Heavy Metals Estimation in Coastal Areas Using Remote Sensing, Field Sampling and Classical and Robust Statistic

Elena Castillo-López, Raúl Pereda, Julio Manuel de Luis, Rubén Pérez, Felipe Piña

Abstract—Sediments are an important source of accumulation of toxic contaminants within the aquatic environment. Bioassays are a powerful tool for the study of sediments in relation to their toxicity, but they can be expensive. This article presents a methodology to estimate the main physical property of intertidal sediments in coastal zones: heavy metals concentration. This study, which was developed in the Bay of Santander (Spain), applies classical and robust statistic to CASI-2 hyperspectral images to estimate heavy metals presence and ecotoxicity (TOC). Simultaneous fieldwork (radiometric and chemical sampling) allowed an appropriate atmospheric correction to CASI-2 images.

Keywords—Remote sensing, intertidal sediment, airborne sensors, heavy metals, ecotoxicity, robust statistic, estimation.

I. INTRODUCTION

SINCE the 1980s, remote sensing has been applied to study parameters related to coastal zones. In the beginning of the 21st century, these methods provided imagery with good temporal and spectral resolution. This fact fostered new systems to acquire reliable imagery, turning remote sensing into a powerful tool to manage water and to detect natural disasters, such as heavy metals pollution.

The spatial resolution of the images to be used is one of the main problems of the coastal studies. Airborne remote sensing is a useful tool in the estimation of physical properties, such as the grain size of intertidal sediments [1].

Local and diffuse pollutions are often deposited as sediments in estuaries and coastal areas. These sediments constitute an essential component of aquatic ecosystems as well as an indicator of the interactions between natural and anthropogenic environments. They are considered to be the last drain of polluting agents introduced both by natural processes as much as anthropogenic ones [2], [3].

In order to give a response to the increasing legal and social demands for a greater environmental protection of the aquatic resources, the scientific community has developed a variety of methods to evaluate the sediment quality [4]-[6]. The use of environmental quantitative quality standards derived from

Elena Castillo-López is with the Department of Geographic Engineering and Techniques of Graphical Expression, University of Cantabria, 39005, Spain (corresponding author, phone: +34 942200895; e-mail: elena.castillo@unican.es).

Raul Pereda, Julio Manuel de Luis and Felipe Piña are part of the Department of Geographic Engineering and Techniques of Graphical Expression, University of Cantabria, 39005, Spain.

Rubén Pérez works in the Department of Transport, and Technology of Projects and Processes, University of Cantabria, 39005, Santander, Spain.

sediment quality guidelines is becoming an important part of the protection and management of marine ecosystems [7].

Remote sensing seems a feasible alternative [8] as it constitutes a synoptic tool that provides global and quantitative information of the area under study. Both satellite and airborne remote sensing techniques have become useful and effective tools to carry out coastal and oceanic pursuits [9]-[13].

II. MATERIALS AND METHODS

The airborne sensor selected for monitoring has been CASI-2 (Fig. 1). Due to its spatial resolution (between 2 and 10 m), it is suitable for the present application and allows identifying optimum time windows. The experiment would provide best chances of success, even though the working bandwidth is not the optimal (400-750 nm), as it only provides information in the part of the electromagnetic spectrum corresponding to the visible and the very near infrared (VNIR). In the case study, 36 spectral bands and a spatial resolution of 2 m have been applied.

Fig. 1 Hyperspectral sensor CASI-2

The study area is located along the northern coast of Spain, in the Bay of Santander, in Cantabria (Fig. 2). Several tourist activities take place in the area, such as beach swimming, fishing, and sailing. Industrial activities, mainly metallurgical and chemical factories, are distributed in the eight coastal municipalities. They have a population of 250,000 inhabitants (35% of the Cantabria region) and a population density of 1,134 inhabitants per square kilometer [15]. Due to the wealth of the ecosystem, fishing is frequently practiced. Several rivers disgorge into the Bay. The most important ones flow into the Boo, Solía, and San Salvador estuaries in the southern

portion of the Bay, and the Cubas Estuary in the western portion of the Bay.

The mining activity around the Bay of Santander was related to the exploitation of iron ores during the last century, generating huge amounts of muddy iron-enriched wastes that were directly discharged into Solía and San Salvador estuaries. Additionally, there were some minor exploitation of Pb and Zn in the eastern part of the Bay [14]. Because of the mining, industrial, and commercial port-related activities, significant dredging and refilling has been carried out in the Bay since 1837, leading to a reduction of 87% of the natural coast.

The main goals of the fieldwork are to correlate satellite and real-time spectral ground measurements, collect soil samples (Fig. 2) at specified points, and develop algorithms on the estimation of the sediment and the bottom.
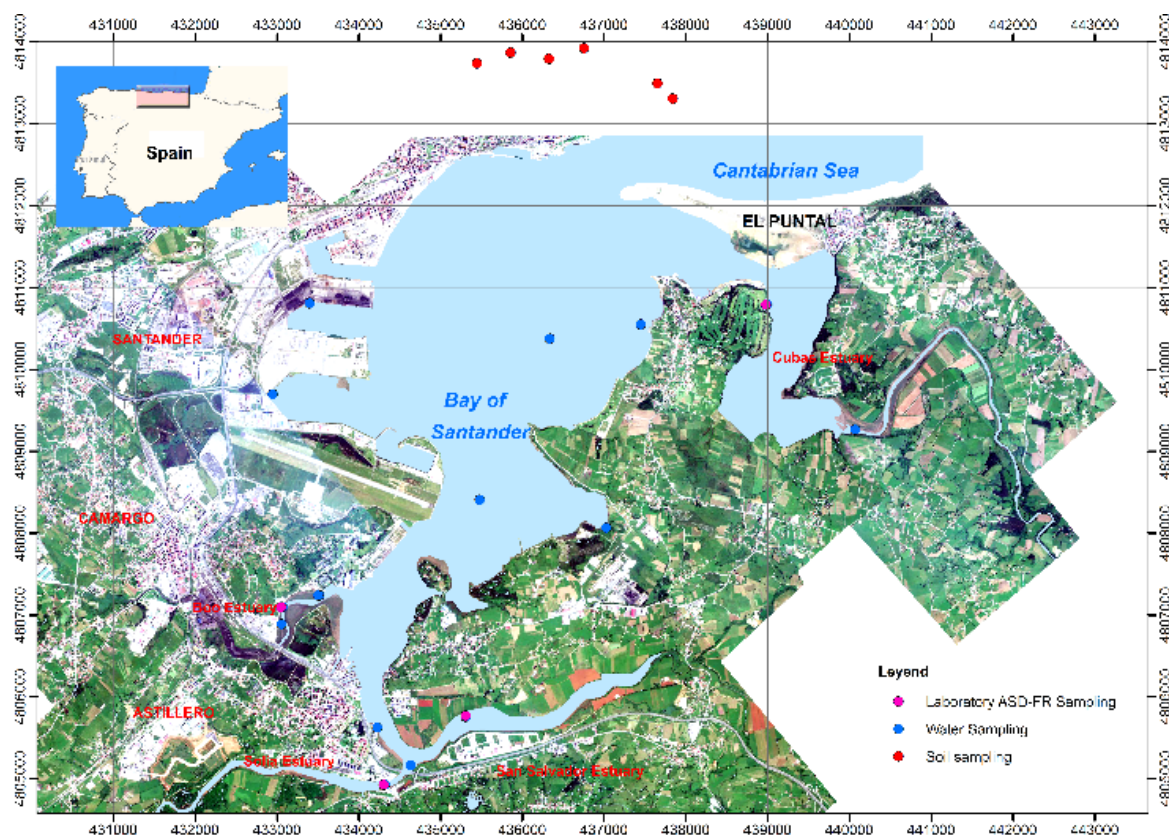

Fig. 2 Location of the study area and the fieldwork

III. METHODOLOGY

The concentration of heavy metals depends on the capacity of exchange in soil, and it is related to the organic matter and clay content in the sediment.

Regarding heavy metals, it should be noticed that lead comes from natural (it is rarely found in its elemental state in the environment, but it can be identified as part of some minerals; the most common ones are the sulfide of lead, galena, and other minerals of commercial interest can be mentioned too, such as lead carbonate, cerussite), and anthropogenic sources. Lead levels in environment have increased over a thousand times during the last three centuries because of human activity.

Local levels can increase through the accumulation of wastewater sediments and the deposition of dust containing lead from the atmosphere. From an industrial approach, the most common application of lead is the manufacture of electric accumulators. It is also used in the production of batteries; as a catalyst in the manufacture of polyurethane foam; or as a component of naval paintings applied to inhibit the inlay in helmets. It is also used for the protection of wood against the attack of marine fungi, as reducing agent in lubricants, as corrosion inhibitor for steel, and in the formulation of pesticides.

Several laboratory studies suggest that the reflectance in the visible and near infrared (VNIR) region can predict characteristics of the soil, such as organic matter and clay content. Metals that are found in low concentration do not have spectral features in the VNIR. However, if they are correlated with other properties of the soil that are spectrally active in these regions, predictions on the concentrations of these parameters of interest (Pb, Zn, MnO, and Fe_2O_3) can be obtained.

The methodology applied comprises two main parts. The first one implies knowing the concentration of heavy metals in some water samples from the intertidal zone of Santander Bay

(Fig. 3). The second stage requires the availability of imagery with a good atmospheric correction, for which it is necessary to have a suitable spectral library, obtained from the analysis of different land and water bodies, to determine the distortions introduced in the satellite imagery as consequence of the atmospheric components. The last step implies the application of robust statistic techniques to CASI-2 data in order to estimate the parameters (heavy metals concentration) and the evaluation of the results obtained by robust methods in comparison to classical estimation techniques.

Fig. 3 Sediment sampling using GPS positioning

IV. RESULTS

Algorithms typically used in remote sensing have been evaluated. Other algorithms have been tested (robust principal component analysis), but they have not provided positive results to estimate the concentrations of heavy metals.

Table I shows the location and results in parts per million or percentage, obtained for the 12 sampled points. The eight sample points that were used during the calibration step are indicated in blue, while the other four points of validations are written in black.

The correlations between the samples used during the calibration and the spectral information provided by sensor, are shown in Table II.

TABLE I
HEAVY METALS WATER SAMPLING

SAMPLE	Pb (ppm)	Zn (ppm)	MnO (%)	Fe2O3 (%)
Sample 1	244	946	0.476	9.1
Sample 2	97	435	0.668	30.28
Sample 3	97	269	0.929	38.21
Sample 4	86	587	0.295	20
Sample 5	12	58	0.003	0.41
Sample 6	23	55	0.167	21.8
Sample 7	28	89	0.0066	3.12
Sample 8	46	188	0.058	5.16
Sample 9	150	828	0.427	17.79
Sample 10	229	2295	0.583	22.16
Sample 11	108	903	0.246	5.32
Sample 12	149	900	0.69	18.95

The correlations between the content of heavy metals in samples, Total Organic Carbon (TOC) and the percentage of clay present in the sediment (Table III) have been calculated. It is should be noticed that there is a highly positive correlation between TOC, lead and zinc, as well as a high negative correlation with ferric oxide.

Results shown in Table III reveal a high correlation between the six parameters analyzed. In the case of the manganese oxide, the obtained correlation is very small because the concentration of this compound is particularly low in the Bay of Santander.

TABLE II
CORRELATION BETWEEN PB AND ZN SAMPLES AND CASI-2 (34 BANDS)

	b1	b2	b3	b4	b5
Lead	-0.482	-0.825	-0.842	**-0.861**	-0.783
Zinc	-0.680	-0.891	**-0.932**	-0.928	-0.857
	b6	b7	b8	b9	b10
Lead	-0.847	-0.818	-0.812	-0.770	-0.748
Zinc	-0.925	-0.878	-0.878	-0.835	-0.821
	b11	b12	b13	b14	b15
Lead	-0.682	-0.617	-0.567	-0.549	-0.543
Zinc	-0.759	-0.692	-0.629	-0.615	-0.609
	b16	b17	b18	b19	b20
Lead	-0.510	-0.487	-0.473	-0.482	-0.482
Zinc	-0.565	-0.539	-0.535	-0.545	-0.545
	b21	b22	b23	b24	b25
Lead	-0.428	-0.397	-0.395	-0.385	-0.394
Zinc	-0.491	-0.452	-0.442	-0.432	-0.437
	b26	b27	b28	b29	b30
Lead	-0.401	-0.389	-0.392	-0.397	-0.396
Zinc	-0.444	-0.426	-0.425	-0.430	-0.426
	b31	b32	b33	b34	b35
Lead	-0.398	-0.381	-0.349	-0.357	-0.329
Zinc	-0.427	-0.406	-0.378	-0.386	-0.338
	b36				
Lead	-0.301				
Zinc	-0.383				

TABLE III
CORRELATION BETWEEN HEAVY METALS SAMPLES, TOC AND CLAY

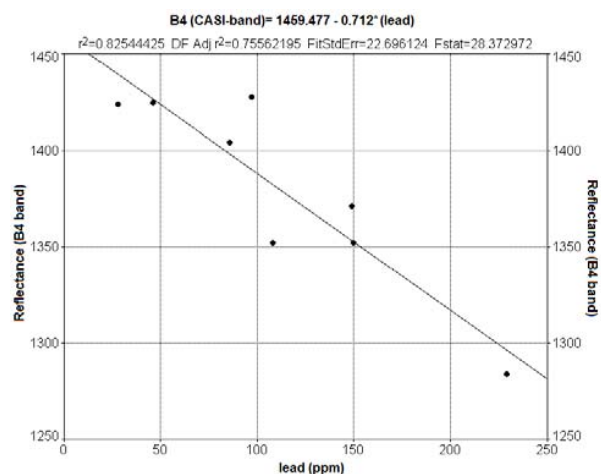|	Clay	TOC	Pb	Zn	MnO	Fe$_2$O$_3$
Clay	1.000	-----	0.937	0.959	**0.817**	0.936
TOC	-----	1.000	0.905	**0.935**	-0.195	-0.846
Lead	0.937	0.905	1.000	**0.942**	0.546	0.178
Zinc	**0.959**	0.935	0.942	1.000	0.443	0.139
MnO	0.817	-0. 195	0.546	0.443	1.000	**0.865**
Fe$_2$O$_3$	0.936	-0.846	0.178	0.139	**0.865**	1.000

Fig. 4 Adjustment function between B4 band of CASI-2 and lead content in calibration samples

Fig. 4 shows the fitting function between the CASI-2 band with a maximum correlation, and the lead content of the sediment in the eight calibration points.

Fig. 5 shows the estimation of lead concentration in the intertidal zone, which has been obtained by applying the adjustment function (Fig. 4) with a R^2 value of 0.82. The validation of this adjustment was rather good with a R^2 value of 0.74.
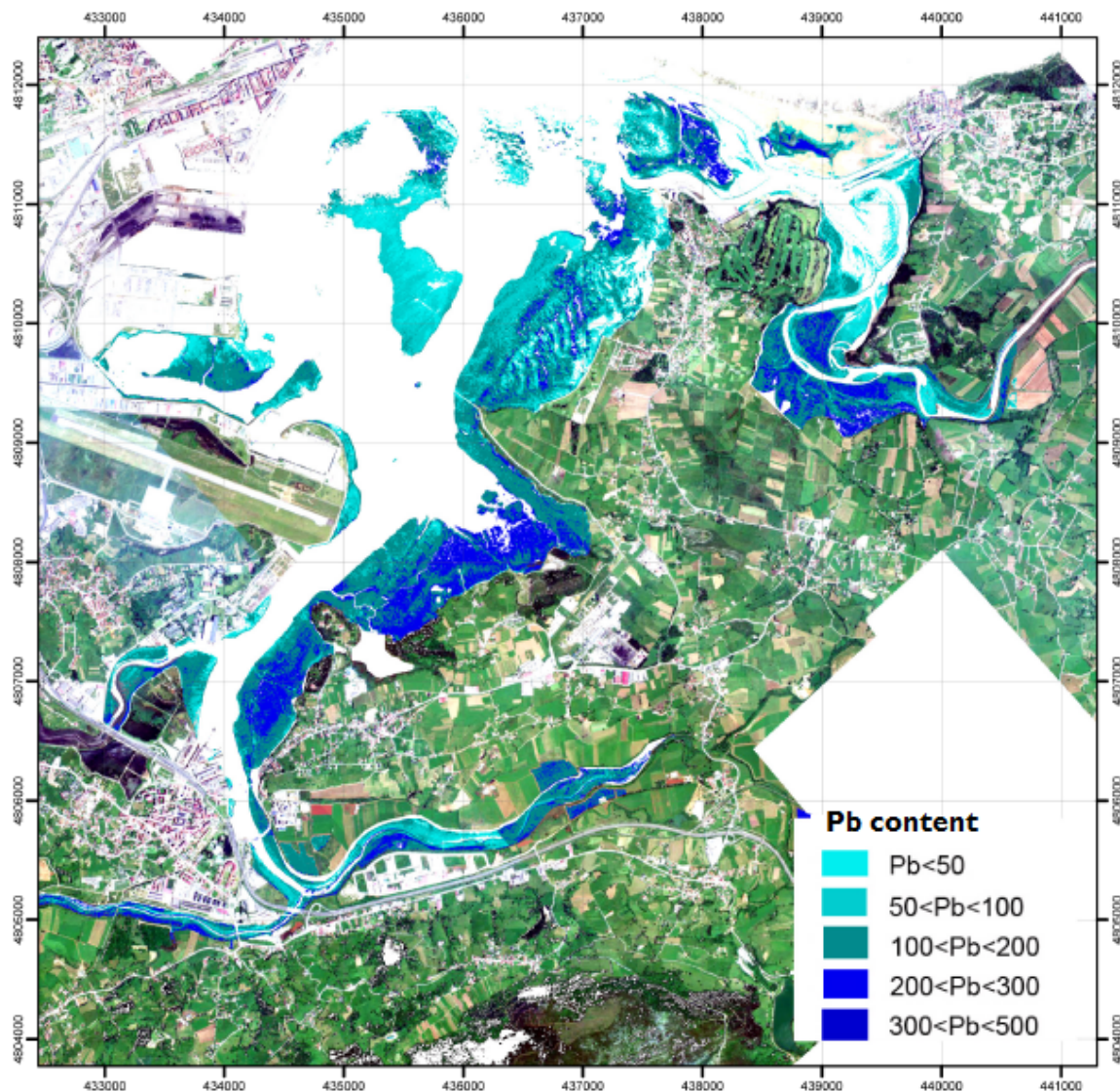

Fig. 5 Results of lead estimation in the intertidal zone using simple band method

V. CONCLUSIONS

The main conclusions of this work are listed next:

- Lead and zinc are highly correlated, which is quite logical if the origins of such discharges are considered, so their spectral response is linked to the same spectral band.
- Manganese oxide and ferric oxide also present a significant correlation.
- Considering the strong absorption of sediments and debris from inorganic origin in the range between 368 nm and the 568 nm, the area of maximum reflectance is in the range between the 590-690 nm. This response differs from that of provided by organic sediments, whose maximums correspond to wavelengths between the 530-570 nm. Therefore, the band of greater correlation with these elements is precisely comprised within this spectral range.
- Despite the fact that the metals that are found in low concentrations do not have important spectral characteristics in a VNIR, if they are correlated with other soil properties that are spectrally active in these regions, predictions about the concentrations of the parameters of interest (Pb, Zn, MnO and Fe2O3) can be performed.

REFERENCES

[1] Castillo, E., Pereda, R., de Luis, J.M., Medina, R. and Viguri, J. Sediment grain size estimation using airborne remote sensing, field sampling and robust statistic. *Environmental Monitoring and Assessment, 181: 431-444, 2011.*

[2] Salomons, W., and Brils, J. *Contaminated sediments in European River Basins.* European Sediment.2004.

[3] Alvarez-Guerra, M., San-Martín, D., and Viguri, J. Predicting toxicity from sediment chemistry using artificial neural networks: Screening tools for sustainable sediment management. In *J.R. 11th Mediterranean Congress of Chemical Engineering,* 2008.

[4] Del Valls, T. A., Andres, A., Belzunce, M. J., Buceta, J. L., Casado-Martínez, M. C., Castro, R., Riba, I., Viguri, J.R. and Blasco, J. *Chemical and Ecotoxicological Guidelines for Managing Disposal of Dredged Material,* 23, 819-828, 2004.

[5] Alvarez-Guerra, M., Viguri, J. R., Casado-Martínez, Carmen, M., & DelValls, A. T. Sediment quality assessment and dredged material management in Spain: Part II, analysis of action levels for dredged material management and application to the Bay of Cádiz. *Integrated Environmental Assessment and Management, 3*(4), 539–551, 2007.

[6] Alvarez-Guerra, M., Viguri, J. R., Casado-Martínez, M. C., & DelValls, T. A. Sediment quality assessment and dredged material management in Spain: Part I, application of sediment quality guidelines in the Bay of Santander. *Integrated Environmental Assessment and Management, 3,* 529–538, 2007.

[7] Campbell, N. A. The decorrelation stretch transformation. *International Journal Remote Sensing, 10,* 1939–1949. Canadian Council of Ministers of the Environment (2001).

[8] Van der Wal, D., & Herman, P. M. J. Regression based on synergy of optical, shortwave infrared and microwave remote sensing for monitoring the grain-size of intertidal sediments. *Remote Sensing of Environment, 111,* 89–106, 2007.

[9] Folving, S. The Danish Wadden Sea: Thematic mapping by means of remote sensing. *Folia Geographica Danica, 15*(2), 1–56, 1984.

[10] Bartholdy, J., & Folving, S. Sediment classification and surface type mapping in the Danish Wadden Sea by remote sensing. *Netherlands Journal of Sea Research, 20,* 337–345, 1986.

[11] Yachts, M. G., Jones, A. R.,

[12] McGrorty, S., & Goss-Custard, J. D. The uses of satellite imagery to determine the distribution of intertidal surface sediments of The Wash, England. Marine. *Coastal and Shelf Science, 36,* 333–344, 1993.

[13] Populus, J., Moreau, F., Coquelet, D., & Xavier, J. P. An assessment of environmental sensitivity to marine pollutions: Solutions with remote sensing and geographical information systems. *International Journal of Remote Sensing, 16*(1), 3–15., 1995.

[14] Populus, J., et al. Remote sensing as a tool for diagnostic of water quality in Indonesian seas. *Ocean and Coastal Management, 27*(3), 197–215, 1995.

[15] Ortega, J. *Formación y Desarrollo de una Economía Moderna.* Santander, España, 1986.

[16] ICANE, Cantabria. https://www.icane.es/.