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Investigation on Possible Contamination of Port Sediments by Means of ATR-FTIR Spectroscopy and Thermal Analysis

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ABSTRACT: This study proposes a method employing thermogravimetric analysis (TG) to predict pollution levels by heavy metals (Cr, Cu, Ni, Zn, Pb, Cd and Hg) in port sediments close to urban and industrial sites from bay of Cádiz. For this purpose, the thermogravimetric results of 14 sediment samples were recorded and showed two characteristic ranges of temperatures (W_1 as weight loss, %: 200-650°C) *vs.* (W_2 as weight loss, %: 650-900°C) as being representative of the sediment characteristics. Samples with a high W_1 were characterized by the prevalence of a thin fraction and high metal content, while samples with a high W_2 were characterized by large sandy fractions and, in general, low metal contents in agreement with the pollution load index (PLI). Furthermore, Fourier transform infrared (ATR-FTIR) analysis proved to be an alternative tool for the simultaneous detection of many components of sediments. Combined with TG, this technique allows for simultaneous, rapid and reliable screening of pollution levels in port sediments.

Key words: ATR-FTIR, Pollution load index, Port sediments, Thermogravimetric,Weight loss

INTRODUCTION

Estuarine marine sediments are constituted by a complex heterogeneous mixture of geochemical phases, and are able to bind metals by means of precipitation, ionic exchange and adsorption processes (Crompton 2001). A consequence of the growth of heavy industry has been the addition of high concentrations of heavy metals originating from anthropogenic inputs, including industrial wastewater discharges and sewage wastewater (Linnik and Zubenko 2000; Lwanga *et al.* 2003; Rodríguez-Barroso et al. 2009a). This occurs to a great extent in harbor or estuarine sediments, where pollution levels are usually quite high due to anthropogenic metal loadings carried by rivers or their tributaries. These metals tend to accumulate in the sediments bound to organic matter, sulfides or fractions of the sediment. However, traditional geochemical metal methods recommended for sediment quality assessment involve, in general, wet digestion of solid samples in hot concentrated acids followed by trace element determination by inductively coupled plasma (ICP) or atomic absorption spectrometry (AAS) (Crompton 2001). Organic carbon, organic matter and nitrogen are usually determined by standard methods. In all cases, these methods are relatively complex, time-consuming and require expensive instrumentation, and are therefore not suitable for performing mapping or monitoring large-scale changes. Additionally, for monitoring purposes, the analysis of many parameters in a large number of samples is also required. As such, fast, cheap and accurate methods are necessary to permit the simultaneous screening of as many parameters as possible (Chapman *et al.*, 2001). Thus, instrumental techniques are gaining importance because they are able to estimate the quality or contamination levels of certain environmental scenarios in short periods of time, for example in environmental monitoring plans in coastal systems, riverbeds, etc. In this context, instrumental techniques such as thermal techniques could become a predictive tool and an alternative to characterization of solid substrates, and are inexpensive than other analytical instrumentation, rapid, require little sample preparation, and give reproducible results.

In recent years, several researchers have been thermal methods such as thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), to characterize organic

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matter in soils and the evaluation of the maturity of compost with different substrates (sewage sludge, waste materials, cow dung, saw dust, tree leaves, etc.) (Ferrase et al. 2003; Magalhães et al. 2008; Zhang *et al.* 2011; Singh *et al.* 2011; Oliveira Silva *et al.* 2011). Another important application of these techniques for the characterization of marine sediments has been performed by several authors (López-Capel *et al.* 2006; Rodríguez-Barroso et al. 2006, 2008, 2009b). We have previously used TG to study the thermal behaviour of sediments from different areas and to perform routine annual thermal analysis of contamination in a littoral ecosystem (Oudghiri *et al.*, 2014). In this work, these techniques have been demonstrated to be suitable for the determination of several parameters in littoral sediments and thus have been employed to determine chemical properties such as organic matter, organic carbon, total nitrogen, clay and carbonates. Another technique used to characterize the sediments is Fourier transform infrared (FTIR) spectroscopy (Tung and Tanner 2003; Moros et al. 2008, 2010), since compound identification is rather complicated with mixtures of specific individual compounds.

A study on the concentration and distribution of heavy metals in Cádiz Bay sediments is important in order to assess the state of contamination of the area and to estimate the possible influence of anthropogenic activities on harbor waters (Hung and Hsu 2004; Morillo *et al.* 2004; Chen *et al.* 2007). In the present study, the physical and chemical properties of sediments in Cádiz Bay were characterized, including mud and sand composition, organic matter content (OM) and the distribution of Cr, Cu, Ni, Pb, Zn, Cd and Hg. The extent of metal contamination was assessed using the contamination factor (CF) and the pollution load index (PLI). The objective of the present study was to assess the applicability of thermal analysis and ATR-FTIR spectroscopy as alternative tools for simultaneous screening of pollution levels in marine sediments.

MATERIALS & METHODS

Three industrial areas near the coast of the Bay of Cádiz were assessed. The Bay of Cádiz is located at the southwestern tip of Europe (W-NW of the province of Cadiz). Approximately 700,000 people live around the bay, and the main industries located in this zone are associated with ship construction and boat maintenance activities, aerospace component manufacturing, power generation and marine transport. All these activities have a negative impact and led to an increase in the pollution of ecosystems in this zone. Estuarine marine sediment samples were collected in 2010 using a Van Veen grab sampler, from 14 stations, including one relatively pristine station. The locations of sampling sites selected is recorded in Table 1, and Fig. 1 shows a map of the sampling points in the three

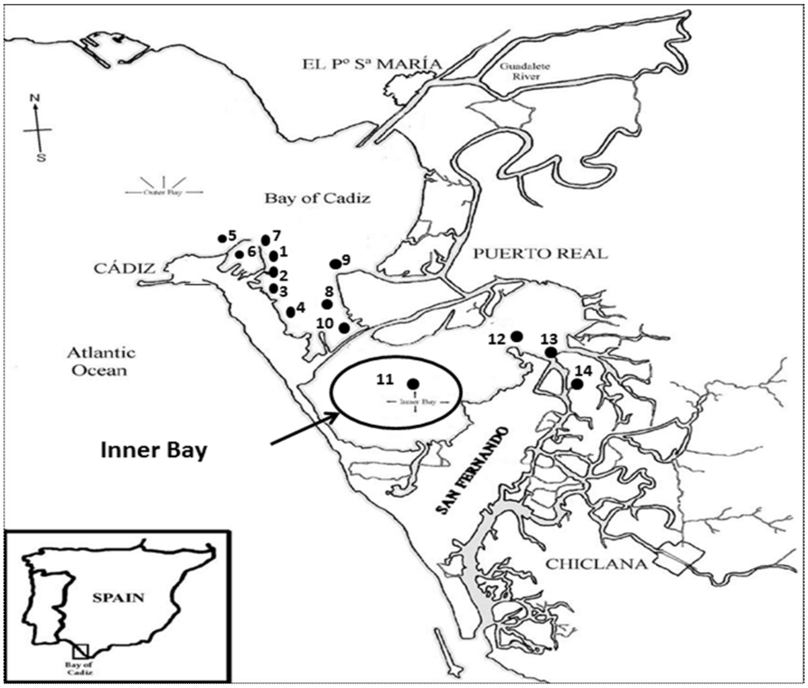

Fig.1. Map of the studied area showing the location of the sampling stations

Table 1. Locations of sampling stations and values of the parameters relating to the granulometric fraction and organic matter (OM) in the sediments.

	Coordinates		Grain size		
Station	**Latitude**	**Longitude**	**% sand (0.063–2 mm)**	**% mud (silt + clay) < 0.063 mm**	**OM (%)**
Samples of industrial origin from the port of Cádiz					
S1	36º32.491´N	006º16.585´W	16.83	83.17	11.81
S2	36º32.184´N	006º16.573´W	10.94	89.06	10.16
S3	36º31.981´N	006º 16.720´W	3.77	96.23	13.05
S4	36º32.041´N	006º 16.907´W	12.02	87.98	12.37
S5	36º32.222´N	006º 16.918´W	4.83	95.17	12.69
S6	36º32.120´N	006º 17.040´W	43.09	56.91	9.39
S7	36º32.595´N	006º 16.717´W	3.77	96.23	12.90
Samples of mainly industrial origin from the Puerto Real shipyard					
S8	36º31.556´N	006º 15.403´W	31.87	68.13	10.50
S9	36º31.402´N	006º 15.329´W	20.75	79.25	12.46
S10	36º31.262´N	006º 15.235´W	4.46	95.54	13.76
Relatively pristine station					
S11	36º30.108´N	006º 14.090´W	65.45	34.55	5.01
Samples of mainly industrial origin from the San Fernando shipyard					
S12	36º30.101´N	006º 11.429´W	10.71	89.29	14.44
S13	36º29.762´N	006º 10.920´W	0.89	99.11	13.62
S14	36º29.497´N	006º 10.797´W	5.67	94.33	11.70

zones: the port of Cádiz in the zone of industrial activity (S1 to S7), the Puerto Real shipyard (S8 to S10) and the San Fernando shipyard in the zone directly affected by the port and the industrial area (S12 to S14); finally, a pristine station located in the inner region of bay was sampled (S11). After sampling, the sediment samples were sealed in clean polyethylene bags, placed in a cooler at 4 °C and transported to the laboratory immediately for further analysis. With granulometric analysis, it is possible to establish the risk levels of contamination in sediment; numerous authors have acknowledged grain size as one of the most significant factors in the capacity to retain trace elements, since finer fractions have a greater capacity to adsorb metal contaminants and organometallic compounds on their surfaces. Additionally, higher contamination concentrations are often associated with sediments with higher organic matter content (Jenne *et al*. 1980; Horowitz and Elrick 1987; Donard *et al*. 2001). Granulometric analyses of the sediments were carried out by wet sieving of the 63 µm particle size fraction (Rodier 1997). Sediment samples were air dried at room temperature and then sieved with a 2 mm sieve. The sieved sample was powdered and finally passed through a 63 µm sieve. For heavy metal content determinations, 0.25 g sediment subsamples were digested according to Förstner and Wittmann (1983) in Teflon vessels with H_2O_2 and an HNO_3 (65%):HCl (37%) mixture (3:1) in a microwave oven (Milestone Ethos 1600). After microwave digestion, the sample solutions were filtered. The sediment extracts were analyzed for Cr, Cu, Ni, Zn, Pb, Cd and Hg by inductively coupled plasma mass spectrometry (ICP-MS). The results are expressed as milligrams per kilogram dry weight. The detection limits were as follows: 0.500 mg/kg for Cr, 0.600 mg/kg for Cu, 0.700 mg/kg for Ni, 0.004 mg/kg for Pb, 0.500 mg/kg for Zn, 0.005 mg/kg for Cd and 0.010 mg/kg for Hg. The accuracy of the analytical procedure was determined by measuring trace element concentrations in reference material (PACS-2) certified by the National Research Council of Canada (NRC) collected from the harbor of Esquimalt. The analysis showed agreement in excess of 90% with the certified values. A Pearson matrix was applied to determine the correlations between trace metal concentrations, using Statistical Program for the Social Sciences (SPSS program version 14.0 for Windows). Group averaging cluster analysis was applied using the city block (Manhattan) distance coefficient.

Attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) was employed to record the spectra of sediment samples.

ATR-FTIR spectra were measured on a Perkin Elmer Spectrum 100™ FTIR. Sediment samples (<2 mm) were placed onto the ATR accessory and a constant force was applied using an integrated torque press. Then, ATR-FTIR spectra were scanned from 4000 to 650 $cm^{"1}$ by averaging 32 scans per spectra at a resolution of 8 $cm^{"1}$. The spectra were obtained with respect to the background and under the same measurement conditions. Afterwards, the internal reflection element (IRE) was carefully cleaned with soft paper and a blank spectrum was recorded in order to verify total elimination of the measured sample to avoid cross-contamination between samples. TG analysis was carried out using a Perkin Elmer STA 6000 simultaneous thermal analyzer. For these experiments, sediments were analyzed after the pretreatment recommended by Rodríguez-Barroso *et al.* (2006, 2008) to eliminate chloride interference before TG analysis. Pretreatment consisted of a prewash of the samples with distilled water under stirring and centrifugation to remove the supernatant. These samples were previously dried for one hour at 105°C and ground before TG analysis.

In the present study, approximately 10 mg of each sediment sample (< 2 mm) was placed in a ceramic (alumina, Al_2O_3) crucible and heated at 100°C for 1 min and then heated again from 100 to 900°C at a constant heating rate of 10°C/min. The measurement cell was continuously purged with nitrogen at a flow rate of 25 mL/min. The percentage of mass loss was calculated according to the equation below:

$$\text{Weight loss (\%)} = \left(\frac{m_i - m_a}{m_i}\right) \text{X100}$$

Where m_i is the initial mass (mg) and m_a is the actual mass (mg).

RESULTS & DISCUSSION

The results of the granulometric analysis (Table 1) show that, despite certain granulometric variability in the samples, most stations were dominated by fine particles (<63 %), ranging between 57% and 99% from station 1 to 14, excepting the control sediment (sample S11) which presented a typically sandy (>63 ìm) texture (65%).

Table 2 presents the total concentration of metals found in the sediments from the studied areas and the average shale values (Turekian and Wedepohl 1961), commonly used as a background reference in sediment studies (Blasco *et al.* 2000; Morillo *et al.* 2002). A comparison of the metal concentrations with average shale values revealed that highest concentrations of Cu, Zn, Pb, Cd and Hg were found at stations 2, 3, 4 and 6 (the port of Cádiz), while the highest Cr and Ni levels were found at station S6 and the three stations in the San Fernando shipyard (S12, S13 and S14), although the data on Ni were lower than the reference background value.

The overall metal contents of sediments at the sites investigated in this study were compared using two indices, the contamination factor (CF) and pollution load index (PLI). The CF is a good tool to differentiate the metal source between anthropogenic and naturally occurring sources and is defined as the ratio obtained by dividing the concentration of each metal in the sediment by the baseline or background value (concentration in uncontaminated sediment):

$$CF = \frac{C_{\text{heavry metal}}}{C_{\text{background}}}$$

CF values were interpreted as suggested by Hakanson (1980), where: CF < 1 indicates low contamination; 1 < CF < 3 indicates moderate contamination; 3 < CF < 6 indicates considerable contamination; and CF > 6 indicates very high contamination.

The CF results are presented in Table 3. The highest CF values for all studied metals were found at stations 2, 3, 4 and 6 (the port of Cádiz), which receives a huge amount of metallic discharge. The CF values for Hg > 6 in the sediments at stations 4 and 6 (next to a cement factory) denote very high contamination with this metal. The CF values for Cr and Ni indicated low contamination, and stations S3, S4 and S6 showed moderate contamination for Cu and Zn. Pb showed considerable contamination at S4 and S6 (also for Cd). Hg showed very high contamination at S4 and S6 and

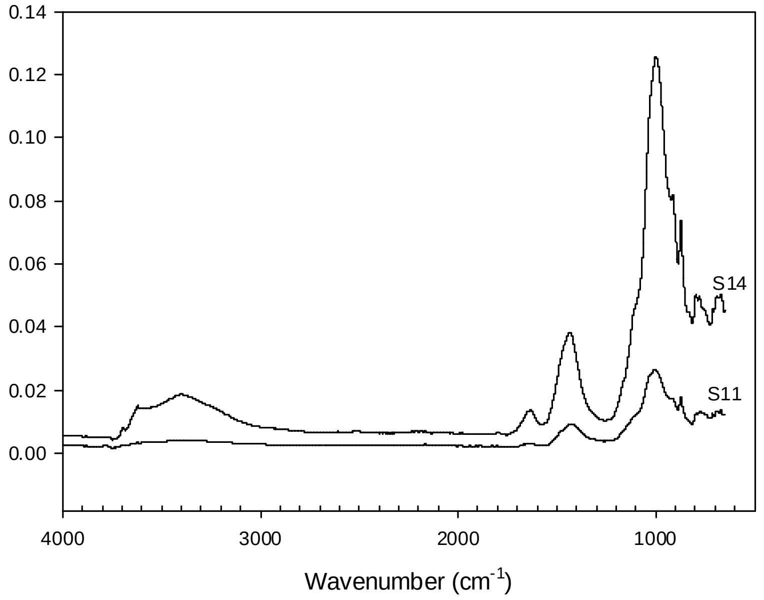

Fig. 2. FTIR absorption spectrums trace for sample sediment (S14) and control (S11)

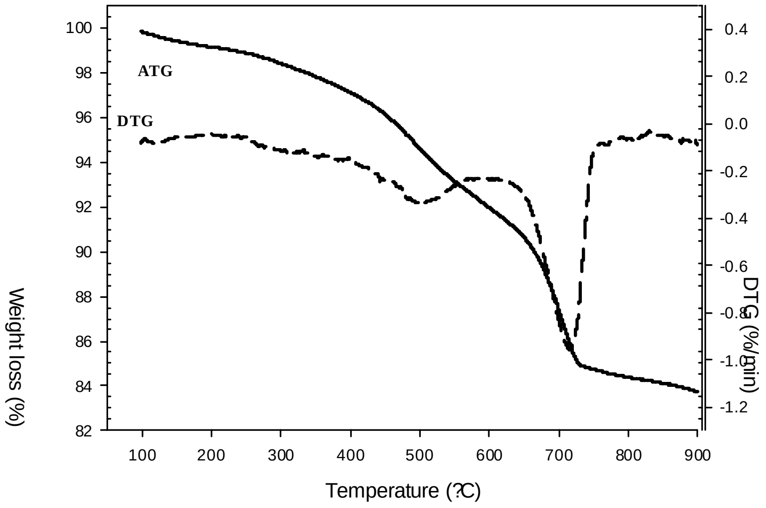

Fig. 3. TG and DTG curves of sediment at a heating rate of 10°C/min under a nitrogen atmosphere. Traces are from one sample (S14)

considerable contamination at S2. The overall metal contents of sediments at the sites investigated in this study were compared using the pollution load index (PLI). This empirical index provides a simple, comparative means for assessing the level of heavy metal pollution. When PLI > 1, it indicates the presence of pollution; otherwise, if PLI < 1, there is no metal pollution (Tomlinson *et al*. 1980).

For the entire sampling site, PLI was determined as the nth root of the product of the n CF:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times ....CF_n},$$

where *CFn* is the concentration of metal *n* in the sample

The PLI values of the eight heavy metals in the three studied areas are summarized in Table 3, and ranged from 1.00 to 2.44, meaning that sediments were moderately polluted to unpolluted, except for S11 (0.81≅ no metal pollution). Two stations in the port of Cádiz showed the highest PLI (S4 and S6), with values of 2.44 and 2.13, respectively, indicating moderate pollution with the investigated heavy metals.

The rapid-scan FTIR method permits the characterization of the sediment matrix. Typical FTIR spectra were observed for all samples (Fig. 2) and an increase in absorbance for all stations was seen compared to the control station (S11). The broad band located around 3430/cm can be attributed to the OH stretching of water molecules, which might also belong to the organic fraction of sediments. The presence of kaolinite could explain the appearance of the two well-defined additional bands at 3699 and 3620/cm (Kotoky *et al*. 2006). The band around 2940/cm could be attributed to the C-H stretching of methyl (-CH_3) and methylene (-CH_2-) groups (Larkin, 2011), mainly due to the presence of organic carbon in the sediments. The asymmetric stretching of metal carboxylate appeared around 1643/cm. This band occurred due to the interaction between the carboxyl group of the organic and/or humic acids and metals. The small band at 999/cm could be attributed to Si–O stretching bands of clay minerals (Sivakumar *et al*. 2012), while the absorption bands at 1433, 873 and 712/cm could be associated with the presence of calcite (Moros *et al*. 2010). Additionally, the presence of different carbonates could be considered responsible for the presence of vibrational bands located at 797 and 693/cm (Kovac *et al*. 2005).

These results provide useful information about the organic and inorganic composition of the sediments and also indicate the formation of metal carboxylate in sediments, indicating that the contamination of these sediments is mainly of anthropogenic origin.

According to Lopez-Capel *et al*. (2006), the mass loss in marine sediments is divided into four intervals: labile organic matter (decomposing between 200 and 400°C), recalcitrant (400–550°C), refractory (550–650°C) and carbonates (650–900°C). This is a simplification that does not take into account mass losses caused by dehydration, dehydroxylation and decomposition of mineral structures, but it may be helpful when considering the considerable amounts of organic contamination involved. While the labile pool is more reactive and susceptible to degradation, the recalcitrant pool has low degradation rates and the refractory pool, composed of either artificial chars or highly aromatic

Table 2. Heavy metal concentrations in sediment samples from the study area and the reference background (Turekian and Wedepohl, 1961)

Stations	Metal concentrations (mg/kg, dry mass)						
	Cr	Cu	Ni	Zn	Pb	Cd	Hg
S1	82.47	42.04	32.64	115.84	29.63	0.45	0.27
S2	77.56	69.53	30.70	148.58	44.24	0.45	0.78
S3	79.88	137.15	31.49	208.60	53.06	0.48	0.52
S4	82.77	186.11	32.05	261.55	75.08	0.51	1.15
S5	83.44	48.62	35.10	118.21	33.80	0.40	0.29
S6	93.33	124.54	40.59	281.47	93.65	0.98	1.18
S7	75.54	34.24	31.15	101.28	29.90	0.43	0.39
S8	78.31	34.00	35.01	102.00	25.22	0.42	0.33
S9	82.41	37.77	33.82	114.41	30.58	0.45	0.30
S10	85.56	36.24	36.75	103.37	24.90	0.40	0.24
S11	74.31	30.14	22.53	97.51	26.77	0.30	0.16
S12	89.16	42.94	37.61	114.90	30.42	0.44	0.27
S13	89.21	40.17	38.46	108.06	25.32	0.49	0.23
S14	88.81	39.31	37.65	107.89	29.80	0.40	0.39
PACS-2	84.20	302.36	40.10	370.55	183.39	2.04	3.00
Reference background	90	45	68	95	20	0.3	0.18

compounds, may remain in sediments for centuries. In the present work, the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves during thermal degradation of sediment samples under nitrogen and at a heating rate of 10ºC/min are presented in Fig. 3 (for one example). The TG curve is characterized by two stages that occur when heating the sample in two temperature ranges, 200–650°C (W_1) and 650–900°C (W_2). In previous studies and according to Lopez-Capel *et al.* (2006), the first weight loss (W_1) is mainly due to decarboxylation of organic matter and dehydroxylation of clay minerals (Oudghiri *et al.* 2014; López-Capel *et al.* 2006), while the second stage (W_2) corresponds to volatilization of different kinds of carbonates (Mg^{2+}, Ca^{2+}, Pb^{2+}, etc.) (Oudghiri *et al.* 2014). The calculated values from TG (W_1, W_2) and their sum as the total weight loss (W_{total}) are given in Table 4.

Table 3. Metal contamination factors (CFs) and pollution load indices (PLIs) for sediments at all studied stations

	Contamination factors (CFs)							
Station	**Cr**	**Cu**	**Ni**	**Zn**	**Pb**	**Cd**	**Hg**	**PLI**
S1	0.92	0.93	0.48	1.22	1.48	1.52	1.52	1.08
S2	0.86	1.55	0.45	1.56	2.21	1.49	4.34	1.45
S3	0.89	3.05	0.46	2.20	2.65	1.59	2.88	1.65
S4	0.92	4.14	0.47	2.75	3.75	1.70	6.39	2.13
S5	0.93	1.08	0.52	1.24	1.69	1.32	1.64	1.13
S6	1.04	2.77	0.60	2.96	4.68	3.27	6.56	2.44
S7	0.84	0.76	0.46	1.07	1.50	1.44	2.18	1.06
S8	0.87	0.76	0.51	1.07	1.26	1.41	1.81	1.02
S9	0.92	0.84	0.50	1.20	1.53	1.51	1.67	1.09
S10	0.95	0.81	0.54	1.09	1.25	1.33	1.31	1.00
S11	0.83	0.67	0.33	1.03	1.34	1.00	0.89	0.81
S12	0.99	0.95	0.55	1.21	1.52	1.45	1.47	1.11
S13	0.99	0.89	0.57	1.14	1.27	1.63	1.26	1.06
S14	0.99	0.87	0.55	1.14	1.49	1.33	2.19	1.13
PACS-2	0.94	6.72	0.59	3.90	9.17	6.81	16.67	3.95

Table 4. Weight losses (% of total sample weight) corresponding to both temperature ranges (°C) in the analyzed sediments

Stations	**ΔW_1 (%) (200-650ºC)**	**ΔW_2 (%) (650-900ºC)**	**Wtotal (%) (200–900°C)**
S1	8.97	11.10	20.07
S2	8.31	10.79	19.1
S3	9.08	10.99	20.07
S4	8.20	11.56	19.76
S5	8.48	11.37	19.85
S6	5.72	8.66	14.38
S7	8.80	10.98	19.78
S8	7.56	10.94	18.5
S9	7.87	10.88	18.75
S10	9.21	10.83	20.04
S11	3.17	9.59	12.76
S12	8.71	9.13	17.84
S13	8.71	11.40	20.11
S14	8.53	6.90	15.43
PACS-2	7.16	2.77	9.93

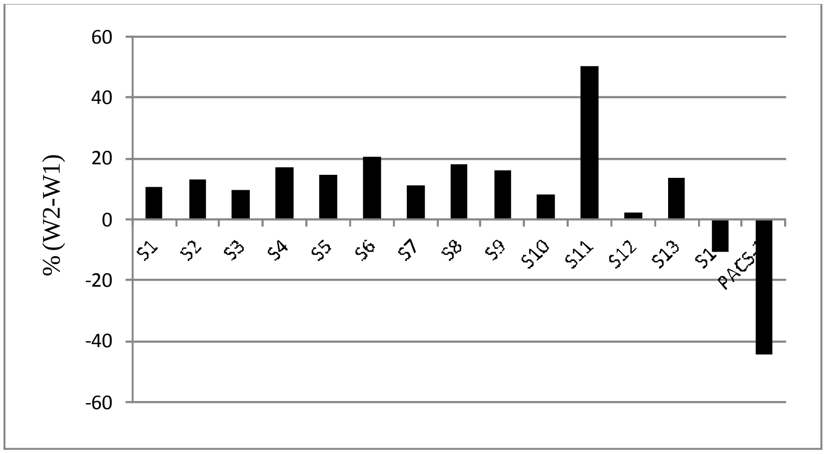

Fig. 4. Percentage difference between W_2 (650–900°C) and W_1 (200-650°C) in the studied samples.

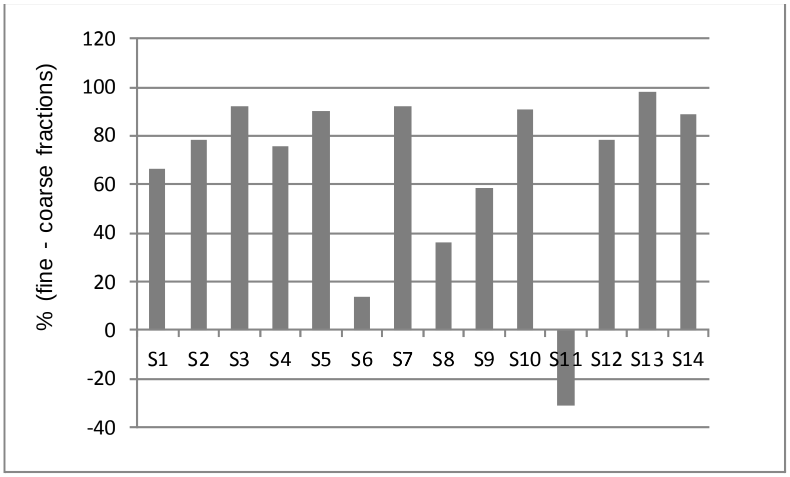

Fig. 5. Percentage difference between the fine and coarse fractions in the studied samples

Most of the samples showed a higher percentage relative to W_{total} in the second range (W_2) than the percentage in W_1 (shown in Fig. 4 as the W_2-W_1 difference). This was emphasized in the control sample (S11), and therefore it can be assumed that these types of sediment are usually coarser and have a lower organic content and metal content. On the contrary, sediment S14 (near a shipbuilding factory) and the reference sample (PACS-2) showed greater percentages in the range of 200–650°C, indicating a high degree of organic pollution, and therefore a high metal content. These are usually fine sediments.

To see the incidence due to grain size in sediments, Fig. 5 shows the differences between the granulometric compositions (represented as the fine fraction subtracted from the coarse fraction, given as a percentage). It was observed that all the sediments had a higher percentage of fine particles (fraction size > 60% with a size < 63 µm), except for the control samples (S11) and S6, which had a lower percentage of fine particles. Therefore, these samples should not be highly contaminated.

Pearson's correlation coefficients were calculated for the thermogravimetric data, grain size and organic matter (OM, Table 1) in the studied sediments. A significant positive correlation ($p < 0.01$) was found between the fine fraction vs. W1 ($r = 0.8$) and OC ($r = 0.70$) and between coarse particles vs. W2 ($r = 0.80$), meaning that samples with (W2-W1) < 0 showed a larger fine fraction and OM content (e.g. S14 with 94.33% and 11.70%, respectively). Samples with high W2 values had a larger coarse fraction (e.g. S11 with 34.55% and 5.01%, respectively). Cluster analysis was used to group sediments based on these five parameters (% fine, % coarse, W1, W2 and OM). Fig. 6 shows an isolated sediment (S11) and two station groups. The first major grouping was formed by several stations (S3, S5, S7, S10 and S13) with a very similar

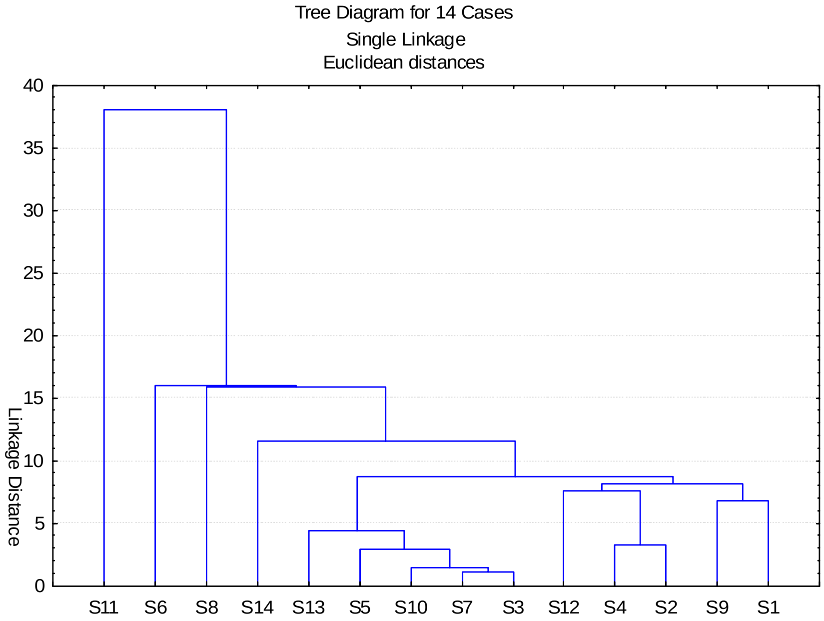

Fig. 6. Dendrogram showing station groups formed by group averaging cluster analysis of the elemental concentrations

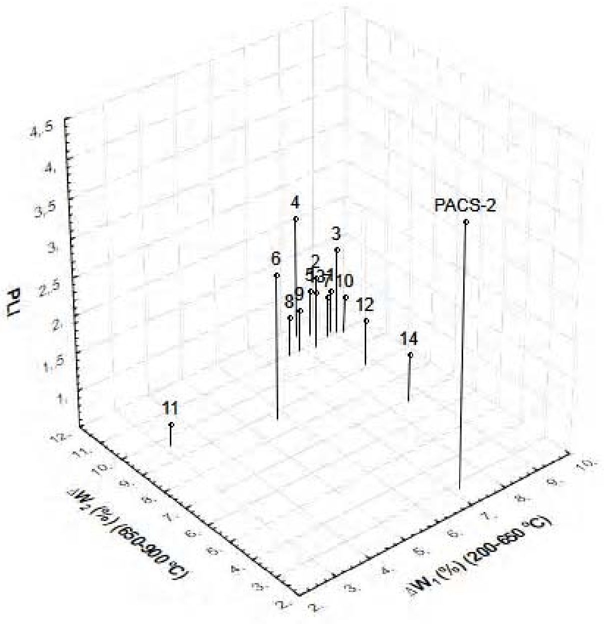

Fig.7. Distribution of polluted sediments in a 3D diagram based on thermogravimetric analysis

content of fine sediments, while the second group was formed by five samples (S1, S2, S4, S9 and S12); another nearby sediment is also shown (S14), characterized by a high fine fraction and OM. These stations are characterized by their shallow waters, low rate of water renewal and the preponderance of sedimentation phenomena, associated with very fine sediment. These zones have a greater anthropogenic influence and, consequently, are closer to sources of contamination. Finally, several sediments showed independent behavior (S6 and S8) with a lower percentage of fine particles.

One conclusion could be that samples with a positive difference (W_2-W_1) will be less contaminated by metals than those with a negative difference. To prove this hypothesis, the pollution load index (PLI) was correlated with the thermal results.

One way to correlate thermal results and PLI is to develop a 3D graphic (Fig. 7), where the values for W1, W2 and PLI are represented on the x, y and z axes, respectively. The sediments were distributed in two groups: (1) stations with the highest PLI and W1 values, characterized by significant organic matter and metal contents, were grouped together and correspond with the right side of the 3D graphic (Fig. 7), and (2) samples with a smaller PLI and W1, placed on the left of the diagram, typically correspond to sandy sediments which retained low metal loads. Finally, in order to check the accuracy of the thermal results, a standard marine sediment was used (PACS-2) (NRC), which presents a high fine particle composition and an elevated heavy metal content, as evidenced by the high PLI (Table 3).

The sandy sediment (S11) is located on the left of the Cartesian diagram, and showed the lowest PLI, while the rest of the stations showed higher PLI values, a prevailing fine granulometric composition and were located on the right side of the diagram. This result is coincident with the station grouping performed by cluster analysis. An exceptional sample (S6) must be taken into account, as it is located on the right side of the diagram, with similar mud and sand fractions and relatively high results for both organic matter and heavy metals, probably due to its location next to a cement factory.

From the results of TG analysis, we confirmed that the two weight losses (W1 and W2) seen in the TG analysis correspond mainly to the presence of carbon compounds present in the decomposition stage of organic matter (W1) and carbonates released by the volatilization of different kinds of carbonates (W2).

CONCLUSIONS

FTIR, TG and DTG were used to evaluate sediments next to littoral zones. FTIR spectroscopy combined with multivariate data analysis and thermal methods was a useful tool to assess pollution levels in marine sediments. These analytical methods are promising for use in the assessment of metal pollution in port sediments due to their comprehensive information and readily available evaluation tools based on statistical methods. Moreover, this method could serve as a simple screening technique for contaminated sediments. In this way, the use of thermogravimetry and ATR-FTIR could alert authorities to possible contamination incidents that would require a more in-depth sediment characterization. Although these results are estimations, the method offers a series of advantages over other standard methods of analysis such since (1) it allows monitoring of an area with low costs, reduced time requirements and with little equipment, for example at a spill site and/or (2) it allows for pre-selecting highly contaminated sediments, such as in environmental monitoring programs or dredging channels to ports.

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REFERENCES

Blasco, J., Sáenz, V. and Gómez-Parra, A. (2000). Metal fluxes at the sediment-water interface of three coastal ecosystems from south-west of the Iberian Peninsula. Sci. Total Environ., **247**, 189-199.

Chapman, P. M. and Wang, F. (2001). Assessing sediment contamination in estuaries. Environ. Toxicol Chem., **20,** 3-22.

Chen, C. W., Kao, C. M., Chen, C. F. and Dong, C. D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbour, Taiwan. Chemosphere, 66, 1431-1440.

Crompton, T. R. (2001). Determination of Metals and Anions in Soils, Sediments and Sludges, Taylor & Francis Books Ltd., United Kingdom.

Donard, O.F.X., Lespes, G., Amouroux, D. and Morabito, R. (2001) In: Ebdon, L., Pitts, L., Cornelis, R., Crews, H., Donard, O.F.X., Quevauviller, P. (Eds). Trace Element Speciation for Environment, Food and Health. Royal Society of Chemistry, Cambridge, pp. 142-175.

Ferrase, J.H., Chavez, S., Arlabosse, P. and Dupuy, N. (2003). Chemometrics as a tool for the analysis of evolved gas during the thermal treatment of sewage sludge using coupled TG–FTIR. Thermochimica Acta, **404**, 97-108.

Förstner, U. and Wittman, G. T. W. (1983). Metal Pollution in the aquatic environment. Singer-Verlang, Berlin.

Hakanson, L. (1980). Ecological risk index for aquatic pollution control: a sedimentological approach. Water Res., **14**, 975-1001.

Horowitz, A. J. (1988). A review of physical and chemical partitioning of inorganic constituents in sediments. In: the role of sediments in the chemistry of aquatic systems. Proceedings of the Sediment Chemistry Workshop (Edited by Horowitz A.J and Bradford W.L.). U.S. Geological Survey 969.

Hung, J. J. and Hsu, C. L. (2004). Present state and historical changes of trace metal pollution in Kaoping coastal sediments, south-western Taiwan. Mar. Pollut. Bull., **49**, 986-998.

Jenne, E. A., Kennedy, V. C. and Burchard, J. M. and Ball, J. W. (1980). Sediment collection and processing for selective extraction and for total trace metal analyses. In: Contaminants and Sediments (Ed. by R.A. Baker). Ann Arbor Science Publishers Inc., Michigan, **2**, 169-189.

Kotoky, P., Bezbaruah, D., Baruah, J., Borah, G. C. and Sarma, J. N. (2006). Characterization of clay minerals in the Brahmaputra River sediments, Assam, India. Current Science, **91**, 1247-1250.

Kovac, N., Faganeli, J., Bajt, O., Orel, B. and Surca Vuk, A. (2005). Investigation of sediment samples from the Gulf of Trieste (northern Adriatic) by FTIR spectroscopy. RMZ Materials and Geoenvironment, **52**, 81-85.

Larkin, P. (2011). Infrared and Raman Spectroscopy: Principles and Spectral Interpretation. Elsevier, San Diego, Calif, USA.

Linnik, P. M. and Zubenko, I. B. (2000). Role of bottom sediments in the secondary pollution of aquatic environments by heavy-metal compounds. Lakes Reservoirs Research and Management, **5**, 11-21.

López-Capel, E., Rosa, J. M., González-Vila, F. J., González-Pérez, J. A. and Manning, D. (2006). Elucidation of different forms of organic carbon in marine sediments from the Atlantic coast of Spain using thermal analysis coupled to isotope ratio and quadruple mass spectrometry. Org. Geochem., **37**, 1983-1994.

Lwanga, M.S., Kansiime, F., Denny, P. and Scullion, J. (2003). Heavy metals in Lake George, Uganda, with relation to metal concentrations in tissues of common fish species. Hydrobiologia, **499**, 83-93.

Magalhães, W. L. E., Job, A.E., Ferreira, C. A. and da Silva, H. D. (2008). Pyrolysis and combustion of pulp mill lime sludge. J. Anal. Appl. Pyrolysis, **82**, 298-303.

Morillo, J., Usero, J. and Gracia, I. (2002). Partitioning of metals in sediments from the Odiel River (Spain). Environ. Int., 28, 263-271.

Morillo, J., Usero, J. and Gracia, I. (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. Chemosphere, **55**, 431-442.

Moros, J., Barciela-Alonso, M. C., Pazos-Capeáns, P., Bermejo-Barrera, P., Peña-Vázquez, E., Garrigues, S. and de la Guardia, M. (2008). Characterization of estuarine sediments by near infrared diffuse reflectance spectroscopy. Anal. Chim. Acta., **624**, 113-127.

Moros, J., Cassella, R. J., Barciela-Alonso, M. C., Moreda-Piñeiro, A., Herbello-Hermelo, P., Bermejo-Barrera, P., Garrigues, S. and de la Guardia, M. (2010). Estuarine sediment quality assessment by Fourier-transform infrared spectroscopy. Vib. Spectrosc., **53**, 204-213.

Oliveira Silva, J., Filho, G. R., da Silva Meireles, C., Ribeiro, S. D., Vieira, J. G., da Silva, C. V. and Cerqueira, D. A. (2012). Thermal analysis and FTIR studies of sewage sludge produced in treatment plants. The case of sludge in the city of uberlândia-MG, Brazil. Thermochimica Acta, **528**, 72-75.

Oudghiri, F., García-Morales, J. L. and Rodríguez-Barroso, M. R. (2014). Rapid screening of estuarine sediments properties using thermogravimetric analysis and attenuated total reflectance (ATR) by Fourier transform infrared (FTIR) spectrometry. Water Air Soil Pollut., **225**, 1-10.

Rodier, J. (1997). L'analyse de l'eau. Eaux naturelles, eaux résiduaires, eau de mer, 8ème édition.

Rodríguez-Barroso, M. R., Ramírez-del Solar, M., Blanco, E., Quiroga, J. M. and García-Morales, J. L. (2006). Thermal analysis in the evaluation of sediment pollution. Environ. Technol., **27**, 1001-1009.

Rodríguez-Barroso, M. R., Ramírez-del Solar, M., Blanco, E., Quiroga, J. M. and García-Morales J. L. (2008). Qualitative estimation of heavy metals in marine sediment using thermal analysis. Soil Sediment Contam., **17**, 107-120.

Rodríguez-Barroso, M. R., Benhamou, Y., El Moumni, B., El Hatimi, I. and García Morales, J. L. (2009a). Evaluation of metal contamination in sediments from north of Morocco: geochemical and statistical approaches. Environ. Monit. Assess., **159**, 169-181.

Rodríguez-Barroso, M. R., Ramírez-del Solar, M., Blanco, E., Quiroga, J. M. and García-Morales, J. L. (2009b). Thermal gravimetry analysis assessed as an alternative method for characterization of sediment contamination. Environ. Eng. Sci., **26**, 279-287.

Singh, S., Wu, C. and Williams, P. T. (2012). Pyrolysis of waste materials using TGA-MS and TGA-FTIR as complementary characterisation techniques. J. Anal. Appl. Pyrolysis, **94**, 99-107.

Sivakumar, S., Ravisankar, R., Raghu, Y., Chandrasekaran, A. and Chandramohan, J. (2012). FTIR Spectroscopic Studies on Coastal Sediment Samples from Cuddalore District, Tamilnadu, India. Indian Journal of Advances in Chemical Science, **1,** 40-46.

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. Helgoländer Meeruntersuchungen, **33**, 566-575.

Tung, J. W. T. and Tanner, P. T. (2003). Instrumental determination of organic carbon in marine sediments. Mar. Chem., **80**, 161-170.

Turekian, K. K. and Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. Geol. Soc. Am. Bull., **72,** 175-192.

Zhang, B., Xiong, S., Xiao, B., Yu, D., Jia, X. (2011). Mechanism of wet sewage sludge pyrolysis in a tubular furnace. International Journal of Hydrogen Energy, **36**, 355-363.