Comparative hydrogeochemical study of the Romanian Black Sea coast and the Spanish Atlantic coast – from Huelva to Cadiz

PhD thesis summary

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The present thesis represents a comparative study of the distribution of heavy metals in the water and sediments of the coastal areas of the Romanian Black Sea and the Andalusian Atlantic, through an overview of the pollution sources and the temporal and spatial dynamics of heavy metal concentrations under the influence of natural or anthropogenic pressures.

In order to achieve the complex objectives of the thesis and meet the requirements of the European directives regarding the monitoring of marine water quality, different methods of analysis have been used, namely atomic absorption spectrometry, graphite electrode atomic emission spectrometry with inductively coupled plasma, XRF and XRD. For the interpretation of data, modern methods of processing and representation, such as graphs and maps of the chemical contents, have been employed.

The thesis consists of *seven* chapters, namely: *I. An overview of previous research; II. Geographical and geological considerations on the areas studied; III. Coastal dynamics in the two areas studied: the Romanian Black Sea coast and the Spanish Atlantic coast – from Huelva to Cadiz; IV. Water chemistry of the Black Sea and the Atlantic Ocean; V. Samples and analytical methodology; VI. Coastal sediment mineralogy; VII. Geochemical distribution of elements in coastal waters and sediments*, followed by C*onclusions* and *Bibliography.*

After an introduction, in Chapter I are presented the main geological, hydrological and geochemical studies performed over time on the Romanian Black Sea coast and the Spanish Atlantic coast. The most significant papers focusing on the hydrology and geochemistry of the waters and sediments of the two coastal areas that have been published in recent years by various researchers have also been mentioned.

Chapter II deals with the main geographical, geomorphological, geological and human-induced features of the two coastal areas studied, with an emphasis on the influence of certain geomorphological and geological elements at different stages of the development of these two areas, in their interaction with coastal processes associated with erosion and the transport and deposition of sediment.

The two area studied are, on the one hand, the entire coastline of Romania, located in the western part of the Black Sea, with a length of about 240 km, and, on the other, the section of the

Spanish coast represented by the Gulf of Cádiz (southwestern Spain). The latter comprises the following: the Huelva coast, the Atlantic coast of the province of Cádiz, Cadiz Bay, and the 6 estuaries of the Atlantic Ocean: Guadiana, Carreras, Piedras, Tinto and Odiel, and the Padre Santo Channel, Guadalquivir, Guadalete. For this area, the Iberian Pyrite Belt mineralizations on the rivers Tinto and Odiel are presented in both geochemical terms and as the main source of pollution for the waters of the Spanish coast stretching between Huelva and Cádiz.

Chapter III deals with the dynamics of the two coastlines studied. The general presentation of the main depositional facies of the coastal system and of the dynamic elements acting upon it (wind, waves, currents, tidal regime) is followed by a description of the main dynamic elements and their influence on both the Romanian seaside and the Spanish coastline. For the Romanian seaside, data on changes in sea level, temperature, humidity, rainfall, sediment input and transport, beach erosion and the impact of human activities have also been provided.

Chapter IV consists of an overview of the water chemistry of the Black Sea and the Atlantic Ocean, respectively, followed by a summary of the chemical and hydrological parameters of the Black Sea, with particular reference to the Romanian seaside and emphasis on the concentrations and residence times of the main chemical species, and a more detailed description of the water chemistry of the Atlantic in the area of the Gulf of Cádiz.

Chapter V describes the sampling process carried out in the two areas and the methods used in the analyses.

For the Romanian coast of the Black Sea, 31 sediment samples were collected at different distances from the shore. The samples went through several preparation steps, and were then analyzed as follows: 25 samples by means of X-ray diffraction, in order to determine the mineralogical composition, and 31 samples through X-ray fluorescence, for the following elements: Zn, Cu, Pb, Co, Ni , Cr, Fe, Mn, Ca, K, Al, Cd, As, Mo, Ba and Br, Ce, Cs, Hf, La, Nb, Nd, Rb, S, Sc, Sr, Th, Ti, U, V , Y, and Zr. The pH of all the samples was measured, as well. The analyses were performed within the Departments of Geology and Physics of the "Alexandu Ioan Cuza" University of Iași.

The study of the Atlantic coastline from Huelva to Cádiz is based on the results published in the paper titled "The assessment of water and sediment quality on the Andalusian coast." For the samples used, which were collected from 80 sampling points, the harvesting and storage conditions, which were in agreement with the parameters analyzed and the norms and recommendations of the "Standard Methods for the Examination of Water and Wastewater" (1998), were described. The methods used in the analyses of the sediment and water samples gathered from the Andalusian coast, analyses which reveal the variety and specificity of the former in relation to the behavior of the element analyzed in the environment under study, were also specified.

The spatial distribution of geochemical elements in coastal sediments was illustrated using the Surfer 9.7 software and the kriging method. The statistical parameters, the histogram and dendrogram of the contents of minor elements were obtained through the statistical processing of analytical data, using the Excel software from Microsoft Office and the SPSS 17.0 software.

Chapter VI presents the mineralogy of the sediment in the two sectors of the Romanian coast. The samples collected here are characterized by a mixture of carbonate minerals, quartz and feldspars. They can be divided into two categories: those gathered in the south (Eforie – Vama Veche) are predominantly composed of calcite (15 samples), while those collected from the northern sector (Năvodari – Constanța) are predominantly made up of quartz (10 samples). The samples MN20 and MN21, collected from the southern sector, are largely composed of quartz, followed by calcite and aragonite, perhaps as a result of the sand-replenishing activities that are often carried out in the area of the Costineşti Obelisk, Venus Beach and Cap Aurora, where storms have been quite frequent recently, and, in order to preserve the beach, large amounts of sand have been brought from other areas and mixed with the ancient sands. Two areas can, thus, be delineated: the Năvodari – Constanța zone, where siliciclastic sands prevail, and the Vama Veche – Eforie zone, where sands rich in calcite are predominant.

The main minerals identified in the Năvodari – Constanța zone are the following: quartz, calcite, dolomite, albite, hematite, orthoclase, microcline, and muscovite.

In the Vama Veche – Eforie zone, in nearly all of the samples, biogenic calcite is predominant. Quartz, hematite, aragonite, muscovite, dolomite, albite and gypsum have also been identified.

The Andalusian coast is composed of fine sand in the northern sector, and medium-grained sand in the central and southern sectors. The mineralogical analyses performed have indicated the predominance of quartz in the sandy fraction. Within the sediment, the heavy fraction never exceeds 5%, the heavy minerals present being zircon, garnet, tourmaline, epidote and andalusite. In the Gulf of Cádiz, the clay fraction is composed of illite (50-70%), kaolinite (10-20%), smectite (5-15%), and I-S (5-15%). The chemical and mineralogical processes that occur in the area of the mouth of River Tinto have also been presented.

The two coastal beaches are composed of medium, fine and very fine sand, mainly siliciclastic and carbonatic in composition. The results obtained were compared with those of other studies carried out on various coastal areas of the world, and they show that the sands of the Romanian seaside have similar contents in terms of light minerals, with a higher content of carbonates and quartz, and a lower content of clay minerals. The Andalusian Atlantic coast is characterized by the presence of clay minerals as a result of the contributions of numerous rivers and of the estuaries along it.

Chapter VII focuses on the geochemistry of sediments and water in the two areas studied. It begins by providing an overview of the sources, concentrations and toxicity of metals in marine waters, and it continues with the geochemical distribution of elements in the waters and sediments of the Romanian Black Sea coast. Thus, the mean annual concentrations of Cu, Pb, Zn, Cd, Fe and Mn in the surface waters of the Romanian seaside and Romanian harbors are presented, followed by the geochemistry of various chemical elements (Co, Cr, Cu, Cd, Mn, Ni, Pb, Zn and As) present in the sediments of the Romanian coast. The spatial distribution of concentrations in different geographic areas displays a high degree of variability, depending on the element, the sediment type, the distance from shore and the influence of anthropogenic factors. Significant differences were noted particularly in the case of Cu, Ni and Cr, elements which exhibit increased accumulations in the sediments found in the area subjected to fluvial influence (Sulina – Portița) and in the aquatorium of Constanța Sud harbor, compared to neighboring areas. Cadmium showed a more uniform distribution along the coastline, the highest mean value having been recorded in Constanța Sud harbor. Normal values for most of the elements investigated were recorded in the central sector of the coast (East Constanța), as well as in the southern extremity (Vama Veche). Based on the results of XRF analyses, distribution maps for all the elements analyzed were created. The distribution graphs reveal sectors with higher concentrations, where the sediments have stored heavy metals as a result of strong terrigenous and anthropogenic influences (the mouths of the Danube, industrial wastewater discharges from the former S.C. "Fertilchim" S.A. Năvodari, the harbors of Constanța, Mangalia and Midia etc.), compared to those where the superficial sediments are low in heavy metals (the sector south of the mouths of the Danube, up to Cape Midia, and several smaller sectors located in the southern part of the Romanian seaside), and in which the influence of the land, although present, is lower in intensity than in the areas mentioned above.

Lower concentrations of heavy metals are found mostly in the sediments collected from the sector located south of the mouths of the Danube.

In the sediments found in the proximity of the mouths of the Danube, the terrigenous and anthropogenic influences are felt with greater intensity, as proven by the higher values, while south of this area, up to Cape Midia, these influences exist, but their impact is greatly diminished.

An important role in the accumulation of heavy metals in the surface sediments of the sectors mentioned is played by the high amount of organic matter, the main ligand of these elements, which contributes to the formation of organometallic compounds that are far more stable and more resistant than the other types of metallic ions.

Based on the arguments above, one may infer that the Romanian seaside can be divided into two distinct areas, one with sediments rich in heavy metals (in the vicinity of the mouths of the Danube and on the premises of harbors), and another with sediment less rich in metallic ions, as a result of the different intensity of anthropogenic and terrigenous influences. The fine fraction

and the organic matter content are particularly significant when it comes to the existence and concentration of heavy metals in surface sediments.

The Andalusian coast has been studied in terms of the concentration levels of the specific pollutants found in its sediments and water that were recorded between 1999 and 2003. For the water samples collected from this coast, the following heavy metals have been determined: Cu, Zn, Ni, Cr (VI), Cd, Pb, As, and Hg. We have carried out measurements of the pH and have analyzed the phosphates, the nitrates (NO_2^-, NO_3^- and PO_4^{3-}), the total organic carbon (TOC), the ammonia, dissolved oxygen, and fatty acids. For the sediment samples, the following heavy metals were analyzed: Cr, Co, Cd, Pb, Ni, Zn, As, and Hg.

The test results are discussed in terms of the mean concentrations, which are illustrated by means of charts, and the Metal Content Index (MCI_8) is calculated.

For the Andalusian coastline, all the sources of pollution are inventoried, being divided into: sewage produced by coastal populations, industrial waste, and the input of rivers crossing areas with mining activity (the Iberian Pyrite Belt).

For each of the sectors of the Andalusian coastline analyzed, grade-based classifications were made based on the results of the analysis of water samples. For the sediments, global quality levels were determined based on heavy metal concentrations.

The water and sediments of the Huelva coast display low levels of contamination, which allows its inclusion, to a degree of over 70%, in the "good" quality class.

The water samples collected from the Atlantic coast of Cádiz show average concentrations of the parameters analyzed lower than those obtained for the entire Andalusian coast, with the exception of cadmium, nitrites and phosphates. The sediments of the Cádiz coast display the lowest average value of the MCI_8, 3.44, of all the areas studied. They also exhibit the lowest average values for Cu, Zn, Ni, Cr, Pb, As and Hg out of all the areas of the Andalusian coast.

In the Cádiz Bay area, located in the southwestern part of the Atlantic coast of Spain, the average concentrations of metals (an average MCI_8 of 0.62) are similar or slightly higher than the average values across the Andalusian coast (an average MCI_8 of 0.58). Among the nonmetallic parameters, nitrites, ammonia and phosphates are elevated. However, in 76.3% of cases, the waters of Cadiz Bay fall within level 1 of quality ("good"). The sediments in this area display a low degree of contamination with heavy metals, corresponding, thus, to quality levels 1 ("good") and 2 ("sufficient"), with the exception of Cd, which makes them correspond to either level 3 ("insufficient") (for 2% of the results) or level 4 ("bad") (for 2% of the results).

The Guadiana estuary has a mean level of heavy metal concentrations below the average determined for all the estuaries. Arsenic displays higher concentrations, while those of Ni are lower. Nonmetallic contaminants are present in low concentrations, relative to the averages established for estuarine environments. Based on the concentration of heavy metals, the water

falls in either category 1 or category 2, while, based on its non-metallic contaminants, it can be included in either class 3 or class 4, due to its suspended solids and nitrates. The average concentrations of metals in the sediments are slightly higher than in the rest of the estuaries, with higher values for As and Zn. Chromium displays the lowest average content out of all the estuaries studied.

The Carreras estuary displays, for all of its metals, the quality levels 1 and 2. Some non-metallic parameters exhibit low percentages, which correspond to level 3. In the sediments, the metal content indices (an average MCI_8 of 15.8) exceed the average value of this parameter in the Andalusian estuaries (an average MCI_8 of 12.1). The presence of relatively high concentrations of As, Hg and Zn can be attributed to the geological substratum.

In the Piedras estuary, the concentrations of all metals are either similar to or slightly lower than the average values obtained for the estuaries studied, with the exception of copper and zinc. The nonmetallic parameters show lower levels, compared to the corresponding average values of the Andalusian estuaries. Based on metal contents and nonmetallic parameters, the water quality corresponds to levels 1 and 2, with the exception of Zn, which reaches level 3 in 5% of cases, dissolved oxygen, nitrates, nitrites, TOC, which reach level 3, and suspended solids, which correspond to level 4. The average concentrations of the heavy metals analyzed (an average MCI_8 of 14.0) are higher than the average values of the other Andalusian estuaries (an average MCI_8 of 12.1), with lower values for Ni, Cr and Hg.

In the Odiel and Tinto estuaries and the Padre Santo Channel – Ria (estuary) Huelva, the concentration levels of the metals in the water are very high, especially for Cu, Zn, Ni, Cd, Pb and As. The Tinto estuary exhibits the highest average MCI (121) of all the areas studied, followed by the Odiel estuary (17.1) and the Padre Santo Channel (3.96). The high concentrations of Ria Huelva phosphates and fluorides are due to industrial waste and phosphogypsum deposits. The quality level of the water is, thus, 4 (“bad”). The nonmetallic parameters of the Tinto estuary reach level 4 due to their pH, dissolved oxygen, TOC, ammonia, phosphates and suspended solids. The sediments of the Odiel estuary have yielded the highest values recorded throughout Andalusia, reaching the threshold for nearly all the metals analyzed (Cu, Pb, As, Hg, Zn and Cd).

In the Guadalquivir estuary, the average concentrations of most of the metals in the water are slightly higher (an average MCI_8 of1.65) than those obtained for Andalusian estuaries (an average MCI_8 of 1.51). This is also true for the TOC content, nitrites and fatty acids. The mean values of the suspended solids, nitrates and phosphates are the highest of all the areas studied. Dissolved oxygen shows the lowest concentrations recorded throughout Andalusia.

The waters of Guadalete estuary exhibit metal contents that are similar to or slightly below those of Andalusian estuarine environments. The nonmetallic parameters are similar to the average concentrations obtained for Andalusian estuaries. It is worth highlighting, nevertheless,

the low nitrate concentration and the high ammonia concentration, the latter being the highest of all the areas studied. The concentrations of metals in the sediments of the Guadalete estuary (an average MCI_8 of 11.1) are similar to or below those of the Andalusian estuarine environments (an average MCI_8 of 12.1). It is, again, worth noting that, out of all the areas studied, As has the lowest concentration in the sediments of Guadalete.

The chapter ends with a comparison between the parameters of the two coastal areas studied. Thus, Cu, Pb, Zn, Cd and As exhibit much lower values in the sediments of the Romanian coast, while the Cr and Mn contents slightly exceed those obtained for the Andalusian coast.

The *Conclusions* of the thesis summarize the main geochemical characteristics of the water and sediments of the two areas studied. The values determined for the heavy metals present in the Romanian coastal areas are typical for the northwestern shelf of the Black Sea, found under the influence of three great rivers: the Danube, the Dnieper and the Dniester.

On the Romanian coast, the most contaminated sediments were found inside marine harbors, in the shallow areas next to the points where sewage is discharged, as well as in the sector in front of the mouths of the Danube. Elevated metal levels in harbor sediments were discovered particularly in the vicinity of ore berths and shipyards.

For each chapter, bibliographic documentation has contributed to the knowledge of the complexity of the issues addressed in deciphering coastal dynamics and the factors that influence sediment transport in coastal areas, with implications in the distribution and dynamics of the concentrations of specific pollutants.

The main achievements of the present thesis are the following:

- a comparative hydogeochemical study of the waters of the Romanian and Spanish coasts, which has entailed the processing of a large number of bibliographic sources;

- the determination of sediment mineralogy and chemistry for the Romanian seaside, based on 31 samples;

- the determination of the concentrations of heavy metals in the sediments and waters of the coastal areas studied;

- the devising of geochemical distribution maps for nine chemical elements present in the sediments of the Romanian coast;

- the illustration of the spatial distribution of pollutants for each of the areas, which allowed the delineation of coastal sectors based on the degree of pollution;

- the classification of the two environments analyzed based on water and sediment quality parameters, in agreement with the environmental standards imposed through global quality levels

- the providing of an explanation for the presence of high concentrations of pollutants, through detailed analyses, for each area (coast, estuaries, bays), of the land-based sources of pollution and the mechanisms through which they act;

- the providing of an explanation for the influence of natural conditions upon the marine environment in terms of the distribution, accumulation and mobility of heavy metals and nonmetallic pollutants between estuaries, bays and the coast.