



Source of detritus and toxic elements of seabed sediments from Acapulco Bay (southern Mexico) and their ecological risk

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ABSTRACT

Total concentrations of Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, and As together with Sr and Pb isotopic compositions of seabed sediments from the worldwide famous tourist destination of Acapulco Bay, Guerrero (southern Mexico) were determined to reveal the origin of detritus and toxic elements (TEs), their potential natural and anthropogenic sources, elemental distribution and their ecological risk. Sediments derive entirely from the nearby Acapulco Granite and their concentrations of TEs are variable and rather low, although, several are above the Local Geochemical Baseline in some sites of the bay. The enrichment factor (EF) and Pb isotopes indicate that TEs derive from the Acapulco Granite with contributions of an anthropogenic source represented, very likely, by ship-bottom paints. Wastewaters are a significant source of Pb and Cu. The ecological risk of TEs is low and only Cu represents a moderate ecological risk in a few sites.

1. Introduction

Oceans are the final reservoir of natural and anthropogenic contaminants which affect seawater, coastlines and beaches, and pose a severe threat to coastal/marine ecosystems and human health (e.g., Islam and Tanaka, 2004; Akcil et al., 2015; Ruiz-Fernández et al., 2018; Nalley et al., 2021). The presence of contaminants in the water can also have serious socioeconomic consequences since coastal/marine resources represent a major source of food and direct/indirect jobs for many people, particularly tourist sites in developing countries (e.g., Chua, 1992; Freire and García-Allut, 2000; Façanha-Câmara et al., 2021). Among the contaminants of greatest concern for the environment and health, toxic elements (TEs) like Ba, Hg, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, and As, and fecal-derived microorganisms stand out due to their persistence in the environment and by the negative effects they cause to

ecosystems and humans (e.g., Sankhla et al., 2016; Jaiswal et al., 2018; Joksimovic et al., 2020; Amqam et al., 2020; Al-Mutairi and Yap, 2021). The TEs are mainly concentrated in sediments and organic matter but they can be released as soluble chemical species or bound to submicron particles both by physico-chemical changes at the water-sediment interphase and by the action of benthonic, filter-feeder organisms, which favor their incorporation into the food chain (e.g., Ruelas-Inzunza and Pérez-Osuna, 2000; Jara-Marini et al., 2013; Webb et al., 2020; Gao et al., 2021). Some elements like Cd, Hg, and As can even be bio-magnified becoming a significant route of intake for higher organisms, including humans (e.g., Zhang and Wang, 2009; Ali and Khan, 2019; Jara-Marini et al., 2020; Du et al., 2021; Gu et al., 2021; Seco et al., 2021). The knowledge of the influence of both natural and anthropogenic processes on the physical and chemical quality of seawater, coasts, and beaches is needed to evaluate the ecological impact they have on the

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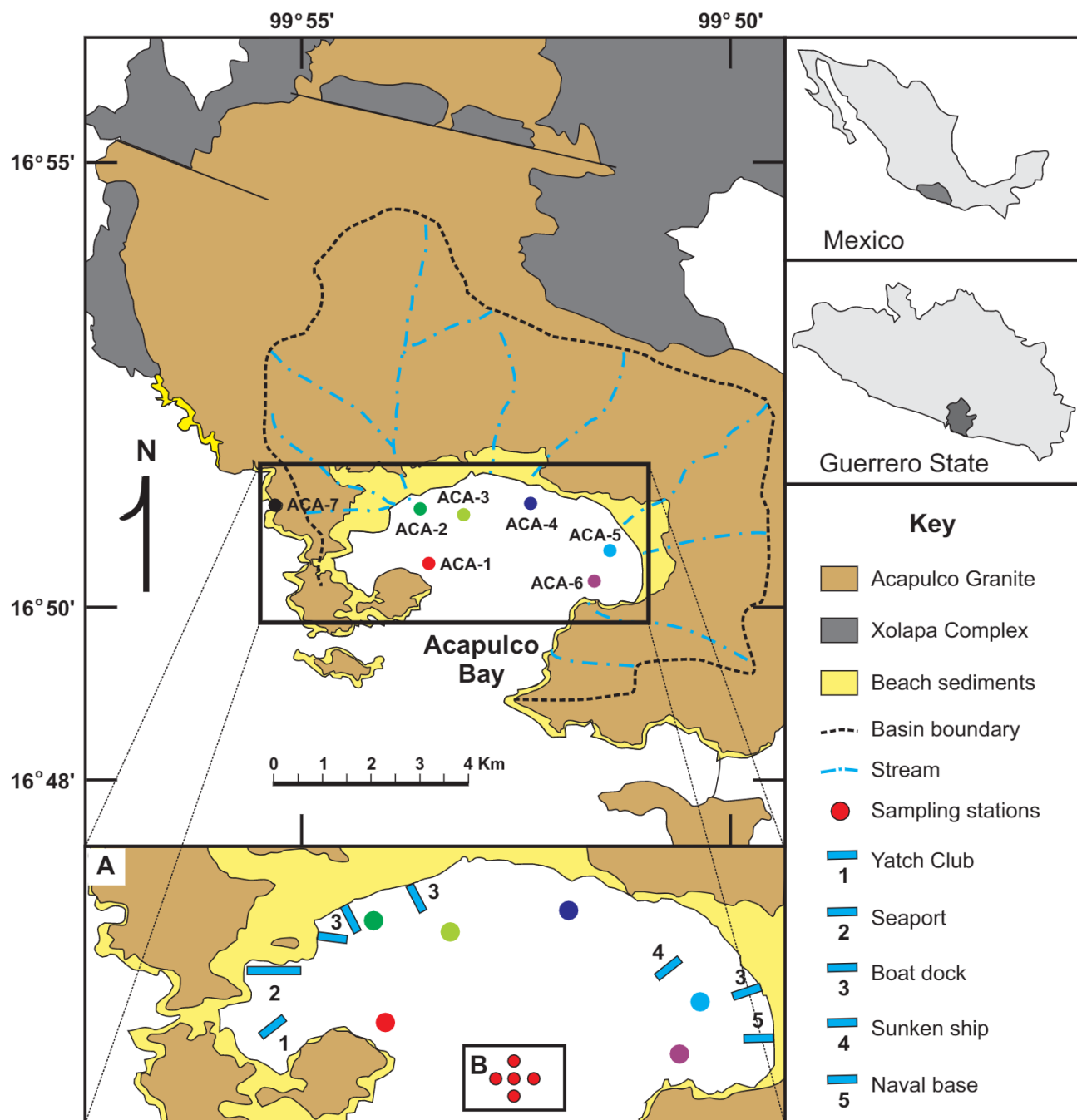


Fig. 1. Geologic map of Acapulco Bay, Guerrero (southern Mexico) after [Hernández-Pineda et al. \(2011\)](#) showing the location of the sampling stations as well as the location of the main ship/boat facilities (A). The approximated distribution of samples in each station is also shown (B).

ecosystems and the potential health risks to inhabitants.

Acapulco, Guerrero in southern Mexico is one of the most famous tourist destinations of the Americas and an important commercial seaport. The physical, chemical and biological conditions of these waters, beaches and marine sediments have been questioned and only four out of twenty-four of Acapulco's beaches meet the Blue Flag cleanliness regulation issued by the Foundation for Environmental Education Mexico. Some studies in the zone (e.g., [Silva-Cazares, 2011](#); [Flores-Mejía et al., 2011](#); [Curiel-Ayala et al., 2012](#)) have reported the presence of pathogenic microorganisms (fecal coliforms and *Enterococcus*) well above acceptable limits. Even then [Silva-Cazares \(2011\)](#) indicated that seawater in this zone met Mexican regulations in metal contents, [Dimas et al. \(2015\)](#) reported that one effluent contains TEs at concentrations

above the Mexican and EPA guidelines and concluded that the effluent is a permanent supply of these pollutants to the bay. This is particularly concerning because mollusks from the shallow rocky shore represent an important source of economic income for many riparian fishermen and are consumed by both inhabitants and tourists. [Jonathan et al. \(2011\)](#) indicated that Acapulco beaches recorded slightly high concentrations of some TEs, which they impute to tourist activities. Finally, [Marmolejo-Rodríguez et al. \(2017\)](#) reported the mean ($n = 3$) concentrations of some TEs in seabed sediments collected at a sole site at the entrance of the Acapulco Bay as part of a wide study of the Pacific Coast of Mexico. The work by [Jonathan et al. \(2011\)](#) is the only known report on the contamination by TEs of the tourist beaches of Acapulco but there are no studies evaluating the state of contamination of seabed sediments of the

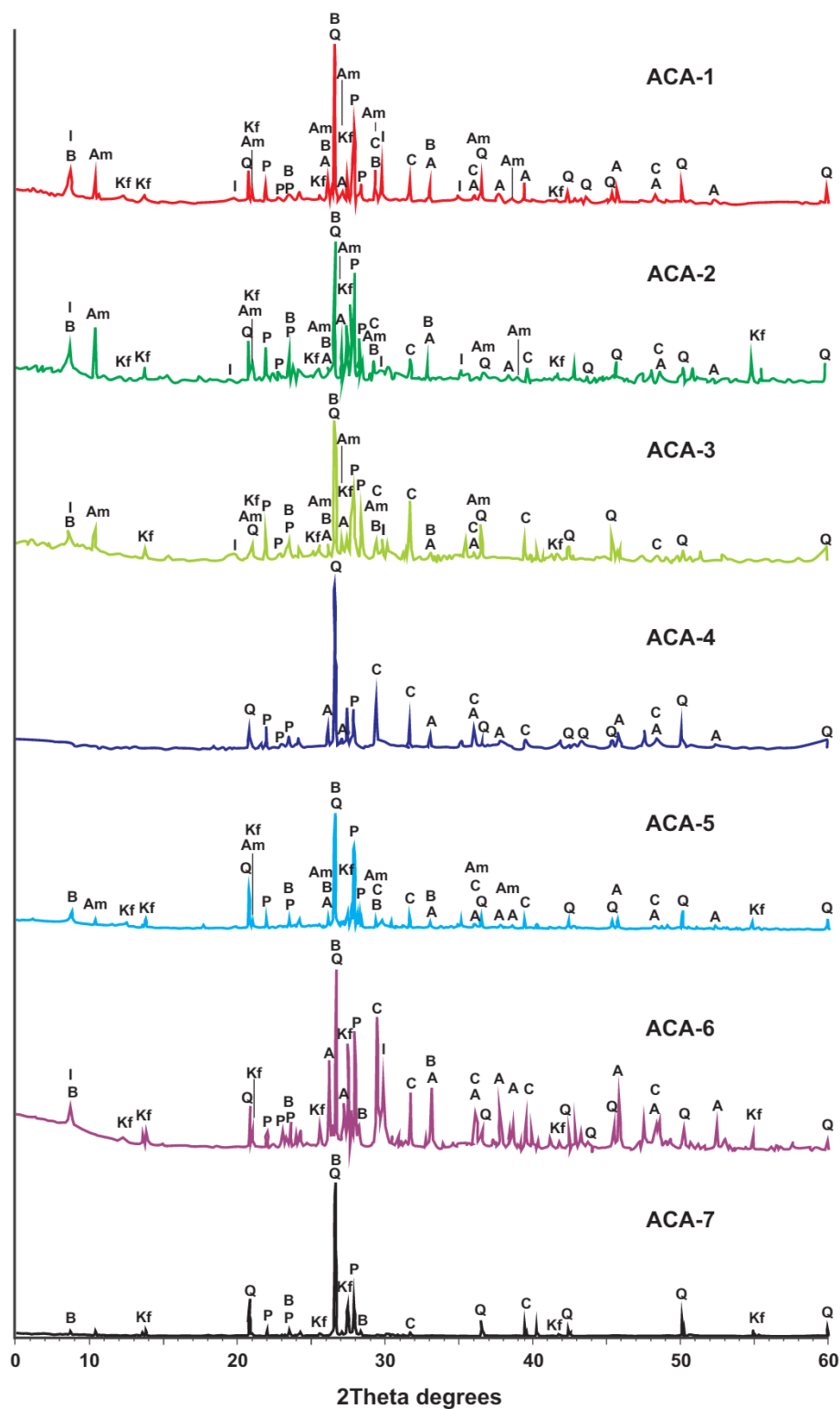


Fig. 2. X-Ray diffractograms of representative samples from all the studied stations.

A = Aragonite; Am = Amphibole; B = Biotite; C = Calcite; I = Illite; Kf = K-feldspar; P = Plagioclase; Q = Quartz.

bay by TEs or their ecological impact in spite of its tourist and economic importance. No studies on the identification of the potential sources of debris or TEs and their apportionment have been carried out in the zone either.

To provide insights into these issues, we carried out a mineralogical, geochemical, and Sr–Pb isotopic study of seabed sediments from the

Acapulco Bay, Guerrero, Mexico. The results provide a suitable framework to evaluate the degree of contamination of seabed sediments by TEs, to reveal their spatial distribution, to identify the potential sources of lithogenic detritus and TEs, and to determine their ecological risk.

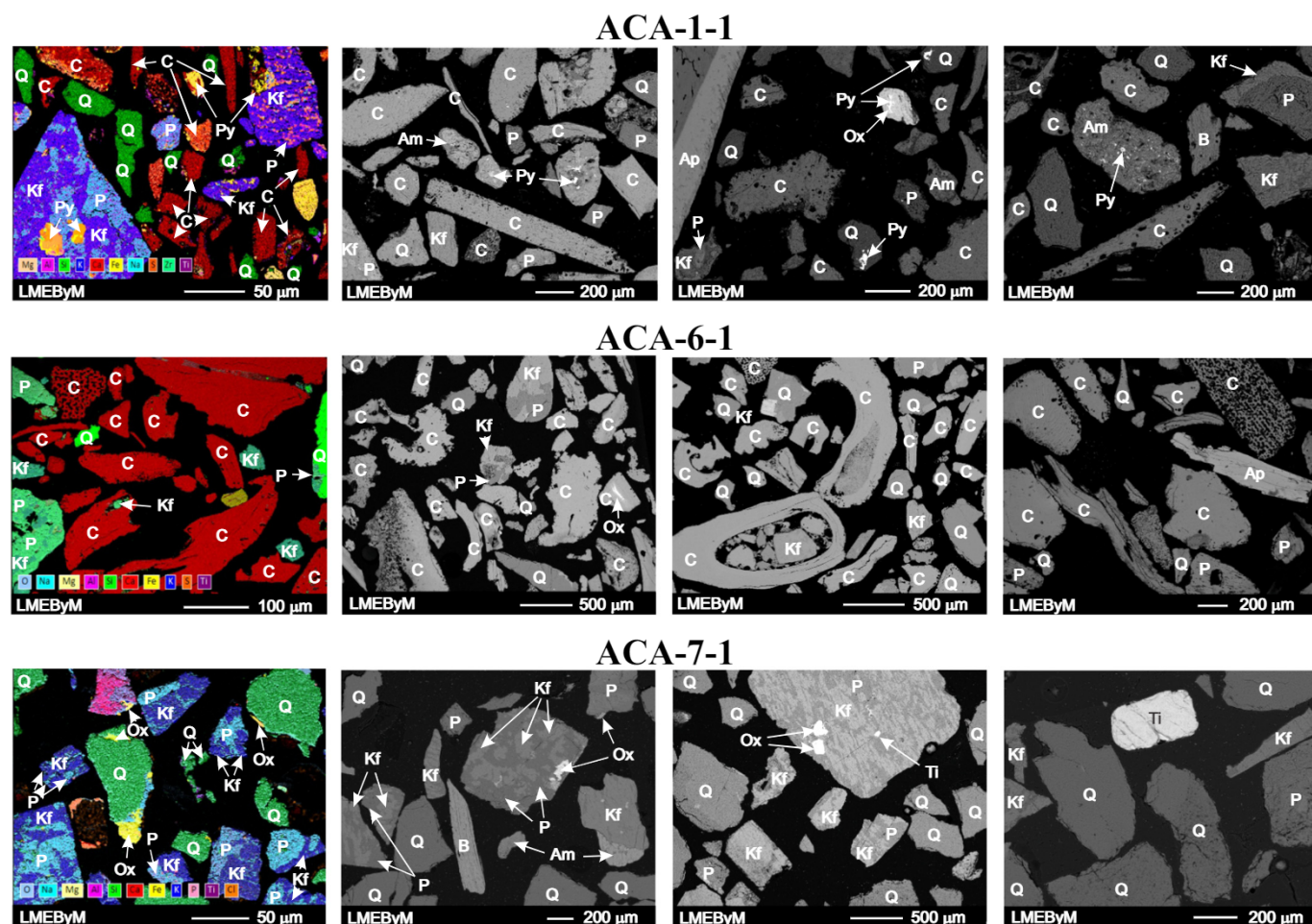


Fig. 3. SEM maps and images of representative mineral phases of seabed sediments from Acapulco Bay, Guerrero. Identification of phases was performed using EDS analysis.

Am = Amphibole; Ap = Apatite; B = Biotite; C = Calcite; I = Illite; Kf = K-feldspar; Ox = Ti-Fe oxide; P = Plagioclase; Py = Pyrite; Q = Quartz; Ti = Titanite.

2. Methodology

2.1. Geological and environmental framework

The Acapulco Bay in the Mexican State of Guerrero is located on the Pacific Coast of southern Mexico at 16° 50' 47.29" N and 99° 52' 39.47" W (Fig. 1). It has a near-circular shape (6 km length and 5.8 km width) surrounded by hills up to 700 m high, and a maximum depth of 62 m. The climate in Acapulco is of type Aw (tropical rainy) with an annual average temperature of 27.8°C and an annual average rainfall of 561 mm (SMN, 2021).

In the bay, lithology is entirely dominated by granitic rocks of the so-called Acapulco Granite (Hernández-Pineda et al., 2011). Mesozoic metamorphic rocks of the Xolapa Complex occur north and west of the area but the drainage in these areas does not flow into the bay and so, its influence in the composition of sediments is limited or null (Hernández-Pineda et al., 2011). Its hydrological system is quite simple and is made up of short fluvial channels arranged radially.

Urban, tourist, and seaport activities are the main sources of contamination in the Acapulco Bay. Even though the municipality assures that only treated waters are discharged into the bay, there is evidence that discharge of untreated waters occurs in some zones and there is suspicion that even some hotels dispose their sewage directly into the bay. The presence of solid wastes in the bay is alarming despite the permanent program of recollection by the municipality. A Naval Base, the dock from the Mexican Oil Company (PEMEX), Yacht Club, boats,

and workshops are significant sources of contamination by hydrocarbons, oils, and fats.

2.2. Sampling

Thirty samples of 1–2 kg of seabed sediment were collected using polyethylene spoons and bags at six sampling stations in the Acapulco Bay to determine their physical, mineralogical, geochemical, and isotopic characteristics (Fig. 1). Sampling was carried out in spring 2019 in the month of May. The stations (ACA-1 to ACA-6) were spatially distributed along the bay and fell within the bathymetric depths of 10 m and 20 m. At each sampling station, five samples were collected following the distribution showed in the inset B of Fig. 1. Samples were taken at distances of between 5 and 10 m from the center point. One additional station (ACA-7) was located 2.5 km NW of the bay at the mouth of an effluent that discharges apparently treated waters from the main regional water treatment plant of the city of Acapulco (Fig. 1). The two samples from this station were used for evaluating the contribution of TEs of wastewaters and for identifying potential anthropogenic sources. The geographic coordinates of the sampling stations are reported in Table S1.

2.3. Sample preparation and geochemical analysis

Samples were air-dried in a dust-free environment at room temperature and then sieved through a No. 10 stainless steel sieve to recover

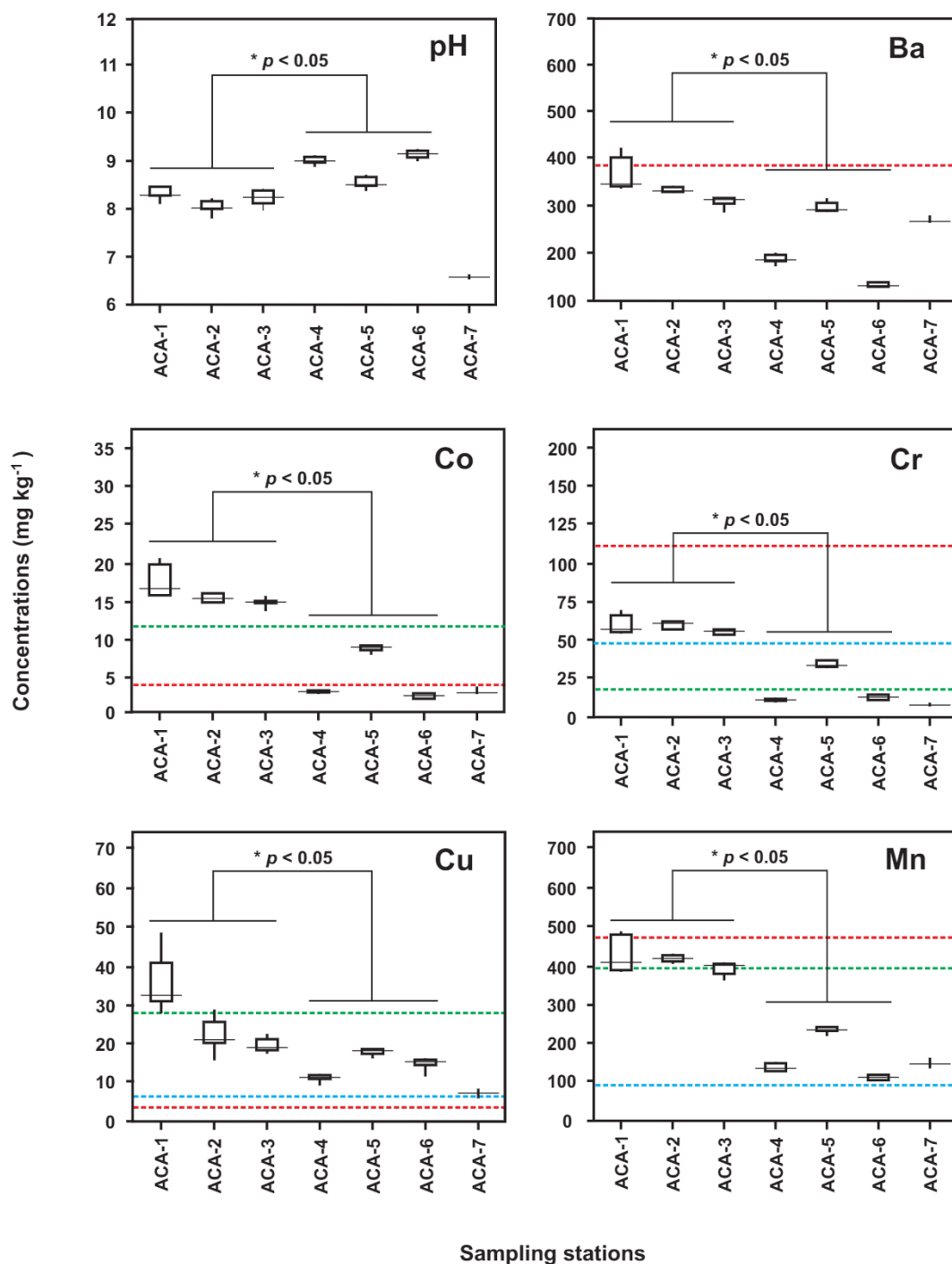


Fig. 4. Box plots of mean pH and TEs of the sediments analyzed from Acapulco Bay, Guerrero. For each station $n = 5$ except in Station ACA-7 where $n = 2$. Statistical differences between samples from Group 1 and 2 are shown. Red dashed line indicates the value of the Local Geochemical Baseline (Hernández-Pineda et al., 2011); blue dashed line indicates the mean concentration of seabed sediments reported by Marmolejo-Rodríguez et al. (2017); and the green dashed line indicates the mean concentration of beach sediments reported by Jonathan et al. (2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

particles <2 mm. Approximately 250 g of this fraction was pulverized using an agate mortar RETSCH-RM100 and the resulting powder was sieved through a No. 230 stainless steel sieve to obtain a grain size <0.063 mm. The pH of each sample was measured in the fraction <2 mm in a sediment/water mix of 1:2 with a portable electrode and buffers of 4, 7, and 10 for calibration. The mineralogical composition of samples was determined in the laboratories of the Earth Sciences Department,

Autonomous University of Guerrero, Mexico by using a combination of Polarizing Microscopy (PM; Leica DM2700P), X-Ray Diffraction (XRD; Bruker D8 ADVANCE ECO) and Scanning Electron Microscopy (JEOL IT300) coupled to an Energy Dispersive Spectrophotometer (SEM-EDS; Bruker QUANTAX).

The total concentration of Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, and As was determined in a PERKIN-ELMER ICP-AES 3200DV at the

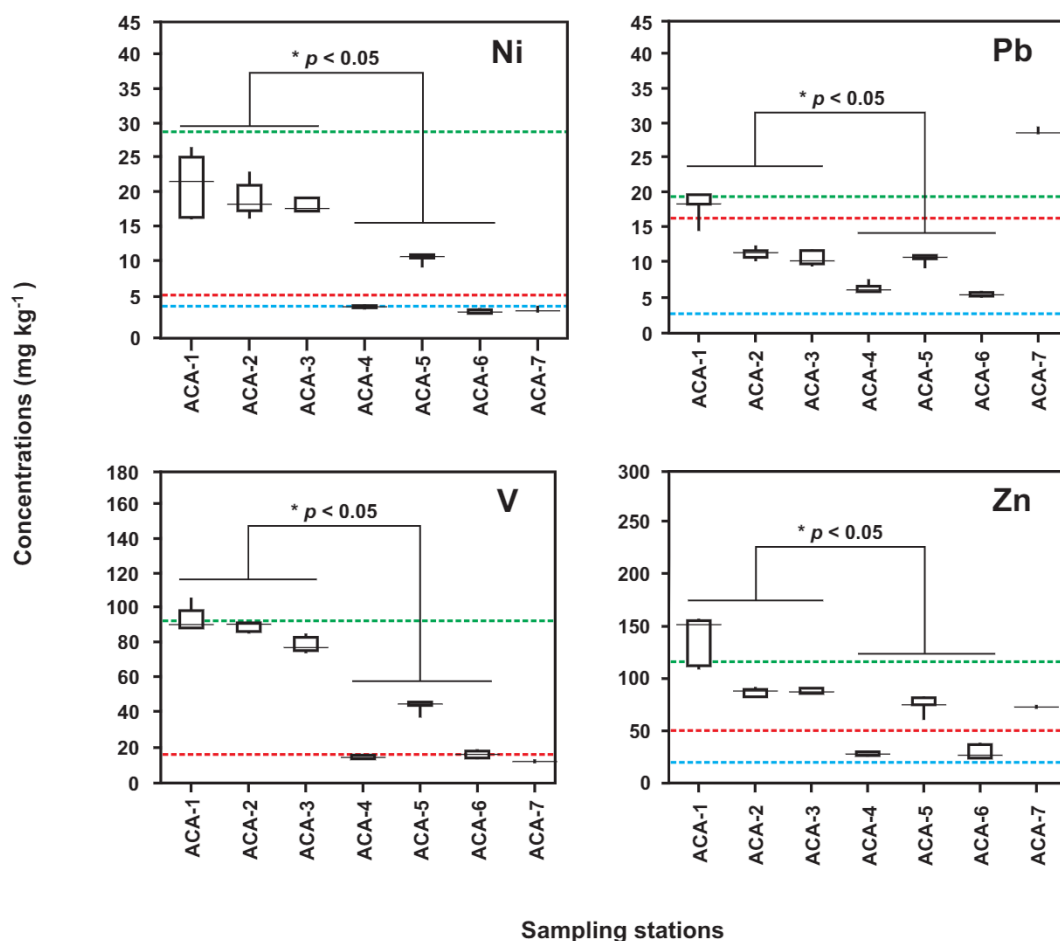


Fig. 4. (continued).

Laboratory of Geochemistry of the Earth Sciences Department, Autonomous University of Guerrero, Mexico after digestion of ~100 mg of the fraction <0.063 mm with HNO₃ and then HF + HClO₄ at high pressure using Parr bombs in a final volume of 12 mL. Four certified High Purity standards (CWW-TM-D, CWW-TM-H, CWW-TM-A, and CWW-TM-E) were used for calibration, the certified solution standard CRM-SOIL-B for checking instrument performance; and, the certified standards CRM-SA-A and CRM-LOAM-B for checking the sample digestion procedure and accuracy of the analytical method. In all standards, recovery was better than 90–110%. The reported detection limit (DL) for the method was determined following the procedure outlined by Talavera et al. (2005), who reported DL as the lowest concentration of an element that the instrument can be accurately determined in a certified standard. This DL is significantly higher than that commonly reported by equipment manufacturers, but ours takes into account the true analytical capacity of the instrument, the weight of the sample digested and the final volume. The reported LD is conservative but is considered the real DL of the instrument for the analytical method used. Thus, for each element, the DL in the study was: 1.25 mg kg⁻¹ (Ba, Co, Cr, Cu, Mn, Ni, Pb, V and Zn); 0.250 mg kg⁻¹ (Cd); and, 0.500 mg kg⁻¹ (As).

2.4. Pb and Sr isotopic analysis

An aliquot of 3 mL of the total digestion (12 mL) of each sample was used for Pb and Sr isotopic determinations. Purification of these elements was carried out by chromatographic techniques using Sr resin (Eichrom Technologies, LLC). The Pb isotopic ratios were measured in ~35 ppb in an Isoprobe MC-ICPMS. The thallium normalization method was used for mass bias correction and the standard NBS-981 was used

for monitoring the isotopic fractionation of the equipment as described by Thibodeau et al. (2013). External errors at the 2σ level were: ²⁰⁶Pb/²⁰⁴Pb = 0.0039; ²⁰⁷Pb/²⁰⁴Pb = 0.0041; ²⁰⁸Pb/²⁰⁴Pb = 0.0101; ²⁰⁷Pb/²⁰⁶Pb = 0.0001; and, ²⁰⁸Pb/²⁰⁶Pb = 0.0003. The Sr isotopic ratios were determined by thermal Ionization Mass Spectrometry in a VGA Instrument and the isotopic fractionation was monitored by analyzing the certified standard NBS-987. The Pb and Sr isotopic determinations were carried out in the Laboratory of Isotopic Geochemistry of the Department of Geosciences, the University of Arizona, USA.

2.5. Statistics and spatial mapping

The enrichment factor (EF) of each element was calculated as the ratio between the arithmetic means of stations (station EF) or the mean of the whole set of samples (bulk EF), and the concentration of the element in the Local Geochemical Baseline (LGBL) calculated from data by Hernández-Pineda et al. (2011). We preferred to compare TEs in sediments against this guideline instead of values of the upper continental crust because, as stated before, the Acapulco Granite is the bedrock and the only lithology providing detritus to the bay. The ecological risk index (ERI) was calculated based on the method proposed by Hakanson (1980) with the toxicity coefficient proposed for Co (2), Cr (2), Cu (5), Ni (5), Pb (5), and Zn (1). Element to element correlations were calculated by using Pearson (r) coefficient. Significant differences in pH values, TEs' concentrations and isotope ratios between stations were tested by unpaired-sample T-student for variables with normal distribution and Mann-Whitney U test for those that did not present a normal distribution using the SigmaPlot 14.0 software. Accepted statistical significance was at $p \leq 0.05$ level. After autoscaling, data were

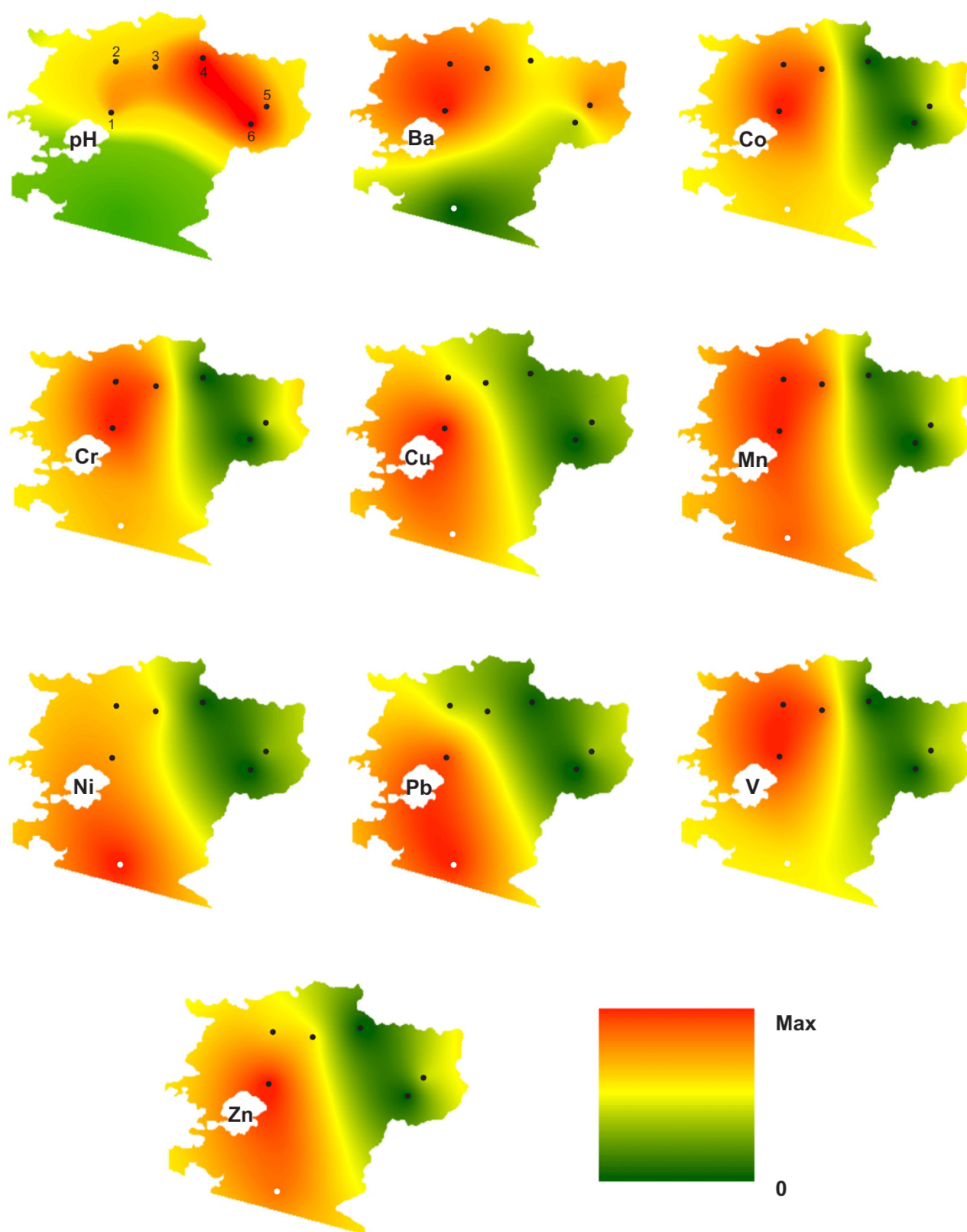


Fig. 5. Spatial distribution of pH and TEs in sediments from Acapulco Bay, Guerrero. The location of stations is indicated by black dots and the location of the sample reported by [Marmolejo-Rodríguez et al. \(2017\)](#) is indicated by a white circle. The number of stations is indicated in the first map. In the scale of colors representing the concentrations of TEs, the range for all the elements is from 0 to the maximum concentration recorded in each element.

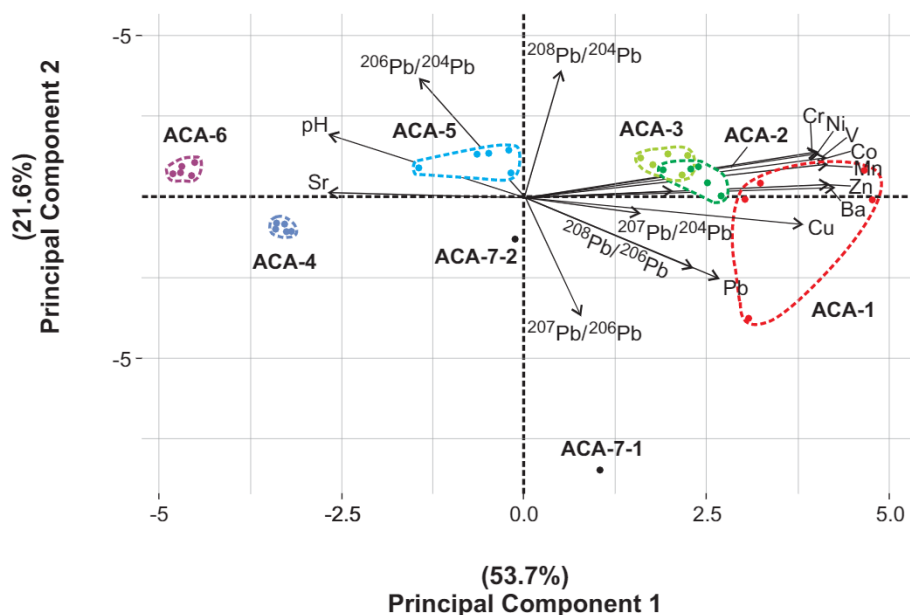


Fig. 6. Plot of the two main components of the PCA for the TEs analyzed in the sediments from Acapulco Bay, Guerrero. Field and samples of each station within the bay are identified by colors and the name of the station is indicated directly in the plot. Samples from the Station ACA-7 are indicated as individual samples.

Table 1

Pearson correlation coefficients for the TEs in the seabed sediments (green) of Acapulco Bay and the Acapulco Granite (orange). Bold numbers indicate statistically significant correlations ($p < 0.05$).

Element	Ba	Co	Cr	Cu	Mn	Ni	Pb	V	Zn
Ba		0.96	0.95	0.83	0.94	0.94	0.87	0.93	0.94
Co	0.06		1.00	0.86	0.99	0.98	0.85	0.99	0.95
Cr	0.36	0.61		0.83	0.99	0.98	0.82	1.00	0.92
Cu	0.02	0.96	0.55		0.82	0.84	0.91	0.81	0.91
Mn	0.14	0.62	0.84	0.51		0.97	0.79	0.99	0.91
Ni	0.00	0.04	0.07	0.07	0.06		0.81	0.91	0.94
Pb	0.07	0.58	0.35	0.49	0.50	0.46		0.80	0.92
V	0.01	0.86	0.78	0.73	0.83	0.00	0.60		0.91
Zn	0.01	0.38	0.53	0.24	0.72	0.18	0.46	0.52	

further submitted to Principal Component Analysis (PCA) with FactoMineR v.2.4 (Lê et al., 2008) and Factoextra v.1.0.7 (Kassambara and Mundt, 2017) in R studio v.1.4.1103 (R-core Team, 2020), and hierarchical cluster analysis (Dendrograms) using the Euclidean distance algorithm by using the Package Cluster v.2.1.1.2 (Maechler et al., 2021). The spatial distribution maps were created with the mean values of pH and the mean concentrations of TEs of each station using the ArcGIS geographical information system. In the construction of the distribution maps, the data reported by Marmolejo-Rodríguez et al. (2017) in sediment samples collected at the entrance of the Acapulco Bay were also included.

3. Results and discussion

3.1. Mineralogical composition of sediments

The mineralogical composition of sediments of Acapulco Bay obtained by PM, XRD, and SEM-EDS is summarized in Table S1. Sediments are composed of mixes of bioclasts and minerals in highly variable proportions with some samples containing up to 90% bioclasts (e.g. sample ACA-6-1) and samples consisting almost entirely of minerals (e.

g. sample ACA-7-1). Bioclasts are fragments of shells with sizes ranging from 0.3 to 2 mm and all showing evident signs of abrasion. They are composed of calcite and aragonite. Minerals range in size from 0.1 to 2 mm and most show subrounded to subangular shapes evidencing some degree of reworking. Recognized mineral phases include quartz, potassium feldspar, plagioclase, biotite, amphibole, chlorite, sericite, epidote, and Fe–Ti oxides. The XRD patterns (Fig. 2) and SEM-EDS imaging and microanalysis (Fig. 3), indicate that the mineralogical composition of samples from all the stations is rather homogeneous. The SEM-EDS images further reveal the presence of micrometric (<25 µm) inclusions of pyrite and zircon in plagioclase and chloritized biotite and isolated crystals of apatite and titanite.

3.2. pH and total concentrations of TEs

The pH and total concentration of TEs in sediments from Acapulco Bay as well as their basic statistics are presented as supplementary material (Table S2) and graphically shown in Fig. 4. In the bay, the pH ranges from 7.87 to 9.24 with samples from Stations ACA-1 to ACA-3 having slightly lower (7.87–8.42) values than those from Stations ACA-4 to ACA-6 (8.38–9.24). Sediments from Station ACA-7, out of the bay, have the lowest (6.58–6.64) pH values. Element concentrations are described in relation to the LGBL and the concomitant EF (Fig. 4). All samples yielded concentrations of Cd and As below the DL and, consequently, below the LGBL. Chromium has concentrations below the LGBL in all the samples with a bulk EF of 0.3. Barium and Mn are also at concentrations below this limit in all the samples excepting ACA-1-3, and have bulk EF of 0.7 and 0.6, respectively. Four out of five samples from Station ACA-1 and the two samples from Station ACA-7 have concentrations of Pb above the LGBL yielding station EF of 1.1 and 1.8, respectively. The remaining samples have concentrations of Pb below this limit and station EF <0.7. The concentration of Co, Ni and V are above the LGBL in Stations ACA-1, ACA-2, ACA-3 and ACA-5 with station EF up to 4.4, 4.1 and 5.2, respectively. Finally, samples from five stations have concentrations of Zn above LGBL with a bulk EF of 1.4, whereas Cu is the only element whose concentrations are above LGBL in all samples with the highest bulk EF = 6.6 recorded. Taking into consideration their pH and elemental concentrations, two distinctive groups of sediments can be clearly identified (Fig. 4): Group 1 include the samples from Stations ACA-1 to ACA-3 having lower pH and the

Table 2

Strontium and lead isotopic ratios of the studied sediments. External errors of Pb isotopic ratios at the 2σ level were: $^{206}\text{Pb}/^{204}\text{Pb} = 0.0039$; $^{207}\text{Pb}/^{204}\text{Pb} = 0.0041$; $^{208}\text{Pb}/^{204}\text{Pb} = 0.0101$; $^{207}\text{Pb}/^{206}\text{Pb} = 0.0001$; and, $^{208}\text{Pb}/^{206}\text{Pb} = 0.0003$.

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
Station ACA-1						
ACA 1-1	0.70891 ± 0.0015	18.7530	15.6450	38.6426	0.8341	2.0606
ACA 1-2		18.7611	15.6474	38.6526	0.8339	2.060
ACA 1-3	0.70914 ± 0.0008	18.7632	15.6449	38.6502	0.8337	2.0599
ACA 1-4		18.7550	15.6445	38.6437	0.8340	2.060
ACA 1-5		18.6886	15.6405	38.5744	0.8368	2.0641
Station ACA-2						
ACA 2-1	0.70741 ± 0.0009	18.7875	15.643	38.6455	0.8325	2.0570
ACA 2-2	0.70742 ± 0.0009	18.7873	15.6436	38.6487	0.8326	2.0573
ACA 2-3		18.7739	15.6387	38.6246	0.8329	2.0574
ACA 2-4		18.7775	15.6401	38.6289	0.8328	2.0573
ACA 2-5		18.7887	15.6447	38.6513	0.8325	2.0572
Station ACA-3						
ACA 3-1	0.70862 ± 0.0014	18.8088	15.6460	38.6670	0.8317	2.0558
ACA 3-2	0.70841 ± 0.0011	18.8032	15.6453	38.6650	0.8319	2.0562
ACA 3-3	0.70836 ± 0.0009	18.8092	15.6465	38.6662	0.8317	2.0557
ACA 3-4		18.8030	15.6455	38.6544	0.8320	2.0559
ACA 3-5		18.8091	15.6454	38.6661	0.8317	2.0558
Station ACA-4						
ACA 4-1	0.70913 ± 0.0010	18.7561	15.6370	38.6149	0.8336	2.0588
ACA 4-2	0.70919 ± 0.0010	18.7548	15.6388	38.6178	0.8337	2.0591
ACA 4-3	0.70929 ± 0.0034	18.7611	15.6407	38.6241	0.8336	2.0587
ACA 4-4		18.7677	15.6401	38.6235	0.8332	2.0580
ACA 4-5		18.7590	15.6386	38.6145	0.8335	2.0585
Station ACA-5						
ACA 5-1	0.70914 ± 0.0018	18.8342	15.6490	38.6803	0.8307	2.0538
ACA 5-2	0.70912 ± 0.0008	18.8154	15.6440	38.6660	0.8313	2.0549
ACA 5-3	0.70908 ± 0.0009	18.8209	15.6440	38.6659	0.8311	2.0545
ACA 5-4		18.8149	15.6438	38.6653	0.8313	2.0551
Station ACA-6						
ACA 6-1	0.70919 ± 0.0010	18.8285	15.6415	38.6335	0.8306	2.0519
ACA 6-2	0.70918 ± 0.009	18.8465	15.6415	38.6434	0.8298	2.0505
ACA 6-3	0.70920 ± 0.0007	18.8128	15.6426	38.6446	0.8314	2.0542
ACA 6-4		18.8197	15.6397	38.6399	0.8309	2.0532
Station ACA-7						
ACA 7-1		18.6412	15.6453	38.5237	0.8392	2.0666
ACA 7-2		18.8285	15.6551	38.6663	0.8313	2.0536

highest concentrations recorded in all the elements; and, Group 2 formed by samples from Stations ACA-4 to ACA-6, which are characterized by higher pH and lower elemental concentrations.

Marmolejo-Rodríguez et al. (2017) reported the mean concentration of TEs of three samples of sediments collected at the entrance of Acapulco Bay. Except for Ni, the concentrations reported by these authors are within the range recorded in our samples: Cu, Mn, Pb, V, and Zn have concentrations like samples from Group 1, whereas Co and Cr match concentrations measured in samples from Group 2 (Fig. 4). On the other hand, the concentrations of Cr, Cu, Mn, Ni, Pb and Zn reported by Jonathan et al. (2011) for beach sediments at Acapulco are very similar to the concentrations recorded in our samples from Group 2. The low concentrations systematically recorded by these authors may be due to the acid extraction method that they used compared to the total extraction we performed.

Maps clearly show that the lowest pH and the highest concentrations of all the analyzed elements having concentrations above DL, are located in the western part of the bay and that this distribution is controlled by samples of Group 1 (Fig. 5). Higher pH values and lower concentrations are recorded in the central and eastern part of the bay and their distribution is controlled by samples belonging to Group 2. Samples from Station ACA-5 clearly represent an anomaly among samples from Group 2 having, in general, lower pH and higher elemental concentrations than the other samples of the group. In general, data reported by Marmolejo-Rodríguez et al. (2017) match with the observed distribution of elements in our samples.

3.3. Statistical analysis

The PCA supports the separation of samples from the Acapulco Bay into two groups and indicates that components one and two explain up to 75% of the variance (Table S3; Fig. 6; Fig. S1). Component one was defined by Cr, Ni, V, Co, Mn, Ba and Cu explaining 53.7% of the variance, whereas component two was defined by Pb and the $^{206}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic ratios, which explain 21.6% of the variance. Component one clearly separates the two groups of samples and vectors representing the variables considered mostly define the samples from Stations ACA-1, ACA-2, and ACA-3, which form Group 1. Samples from Stations ACA-4, ACA-5, and ACA-6 forming Group 2, fall in opposite quadrants. As detailed before, samples from Station ACA-5 show a clear tendency toward the samples from Group 1 corroborating their geochemical connection. The two samples from Station ACA-7 are defined by different variables and are placed apart from each other, and from the rest of stations. In the dendrogram (Fig. S1), distinction of the two groups of samples is not as evident as in the PCA and actually, 3 distinctive clusters can be recognized: (1) Station ACA-1 samples; (2) Stations ACA-2, ACA-3 and ACA-5 samples; and, (3) Stations ACA-4 and ACA-6 samples. Cluster analysis also highlights the geochemical similarity of samples from the Station ACA-5 (Group 2) with samples from the Stations ACA-2 and ACA-3 (Group 1). Samples from Station ACA-7, from out of the bay, separate from the samples from the other stations.

The correlation among all the TEs in the sediments is high

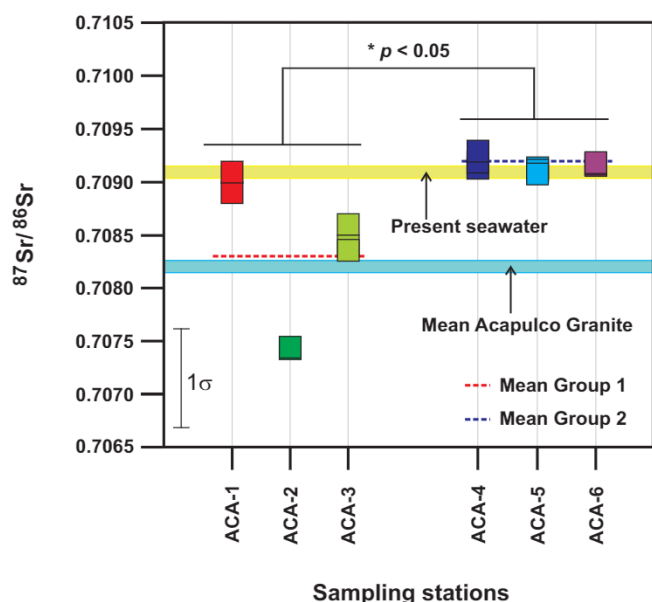


Fig. 7. Strontium isotopic composition of sediments from Acapulco Bay Guerrero, Mexico. The mean Sr isotopic compositions of samples from Group 1 and Group 2 are indicated as red and blue dashed lines, respectively. The mean Sr isotopic composition of the Acapulco Granite (Hernández-Pineda et al., 2011) and the Sr isotopic composition of present seawater (Spooner, 1976) are also presented. Statistical differences between the two groups of samples are indicated. Average error bar is at 1σ level. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(0.80–0.90) to very high (>0.90), which contrasts strongly with the correlations found in the parental rocks of the Acapulco Granite, that only shows high correlation between Cr–Mn (0.84), Co–V (0.86) and V–Mn (0.83), and very high between Cu–Co (0.96; Table 1). These facts suggest that correlations of the parental rock were severely modified by secondary processes, very likely of anthropogenic origin.

The T-student and Mann-Whitney U tests applied to the samples revealed that differences in the pH and concentrations between samples of both groups are statistically significant ($p < 0.05$) in all the elements analyzed, which also supports their separation into the two groups.

3.4. Strontium and lead isotopic signatures of sediments

The Sr isotopic composition is variable and clearly justifies the separation of samples into two distinctive groups with samples from Group 1 having less radiogenic isotopic compositions relative to samples from Group 2 (Table 2, Fig. 7). In Group 1, ratios were statistically indistinguishable from the mean isotopic composition of the Acapulco Granite reported by Hernández-Pineda et al. (2011). The isotopic compositions of samples from Group 2 are slightly more radiogenic and identical to the Sr isotopic composition of seawater reported by Spooner (1976). It is well assessed that carbonates in the shells of mollusks record the Sr isotopic composition of seawater at the time of growth (e.g., Quing et al., 1998) and thus, it is very likely that the Sr isotopic composition of sediments from Group 2 is influenced by shell fragments in the sediments.

The Pb isotopic composition of samples from the two groups (Table 2) is rather homogeneous since no significant statistical

Table 3

Ecological risk index of sediments studied. Statistical differences between samples from Group 1 and 2 are significant ($p < 0.05$).

	Station	Co	Cr	Cu	Ni	Pb	Zn
Group 1	ACA-1	8.9	1.1	62.3	20.6	5.6	2.5
	ACA-2	7.7	1.0	39.3	18.3	3.4	1.7
	ACA-3	7.3	0.9	33.8	17.6	3.2	1.6
Group 2	ACA-4	1.4	0.2	19.3	3.7	1.9	0.5
	ACA-5	4.5	0.6	26.0	10.1	3.2	1.4
	ACA-6	1.3	0.2	11.8	2.7	1.7	0.6
	ACA-7	1.8	0.1	44.9	3.2	8.9	1.3

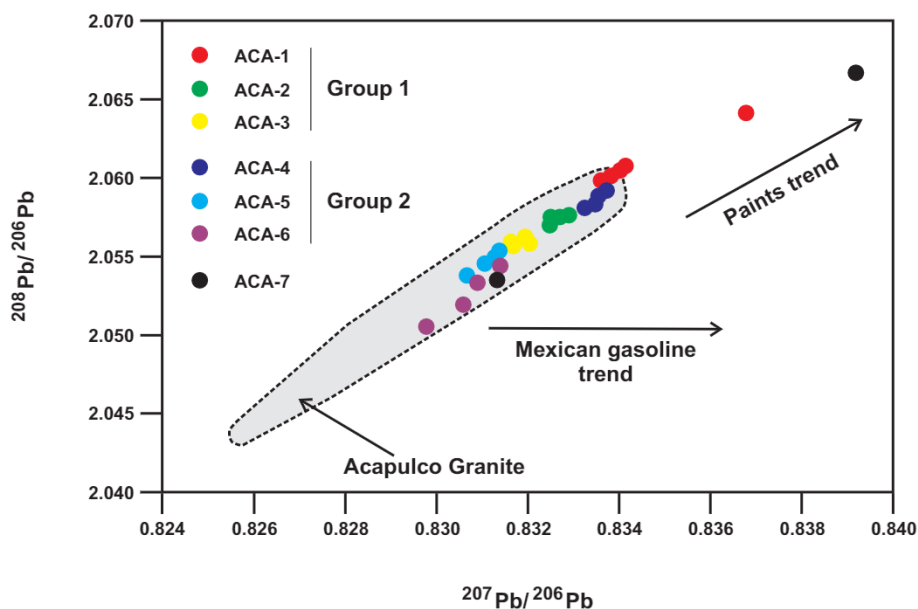


Fig. 8. Biplot of $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ showing the isotopic composition of sediment samples from Acapulco Bay, Guerrero. The field of the isotopic composition of the Acapulco Granite after Hernández-Pineda et al. (2011) is indicated as well as the trends of the isotopic signatures of Mexican gasolines and paints according to data from Martínez et al. (2004) and Morton-Bermea et al. (2011). 2σ external errors of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ are 0.0001 and 0.0003, respectively.

differences ($p > 0.05$) exist between samples from the two defined groups (Fig. S2). However, in the biplot of the radiogenic ratios $^{207}\text{Pb}/^{206}\text{Pb}$ vs $^{208}\text{Pb}/^{206}\text{Pb}$ (Fig. 8), it is evident that samples from Group 1 have a slightly more radiogenic composition and that the two samples from Station ACA-7 have contrasting isotopic signatures. Notwithstanding, as a whole, the Pb isotopic composition in most of the samples matches the isotopic composition reported for the Acapulco Granite (Hernández-Pineda et al., 2011). Some samples from Station ACA-1 and one sample from Station ACA-7 have less radiogenic isotopic compositions indicating the contribution from a different source. These samples follow the trend of the isotopic composition of paints collected by Vázquez-Bahéna et al. (2017), pointing to paints as the most likely source responsible for this trend. No contribution of Mexican gasoline is evident.

3.5. Origin of sediments and TEs

Geomorphological, geohydrological, and geological evidence indicates that the Acapulco Granite is the only lithology shading sediments to Acapulco Bay. This is confirmed by the mineralogical composition of sediments, which matches that of the Acapulco Granite reported by Hernández-Pineda et al. (2011). Indeed, the low concentrations of Ba, Cd, Cr, Mn, and As below the LGBL in all the samples strongly suggest derivation from lithogenic sources. However, the selective enrichment in Ba, Cr, and Mn recorded in samples from Group 1 and to a lesser extent in samples from Station ACA-5 suggests contribution from an additional source of possibly anthropogenic origin. The possibility of a different source of anthropogenic origin is confirmed by the enrichment recorded in Co, Cu, Ni, Pb, V, and Zn in many samples, relative to LGBL. The strong correlation among TEs recorded in sediments but not in the parental lithology further supports contribution from additional sources as the best explanation.

The Sr isotopic composition indicates that the Acapulco Granite is the main source of detritus in Acapulco Bay but that shells of mollusks play a relevant role in the Sr isotopic composition of some samples. There are no studies reporting the presence of TEs in the shells of mollusks from Acapulco Bay so, their contribution to the chemistry of sediments is still unknown. Meanwhile, the Pb isotopic composition of sediments is also consistent with derivation of detritus from the Acapulco Granite but the composition of some samples from Stations ACA-1 and ACA-7 clearly indicate that at least, one additional source is required to explain their variations and point to paints as the most likely source. It is known that ship-bottom paints are a significant source of TEs like Cu, Pb, Zn, Sn, Ni, Cr, and Ba in the marine environment, which affect seawater, bottom sediments, and marine organisms (e.g., Beltinger and Benham, 1970; Baptista-Neto et al., 2005; Rees et al., 2014; Turner et al., 2015; Barnett et al., 2020; Castro et al., 2021).

These interpretations are consistent with the spatial distribution maps of TEs (Fig. 5) which show that the western part of the bay records the highest concentrations of TEs, and it is in this part of the bay where the seaport, yacht club and boating dock are located (Fig. 1). Samples from Station ACA-5, in the western part of the bay, also show enrichment in most TEs, even though of lower proportion than samples of Group 1. There is a Mexican Naval Base located there and there is also a sunken ship close to this Station which also supports the conclusion that ship-bottom paints might be the most likely anthropogenic source of contamination by TEs in the area.

The high concentrations of Pb and, to a lesser extent of Zn, in samples from Station ACA-7, indicate that wastewater could be a significant source of contamination of these elements in agreement with Dimas et al. (2015). The Pb isotopic composition of one sample from this station indicates that paints may be the source of these elements but the existence of an alternate not yet identified source with a similar Pb isotopic signature cannot be ruled out.

3.6. Ecological risk assessment

The ERI evaluates the potential risk that individual TEs pose to soils, sediments, and organisms in terrestrial, coastal, and marine environments. According to Hakanson (1980) an $\text{ERI} < 40$ indicates low ecological risk; $40 \leq \text{ERI} \leq 80$, moderate ecological risk; $80 \leq \text{ERI} \leq 160$, considerable ecological risk; $160 \leq \text{ERI} \leq 320$, high ecological risk; and, $\text{ERI} > 320$, very high ecological risk. Table 3 presents ERI values of seven elements assessed in sediments for each sampling station. With the exception of Cu in Station ACA-1 and ACA-7, all the elements evaluated have ERI values < 40 indicating low ecological risk. In Station ACA-1, Cu has an ERI of 62.3 whereas in Station ACA-7 the ERI is 44.9 which indicates moderate ecological risk. In Station ACA-2, the ERI for Cu is 39.3, very close to reaching a moderate ecological risk level.

4. Conclusions

Several lines of evidence (geology, geomorphology, geohydrology, mineralogy, EF, Sr, and Pb isotopes) indicate that seabed sediments of the world famous tourist site, Acapulco Bay are of local origin and derive almost entirely from the nearby Acapulco Granite. Their total concentrations of Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, Zn, and As are variable and rather low but some are above the LGBL in some sites of the western part of Acapulco Bay and near the Mexican Naval Base in the eastern part of the bay. The EF and Pb isotopes indicate that these TEs derive from the Acapulco Granite parental rock with a slight contribution from an anthropogenic source represented most likely by the ship-bottom paints. Moreover, wastewater could also be a non-negligible source of Pb and Cu and even though many of the analyzed TEs have either station or bulk $\text{EF} > 1$ relative to the LGBL, their ecological risk is low and only Cu represents moderate ecological risk in Stations ACA-1 and ACA-7.

CRediT authorship contribution statement

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Sergio García-Ibañez: Data curation, software, review & editing.

Alicia Sarmiento-Villagrana: Conceptualization, Formal analysis, Methodology, review & editing.

José Luis Aguirre-Noyola: Software, Data curation, review-editing.

Sergio Adrián Salgado-Souto: Conceptualization, Formal analysis, founding acquisition, review-editing.

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Victor Manuel Rosas-Guerrero: Conceptualization, Methodology, review-editing.

Oscar Talavera-Mendoza: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing-original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2021.112797>.

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