in sediment cores from the Psyttaleia-Keratsini Strait identifying the pollution load of the sewage sludge deposited there before the operation of the wastewater treatment plant (WWTP) in Psyttalia. In addition, Galanopoulou et al. (2005, 2009) have determined the concentrations of heavy metals and synthetic organic compounds in the surface sediments of the Keratsini Port, characterizing the sediments as highly-heavily polluted, exceeding the toxic effect range.



Figure 1 - Location map of the Drapetsona-Keratsini coastal area showing the sampling positions of: (a) the analysed sediments (1-12); and (b) the reference sediment (DSS-5).

3. Laboratory Analyses and Data Processing

During the winter of 2010 twelve sediment samples (Figure 1) were collected from the Drapetsona-Keratsini coastal area using a grab sampler. All samples were separated into the different grain-size fractions using a set of sieves for the coarser fraction (>0.063 mm) and a grain size analyser (Sedigraph 5100) for the finer fraction (<0.063 mm). The sediment texture was classified according to Folk (1974) nomenclature. Total carbon was measured by a CHN elemental analyser (EA-1108, Fisons Instruments) with the precision of the method being within 5% (Karageorgis et al., 2005), whilst the organic carbon (orgC) portion was determined following the procedure described by Verardo et al. (1990) with the detection limit of the method being 2.3 µg/g per 10 mg of dry sample. The elemental geochemistry of the bulk sediment samples (<1 mm) was determined using a Philips PW-2400 X-Ray Fluorescence (XRF) system, with the relative uncertainties of the system being within 2% for the major element concentrations (Al, Ca, Fe, K, Mg, Na, P, Si, Ti, S) and within 5% for the trace element concentrations (As, Ba, Bi, Br, Ce, Co, Cr, Cu, Hf, I, La, Mn, Mo, Nd, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Th, V, Y, Zn, Zr) (Karageorgis et al., 2005). In addition, Cd concentrations were determined using the inductively coupled plasma combined with mass spectroscopy technique (ICP-MS), while Hg concentrations were estimated using cold vapor atomic absorption spectrometry.

The determination of major and minor element interrelationships and their association with grain size fractions and organic carbon content was achieved through a principal component analysis (PCA) using Varimax Rotation together with Kaiser Normalization (IBM SPSS statistics).

The assessment of the pollution status and toxicity of examined sediments was based on the following indices: (a) Geoaccumulation Index (*Igeo*) (Müller, 1969, 1981); (b) Pollution Load Index (*PLI*) (Tomlinson et al., 1980); (c) Potential Ecological Risk Factor (*Eri*) and Index (*RI*) (Hakanson, 1980); (d) Modified Contamination Degree (*mCd*) (Abraham and Parker, 2008); and (e) Combined Contamination Index (*W*) (Widianarko et al., 2000). The reference concentrations taken into account for the calculation of *RI*, *PLI*, *mCd*, and *W* were the element contents in the deepest sample (20-22 cm) of a box-core (DSS-5) recovered from the inner Saronikos Gulf at 71 m depth (Figure 1). Due to the low sedimentation rates recorded in the area (<0.6 cm 100 y⁻¹; Lykousis and Anagnostou, 1992); this sediment represents pre-industrial period and can be considered as non-contaminated. The baseline for the *Igeo* calculation was taken from the average composition of continental shale (Turekian and Wedepohl, 1961). The adverse effects of heavy metals, such as As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn, on the aquatic organisms were estimated by the use of two sets of empirical Sediment Quality Guidelines (SQGs) developed by the National Oceanic and Atmospheric Administration (NOAA), i.e., the Effects Range Low (ERL) and Effects Range Median (ERM) approach (Long et al., 1995) and the Threshold Effects Level (TEL) and Probable Effects Level (PEL) approach (McDonald et al., 1996).

4. Results

4.1 Sediment Physical Characteristics

The sediments of the coastal seabed of Drapetsona-Keratsini are characterized as sandy silt (sZ) and silty sand (zS) according to Folk (1974) nomenclature. The sand, silt and clay contents (see Table 1) range from ~19-90% (average ~53%), ~10-81% (average ~46%) and 0-8% (average 1.2%), respectively. The clay fraction is almost absent from all the examined sediment samples except in KER 2 and KER 8, where its proportion is less than 10%. The highest sand contents are found within the Keratsini Port (KER 11, 89.6%) and near the Sfageion Bay (KER 2, 73%), while the highest silt contents occur within the Keratsini Port (KER 10, 80.8%) and in front of the Krakaris jetty (KER 1, 77.4%) outside the Piraeus Port. The organic carbon (orgC) content (Table 1) can not be considered as very high, since its maximum value reaches ~2.8% (KER 10), whereas

the water content (w) and wet bulk density (ρ_t) of the analysed sediments fluctuated from ~14-117% and 1442-1989 kg/m³, respectively (Table 1).

4.2 Sediment Chemical Characteristics

A synopsis of the results of the geochemical analysis is presented in Table 1.

The spatial distribution of several chemical elements shows that their highest concentrations (in $\mu\text{g/g}$) occur mainly in two sectors: (a) in front of the Drapetsona coast (particularly nearby the Piraeus Port exit) [Fe (289,400), P (4800), Hg (0.71), La (28.5), Nd (26.3), Y (47.9), and Zr (88.3)], in the Sfageion Bay [Si (138,200), As (2677), Bi (19.1), Cd (15.4), Ce (84.2), Co (40), Cu (567), Hf (25.2), Mn (1477), Pb (1394), Sb (45) and Zn (4821)] and the Drapetsona Bay [Sn (18); and (b) in the central part of the Keratsini Port [Al (33,500), S (10,900), Ba (247), Cr (428), Mo (6.3), Ni (122), Rb (39.6), Sc (12.5), and V (74.4)].

In contrast, minimum element contents (in $\mu\text{g/g}$) are mainly found in two sites of the Keratsini Port: (a) between the piers I and II (KER 9), where Fe=5700, K=1300, Na=430, P=200, S=700, Si=19,400, Ti=600, As=8.1, Ba=14.3, Bi=1.4, Br=26.9, Ce=18.2, Co=2.4, Cr=81.8, Cu=17.7, Hf=2.9, La=4.8, Mo=1, Nd=4.3, Pb=18.1, Rb=5.3, Sr=190, V=10.9, Y=3.2, and Zn=53.3; and (b) in the inner Keratsini (Heracleous) Port (KER 11), where Al=10,200, Cd=0.2, Hg=0.05, I=10.8, Mn=99.7, Ni=25.3, and Zr=1.1.

Finally, the spatial distribution pattern of Ca, Sr and Th shows an inverse trend, compared to that of all the other elements, with higher contents occurring in KER 11 and lower ones being in front of the Drapetsona coast (KER 1 and KER 2).

Table 1 - Physical and chemical characteristics of the surface sediments in the Drapetsona-Keratsini coastal area.

| | Min | Max | Mean | StDev | | Min | Max | Mean | StDev |
|---|-------|--------|-------|-------|--------------------------------------|-------|--------|-------|--------|
| Sand % | 19.3 | 89.6 | 53.3 | 22.1 | Co $\mu\text{g/g}$ | 2.4 | 40.0 | 10.0 | 10.6 |
| Silt % | 10.4 | 80.8 | 45.6 | 22.9 | Cr $\mu\text{g/g}$ | 81.8 | 427.7 | 229.1 | 105.9 |
| Clay % | 0.0 | 8.0 | 1.2 | 2.7 | Cu $\mu\text{g/g}$ | 17.7 | 566.7 | 189.5 | 168.6 |
| w % | 13.7 | 117.0 | 55.7 | 25.9 | Hf $\mu\text{g/g}$ | 2.9 | 25.2 | 7.0 | 6.4 |
| ρ_t kg/m³ | 1442 | 1989 | 1.702 | 0.148 | Hg $\mu\text{g/g}$ | 0.05 | 0.71 | 0.23 | 0.19 |
| orgC % | 0.295 | 2.812 | 1.615 | 0.754 | I $\mu\text{g/g}$ | 10.8 | 72.9 | 38.0 | 17.6 |
| CaCO₃ % | 24.0 | 86.3 | 54.5 | 18.6 | La $\mu\text{g/g}$ | 4.8 | 28.5 | 14.6 | 7.0 |
| Al % | 1.02 | 3.35 | 2.17 | 0.76 | Mn $\mu\text{g/g}$ | 99.7 | 1476.8 | 391.1 | 386.4 |
| Ca % | 9.69 | 34.86 | 22.02 | 7.52 | Mo $\mu\text{g/g}$ | 1.0 | 6.3 | 3.3 | 1.6 |
| Fe % | 0.57 | 28.94 | 5.43 | 8.20 | Nd $\mu\text{g/g}$ | 4.3 | 26.3 | 12.2 | 5.9 |
| K % | 0.13 | 0.79 | 0.50 | 0.21 | Ni $\mu\text{g/g}$ | 25.3 | 122.1 | 77.6 | 32.7 |
| Mg % | 1.22 | 3.78 | 2.00 | 0.73 | Pb $\mu\text{g/g}$ | 18.1 | 1393.6 | 330.6 | 403.3 |
| Na % | 0.43 | 1.87 | 1.26 | 0.42 | Rb $\mu\text{g/g}$ | 5.3 | 39.6 | 26.6 | 9.2 |
| P % | 0.02 | 0.48 | 0.13 | 0.15 | Sb $\mu\text{g/g}$ | 4.5 | 45.0 | 22.1 | 17.0 |
| S % | 0.07 | 1.09 | 0.55 | 0.30 | Sc $\mu\text{g/g}$ | 5.3 | 12.5 | 10.2 | 2.1 |
| Si % | 1.94 | 13.82 | 7.25 | 3.23 | Sn $\mu\text{g/g}$ | 1.2 | 18.3 | 9.0 | 5.8 |
| Ti % | 0.06 | 0.23 | 0.15 | 0.05 | Sr $\mu\text{g/g}$ | 190.0 | 2435.9 | 649.0 | 707.5 |
| As $\mu\text{g/g}$ | 8.1 | 2677.4 | 411.3 | 802.6 | Th $\mu\text{g/g}$ | 4.4 | 32.4 | 11.6 | 8.5 |
| Ba $\mu\text{g/g}$ | 14.3 | 246.7 | 147.6 | 72.0 | V $\mu\text{g/g}$ | 10.9 | 74.4 | 42.6 | 16.6 |
| Bi $\mu\text{g/g}$ | 1.4 | 19.1 | 6.1 | 5.5 | Y $\mu\text{g/g}$ | 3.2 | 47.9 | 17.7 | 12.6 |
| Br $\mu\text{g/g}$ | 26.9 | 154.3 | 91.5 | 38.1 | Zn $\mu\text{g/g}$ | 53.3 | 4820.9 | 908.2 | 1369.9 |
| Cd $\mu\text{g/g}$ | 0.20 | 15.39 | 2.52 | 4.36 | Zr $\mu\text{g/g}$ | 1.1 | 88.3 | 44.4 | 24.4 |
| Ce $\mu\text{g/g}$ | 18.2 | 84.2 | 39.1 | 19.8 | | | | | |

The results from the applied statistical analysis (PCA) (Table 2) allowed us to classify the geochemical elements, grain-size fractions and organic carbon contents into four groups (components). The first group is characterized by a high positive interrelationship among Al, Ti, K, Mg, Rb, Na, V, and to a lesser extent among Ni, Si, Mo, Cr, Ba. This group clearly represents the “terrigenous aluminosilicates” component, since its principal element, i.e., aluminium, is mainly derived by terrestrial sources and it is extremely immobile in the marine environment (Bischoff et al., 1979). The second group demonstrates high positive loadings primarily for As, Bi, Zn, Cu, Pb, Y, Sb, Ce, Mn, La, Fe, Co, Hf, Cd, P, Nd, Si, Mo, S and secondarily for Ba and Hg. The strong inter-correlation among almost all the harmful heavy metals (i.e., As, Cd, Cu, Pb, Zn) implies their common origin from anthropogenic activities. The third group mainly consists of Br, Sn, I, Cr, Hg, Zr, Ni, Sc, Ba, Rb, and organic carbon, but also V, P, S, Fe are markedly loaded in this group. The third group corresponds to the “organic component” that represents the organic rich silty sediments that scavenge effectively some metals, eventually in the form of sulfides (Calvert and Pedersen, 1993). Finally, a strong correlation is evident among Ca, Sr, Th, and sand contents, which constitute the fourth group. However, this group shows an inverse geochemical behavior compared to the other defined components (i.e., “aluminosilicate”, “anthropogenic” and “organic”). The fourth group represents the autochthonous biogenic fraction of the sediments, comprising shells of calcareous organisms and their fragments. Strontium often substitutes for Calcium due to their similar ionic radii (Shankar et al., 1987).

Table 2 - Principal component analysis (PCA) using Varimax Rotation (rotation converged in 7 iterations).

| Element | Components | | | | Element | Components | | | |
|---------|------------|-------|-------|-------|---------|------------|-------|-------|-------|
| | 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 |
| Al | .070 | .190 | .964 | -.082 | Hf | .840 | .176 | .225 | -.274 |
| Ca | -.881 | -.392 | -.173 | .116 | Hg | .451 | .789 | -.082 | .097 |
| Fe | .866 | .447 | .105 | -.157 | I | .121 | .814 | .210 | -.023 |
| K | .193 | .288 | .911 | -.129 | La | .870 | .259 | -.012 | .073 |
| Mg | .127 | .120 | .696 | .174 | Mn | .877 | .171 | .349 | -.226 |
| Na | .440 | .335 | .639 | .094 | Mo | .743 | .197 | .530 | .137 |
| P | .796 | .574 | .073 | -.023 | Nd | .788 | .349 | .042 | .196 |
| S | .666 | .531 | .248 | .270 | Ni | -.020 | .669 | .660 | -.176 |
| Si | .750 | .078 | .586 | -.114 | Pb | .913 | .216 | .322 | .015 |
| Ti | .275 | .149 | .932 | -.128 | Rb | .115 | .619 | .659 | .172 |
| As | .950 | .198 | .099 | .032 | Sb | .910 | -.333 | .000 | -.192 |
| Ba | .519 | .635 | .453 | .001 | Sc | .453 | .650 | .571 | -.029 |
| Bi | .939 | .227 | .161 | -.016 | Sn | .270 | .837 | .194 | .241 |
| Br | .219 | .838 | .294 | .087 | Sr | -.025 | .015 | .038 | .945 |
| Cd | .840 | .142 | .155 | -.385 | Th | -.392 | .213 | -.055 | .848 |
| Ce | .908 | .218 | .276 | -.175 | V | .391 | .606 | .616 | .010 |
| Co | .856 | .150 | .294 | -.270 | Y | .911 | .361 | .090 | .089 |
| Cr | .215 | .813 | .461 | .005 | Zn | .926 | .209 | .284 | .008 |
| Cu | .925 | .279 | .221 | -.011 | Zr | .480 | .693 | .288 | -.299 |

5. Assessment of Heavy Metal Pollution in Sediments

5.1 Pollution Indices

The Geoaccumulation Index (*Igeo*) values of As, Cd, Pb, and Zn (Table 3) are greatly enhanced in front of the Drapetsona coast (particularly nearby the Piraeus Port exit) and in the Sfageion and Drapetsona bays, indicating strongly, strongly-to-extremely and extremely contaminated sediments, respectively. Slightly lower values are found westwards up to the Drapetsona jetty as well as in the central basin of the Keratsini Port. Therein, the *Igeo* values reveal moderate and moderate-to- strong contamination. At the other sites the *Igeo* values are low indicating an absence of pollution. The *Igeo* values of Cr, Cu and Sn (Table 4) show a similar trend to those of As, Cd, Pb, and Zn, but being quite lower. They indicate moderate or moderate-to-strong contamination for the sediments in the Drapetsona coastal area and in the central basin of the Keratsini Port, but no-to-moderate contamination for the sediments of the other sites. The *Igeo* values of Co, Hg, Mn, and Ni (Table 4) range into the classes 0 and 1, suggesting uncontaminated or uncontaminated-to-moderately contaminated sediments. Finally, the *Igeo* values of Fe are higher (2.0) nearby the Piraeus Port exit, lower (0.1-0.9) in the Sfageion and Drapetsona bays, and minimum (<0) in the rest of the study area (Table 4). This distribution pattern exhibits an increasing trend for Fe towards the Piraeus Port.

The Pollution Load Index (*PLI*) is a quick tool for determining the pollution status of sediments in different sites. The *PLI* of most of the examined sediments is extremely high indicating “progressive deterioration”. Only the surface sediments located between the piers I and II of the Keratsini Port (KER 9) exhibit “baseline pollution” (Table 4).

The Potential Ecological Risk Index (*RI*) implies “severe” and “serious” risk for the majority of the sediments, except for these that occur in the inner basin of the Keratsini Port (low risk) and at the sites KER 7-KER 9, where the risk is moderate (Table 4).

Table 3 - The Geoaccumulation Index (*Igeo*) of twelve elements in the analysed sediments (KER) is presented. The *Igeo* is categorized into seven classes: 0 (values ≤ 0 , uncontaminated), 1 (values 0-1, uncontaminated to moderately contaminated), 2 (values 1-2, moderately contaminated), 3 (values 2-3, moderately to strongly contaminated), 4 (values 3-4, strongly contaminated), 5 (values 4-5, strongly to extremely contaminated), and 6 (values >5 , extremely contaminated).

| ID | <i>Igeo</i> As | <i>Igeo</i> Cd | <i>Igeo</i> Co | <i>Igeo</i> Cr | <i>Igeo</i> Cu | <i>Igeo</i> Hg | <i>Igeo</i> Fe | <i>Igeo</i> Mn | <i>Igeo</i> Ni | <i>Igeo</i> Pb | <i>Igeo</i> Zn | <i>Igeo</i> Sn |
|----|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| 1 | 5.1 | 4.6 | -1.1 | 1.0 | 2.7 | 0.2 | 2.0 | -1.3 | -0.5 | 4.2 | 3.2 | 0.5 |
| 2 | 7.1 | 6.7 | 0.5 | -0.1 | 3.1 | -2.6 | 0.1 | 0.2 | -1.1 | 5.5 | 5.1 | -1.9 |
| 3 | 6.0 | 5.2 | -0.5 | 1.3 | 2.3 | -0.8 | 0.9 | -0.8 | -0.1 | 4.6 | 3.9 | 1.0 |
| 4 | 2.9 | 2.7 | -2.4 | 0.9 | 1.2 | -0.7 | -1.3 | -2.3 | -0.4 | 2.9 | 1.7 | 0.6 |
| 5 | 1.2 | 1.5 | -2.8 | 0.5 | 0.8 | -0.9 | -2.3 | -2.7 | -0.8 | 2.0 | 0.9 | 0.2 |
| 6 | 1.1 | 2.5 | -2.4 | 1.3 | 1.3 | -1.1 | -1.7 | -2.3 | 0.2 | 2.4 | 1.7 | 0.6 |
| 7 | -0.1 | 1.3 | -2.1 | 0.4 | 0.2 | -2.2 | -2.2 | -2.6 | -0.3 | 1.3 | 0.5 | -0.6 |
| 8 | -0.2 | 0.9 | -2.2 | 0.5 | 0.2 | -2.9 | -2.3 | -2.7 | -0.1 | 1.1 | 0.3 | -0.6 |
| 9 | -1.3 | 2.0 | -3.6 | -0.7 | -1.9 | -3.1 | -3.6 | -3.7 | -1.8 | -0.7 | -1.4 | -2.9 |
| 10 | 1.0 | 3.1 | -2.0 | 1.7 | 1.6 | -1.9 | -1.4 | -2.1 | 0.3 | 4.0 | 2.3 | 0.9 |
| 11 | -0.2 | 0.4 | -3.6 | -0.6 | -0.7 | -3.5 | -3.5 | -3.7 | -2.0 | 0.7 | -0.3 | -1.6 |
| 12 | 0.9 | 2.3 | -2.1 | 0.9 | 0.5 | -2.7 | -1.7 | -2.0 | 0.2 | 2.1 | 0.8 | -0.8 |

Table 4 - The Pollution Load Index (*PLI*), Potential Ecological Risk Index (*RI*), Modified Degree of Contamination (*mCd*), and Combined Contamination Index (*W*) of the analysed sediments (KER) are presented. *PLI* indicates “perfection”, “baseline pollution” and “progressive deterioration”, when values are 0, 1 and >1, respectively. *RI* demonstrates “low risk” (values <150), “moderate risk” (values 150-300), “severe risk” (values 300-600), and “serious risk” (values >600). *mCd* shows whether the degree of contamination is zero to very low (values 0-1.5), low (values 1.5-2), moderate (values 2-4), high (values 4-8), very high (values 8-16), extremely high (values 16-32), and ultra high (values >32). *W* classifies the sediments as unpolluted (values ≤0), slightly polluted (values 0-1), polluted (values 1-2), and heavily polluted (values >2).

| ID | <i>PLI</i> | <i>RI</i> | <i>mCd</i> | <i>W</i> |
|-------------|------------|-----------|------------|----------|
| 1 | 31,519 | 2652 | 23.1 | 9.0 |
| 2 | 92,130 | 9157 | 75.8 | 9.9 |
| 3 | 58,846 | 3758 | 33.6 | 9.5 |
| 4 | 1254 | 792 | 7.3 | 6.2 |
| 5 | 147 | 420 | 3.9 | 4.3 |
| 6 | 649 | 607 | 5.8 | 5.6 |
| 7 | 39 | 276 | 2.8 | 3.2 |
| 8 | 24 | 219 | 2.5 | 2.8 |
| 9 | 1 | 291 | 1.7 | 0.1 |
| 10 | 1656 | 801 | 8.4 | 6.4 |
| 11 | 3 | 149 | 1.5 | 1.0 |
| 12 | 144 | 450 | 4.1 | 4.3 |
| Mean | 15,534 | 1631 | 14.2 | 5.2 |

The Modified Degree of Contamination (*mCd*) reveals low pollution for KER 9 and KER 11 (Keratsini Port), moderate pollution for KER 5, KER 7 and KER 8, high pollution for KER 4, KER 6 and KER 12, very high pollution for the central basin of the Keratsini Port; extremely high pollution for the site nearby the Piraeus Port exit, and Ultra high pollution for the Sfrageion and Drapetsona bays (Table 4).

Finally, the Combined Contamination Index (*W*) suggests that the sediments in the inner basin of the Keratsini Port and in the sector between the piers I and II are slightly polluted. For the rest of the study site, the *W* index indicates heavily polluted sediments (Table 4).

5.2 Sediment Quality Guidelines

The biological impact of heavy metal concentrations on aquatic life has been assessed by comparing these concentrations to the marine ERL/ERM and TEL/PEL thresholds (Figure 2). The sedimentary seabed stretching from the Piraeus Port exit to the Aktokeramos Harbour is an area of high concern, since the enhanced contents of As, Cd, Cr, Cu, Ni, Pb, and Zn can cause irreversible adverse effects to marine organisms. To a lesser extent this may also happen in the central basin of the Keratsini Port. However, the rest of the study area does not face this threat.

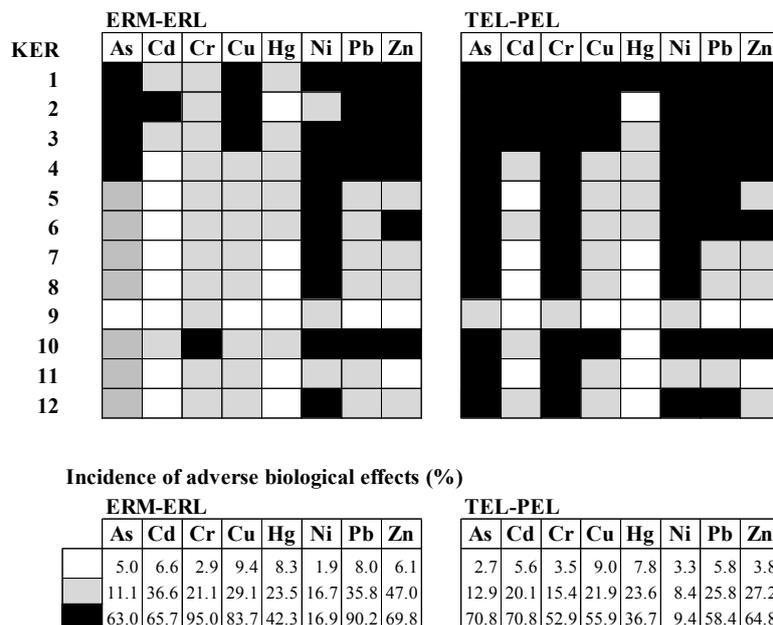


Figure 2 - Evaluation of aquatic life impairment due to the heavy metal load of the study area sediments using the marine ERM/ERL and TEL/PEL Guidelines.

6. Conclusions

The Drapetsona-Keratsini coastal area is a highly polluted area, since it has received for decades untreated urban sewage effluents (until the operation of the Psyttalia WWTP in 1994), industrial solid and liquid wastes and by-products of shipping activities. The distribution patterns of harmful chemical elements, organic carbon content, values of various pollution indices (*Igeo*, *PLI*, *RI*, *mCd*, and *W*) and the Sediment Quality Guidelines of NOAA show that the sector in front of the Drapetsona coast (from the Piraeus Port exit to the Drapetsona jetty), and particularly in the bays of Sfageion and Drapetsona (Foron), is extremely polluted with great possibility for the marine life to be severely and irreversibly impaired. However, the quality of the surface sediments in the adjacent Keratsini Port is relatively better, although the pollution conditions in the central basin of the port are comparable to those of the Drapetsona coast.

7. References

- Abraham G.M.S. and Parker P.J. 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediment from Tamaki Estuary, Auckland, New Zealand, *Environmental Monitoring and Assessment*, 136, 227-238.
- Berkowitz B., Dror I. and Yaron B. 2008. *Contaminant Geochemistry: Interactions and Transport in the Subsurface Environment*, Springer-Verlag, Berlin, 412 pp.
- Calvert S.E. and Pedersen T.F. 1993. Geochemistry of recent oxic and anoxic marine sediments: Implications for the geological record, *Marine Geology*, 113, 67-88.
- Folk R.L. 1974. *Petrology of Sedimentary Rocks*, Hemphill Publications Company, Texas, 182 pp.
- Forstner U. 1990. Contaminated sediments, *Lecture Notes in Earth Science*, vol. 21, Springer-Verlag, Berlin, 157 pp.
- Galanopoulou S., Vgenopoulos A. and Conispoliatis N. 2005. DDTs and other chlorinated organic pesticides and polychlorinated biphenyls pollution in the surface sediments of Keratsini harbour, Saronikos gulf, Greece, *Marine Pollution Bulletin*, 50, 520-525.

- Galanopoulou S., Vgenopoulos A. and Conispoliatis N. 2009. Anthropogenic Heavy Metal Pollution in the Surficial Sediments of the Keratsini Harbor, Saronikos Gulf, Greece, *Water, Air, and Soil Pollution*, 202 (1-4), 121-130.
- Gkaragkouni 2005. Heavy metals and natural radionuclides in marine sediments from the Psytalia-Keratsini strait, Saronikos Gulf, *MSc thesis*, University of Patras, 180 pp.
- Hakanson L. 1980. Ecological risk index for aquatic pollution control. A sedimentological approach, *Water Research*, 14 (5), 975-1001.
- Karageorgis A.P. Anagnostou C.L. and Kaberi H. 2005. Geochemistry and mineralogy of the NW Aegean Sea surface sediments: implications for river runoff and anthropogenic impact, *Applied Geochemistry*, 20, 69-88.
- Krasakopoulou E. and Karageorgis A. 2005. Spatial and temporal distribution patterns of suspended particulate matter and particulate organic carbon in the Saronikos Gulf (eastern Mediterranean, Greece), *Geo-Marine Letters*, 25, 343-359.
- Long E.R., MacDonald D.D., Smith S.L. and Calder F.D. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management*, 19 (1), 81-97.
- Lykousis V. and Anagnostou C. 1992. Sedimentological and paleogeographic evolution of the Saronikos Gulf in the end of Quaternary, *Bull. Geol. Soc. Greece*, 28(1), 501-510.
- MacDonald D.D. Scott C.R., Calder D.F., Long R.E. and Ingersoll G.C. 1996. Development and evaluation of sediment quality guidelines for Florida coastal waters, *Ecotoxicology*, 5, 253-278.
- Müller G. 1969. Index of geoaccumulation in sediments of the Rhine River, *Journal of Geology*, 2 (3), 108-118.
- Müller G. 1981. Die Schwermetallbelastung der sedimente des Neckars und seiner Nebenflüsse: eine standsaufnahme, *Chemiker Zeitung*, 105, 157-164.
- Solomon W. and Forstner U. 1984. Metals in the Hydrocycle. *Springer-Verlag*, New York, 349 pp.
- Theodorou A. J. and Perissoratis C. 1991. Environmental considerations for design of the Athens sea outfall, Saronikos Gulf, Greece, *Environmental Geology*, 17 (3), 233-248.
- Tomlinson D.C., Wilson J.G., Harris C.R. and Jeffery D.W. 1980. Problems in the assessment of heavy metals levels in estuaries and the formation of a pollution index, *Helgol. Wiss. Meeresunters*, 33 (1-4), 566-575.
- Turekian K.K. and Wedepohl K.H. 1961. Distribution of the elements in some major units of the earth's crust, *Geological Society of America Bulletin*, 72 (2), 175-192.
- Verardo D.J., Froelich P.N. and McIntyre A. 1990. Determinations of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Analyzer, *Deep-Sea Research*, 37, 157-165.
- Widianarko B., Verweij R.A., van Gestel C.A.M. and van Straalen N.M., 2000. Spatial distribution of trace metals in sediments from urban streams of Semarang, Central Java, Indonesia, *Ecotoxicology and Environmental Safety*, 46, 95-100.
- Wu Y., Hou X., Cheng X., Yao S., Xia W. and Wang S. 2007. Combining geochemical and statistical methods to distinguish anthropogenic source of metals in lacustrine sediments: a case study in Dongjiu Lake, Taihu Lake catchment, China, *Environmental Geology*, 52, 1467-1474.