Sediment geochemistry of marine shallow-water hydrothermal vents in Mapachitos, bahía Concepción, Baja California peninsula, Mexico

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ABSTRACT

The objective of this study was to determine the influence of marine shallow-water hydrothermal systems in Mapachitos, bahía Concepción, on the composition of surficial sediments in the surrounding area of this bay. The following elements Al, As, Ba, Ca, Cd, Co, Cs, Cu, Fe, Hg, Li, Mn, Mo, Ni, Rb, S, Ti, U, V, Zn, C_{org}, and C_{inorg} were determined in sediment samples. The calculated $CaCO_3$ values in the sediments within some spots of the study area were as high as 90% (with an average of 61 %). The concentration of organic carbon in the sediments was approximately 1%. The total element contents in the sediments were compared with Earth's crustal average, and enrichment factors (EF) were calculated using Al as normalizing element. The results showed that the most of the elements (Ba, Co, Cs, Cu, Fe, Li, Mn, Ni, Rb, Ti, U, V, and Zn) are conservative, with average EF close to unity. Lithium, mollybdenum and uranium were enriched in the sediments with average values of EF between 2 and 10. The highest average EF determined in the study were for the following elements: As, Ca, Cd, and Hg. The average concentrations of potentially toxic elements in the sediments from the Mapachitos vents were 60 mg kg^{-1} for As, and 21849 µg kg^{-1} for Hg. The surface sediments of the adjacent area, however, have low average concentrations for As and Hg: 3.7 mg kg^{-1} and 52 µg kg^{-1}, respectively. Other elements such as Cd (0.9 mg kg^{-1}) and Ca (28.3%) are highly enriched in the sediments of the study area, comparing to their average crustal abundances. The results of Principal Component Analysis allowed to determine three factors which explain 91% of data variance, as well as to differentiate four associations including terrigenous elements, calcareous components, elements of the hydrothermal origin and redox-sensitive elements in the surface sediments off the Mapachitos in the north-western portion of bahía Concepción. Furthermore, the results confirmed the influence of the hydrothermal inputs of some trace elements on the sediments of the area surrounding the vents, in particular As and Hg, and to a lesser extent Al, Fe, and Mn at the venting site.

Key words: marine shallow-water hydrothermal systems, trace elements, marine sediments, bahía Concepción, Baja California Sur, Mexico.

RESUMEN

El objetivo de este estudio fue determinar la influencia de las ventilas hidrotermales someras en Mapachitos, Bahía Concepción, en la composición de los sedimentos superficiales del área circundante de esta bahía. Los siguientes elementos Al, As, Ba, Ca, Cd, Co, Cs, Cu, Fe, Hg, Li, Mn, Mo, Ni, Rb, S, Ti, U, V, Zn, C_{org} y C_{inorg} fueron determinados en muestras de sedimentos. Los valores de $CaCO_3$ calculado en los sedimentos dentro de algunos puntos del área de estudio son tan altos como 90% (con un promedio de

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61%). La concentración de carbono orgánico en los sedimentos fue aproximadamente 1%. Los contenidos totales de los elementos fueron comparados con las abundancias promedios para la corteza continental, y los factores de enriquecimiento (EF) fueron calculados usando Al como elemento normalizador. Los resultados demostraron que la mayoría de los elementos (Ba, Co, Cs, Cu, Fe, Li, Mn, Ni, Rb, Ti, U, V, y Zn) son conservativos, con promedios de EF cercanos a la unidad. El litio, el molibdeno y el uranio fueron enriquecidos en los sedimentos con valores promedios EF entre 2 y 10. Los mayores promedios de EF en el estudio fueron para los siguientes elementos: As, Ca, Cd y Hg. Las concentraciones promedio de elementos potencialmente tóxicos en los sedimentos de las ventilas en Mapachitos, fueron 60 mg kg^{-1} para As y 21849 µg kg^{-1} para Hg. Los sedimentos superficiales del área adyacente, sin embargo, tienen bajas concentraciones promedios para As y Hg: 3.7 mg kg^{-1} y 52 µg kg^{-1}, respectivamente. Otros elementos tales como Cd (0.1 mg kg^{-1}) y Ca (64%) son altamente enriquecidos en los sedimentos del área de estudio, comparando sus abundancias promedios con los de la corteza. Los resultados del Análisis de Componentes Principales permitieron identificar tres factores los cuales explican el 91% de la varianza de los datos, así como también diferenciar algunas asociaciones incluyendo elementos terrígenos, componentes calcáreos, elementos de origen hidrotermal y elementos de reducción-oxidación sensibles en los sedimentos superficiales frente a Mapachitos en la porción noroeste de la bahía Concepción. Además, los resultados confirman la influencia de las agregaciones hidrotermales de algunos elementos traza en el área circundante a las ventilas, en particular, As y Hg, y en grado menor Al, Fe y Mn en el sitio de las ventilas.

Palabras clave: Ventilas hidrotermales someras, elementos traza, sedimentos marinos, bahía Concepción, Baja California Sur, México.

INTRODUCTION

Submarine hydrothermal activity is primarily studied at deep-sea high temperature vent systems and typically includes the characterization of the chemistry of hydrothermal fluids, related geological formations, and the chemical and biological transformations that occur within the hydrothermal plumes (Lilley *et al*., 1995). In the coastal zone this phenomenon is less evident; however, the hydrothermal fluids dispersed in shallow areas are also important sources of trace elements to marine ecosystems (Chester, 2003; Tarasov *et al*., 2005). Shallow hydrothermal systems at the depth less than 200 m are typically associated with tectonic extensions of the crust (Vidal *et al*., 1981). Edmond *et al*. (1979) showed that, for some elements, fluxes of the hydrothermal zone (low-temperature systems) are comparable with, or are greater than, fluxes associated with riverine inputs into the sea. Several studies are focused on the chemical behavior of elements in hydrothermal fluids and formation of minerals (Pichler and Veizer, 1999). The majority of authors agree that marine shallow-water hydrothermal systems could have significant chemical and ecological impacts on surrounding environments. A number of geochemical studies of the hydrothermal influence on shallow ecosystems have already been conducted (Pichler and Veizer, 1999; McCarthy *et al*., 2005; Price and Pichler, 2005). The principal minerals found close to hydrothermal sources are Fe-oxyhydroxides containing potentially toxic elements such as As (Price *et al*., 2007). Off the Pacific coast of Mexico, there are hydrothermal vent systems which are related to the tectonic evolution of the upper crust. This type of hydrothermal systems has been identified in Punta Mita (State of Nayarit), bahía Banderas near Puerto Vallarta (State of Nayarit), Punta Banda (State of Baja California) and bahía Concepción (State of Baja California Sur; Vidal *et al*., 1981; Kostoglodov and Bandy, 1995; Prol-Ledesma, 2003; Prol-Ledesma *et al.,* 2002; Canet *et al.,* 2003, respectively).

Bahía Concepción is located in the central part of Baja California Peninsula (Figure 1). This bay is just south of latitude 26ºN. It is 23 km long, 3 to 5 km wide, and is parallel to the Gulf of California, to which it is connected in the north by narrow mouth. The climate in this region is semi-arid with maximum temperatures during the summer (june to september) of 32.2º C to 35º C and with minimum temperatures of 6.6 ºC during the winter. The rain fall is infrequent (average annual precipitation is approximately 100 to 250 mm) and commonly associated with the occurrence of tropical cyclones during august and september coming from the south (Aschmann, 1959).

The geology around the bay is characterized by a presence of a basement complex of Cretaceous granodiorite and quartz monzonite with small inclusions and roof pendants of older schists. These rocks belong to the Comondú Group and are composed of gabbro stocks with numerous associated diorite dikes and subsequently large tonalite stock (McFall, 1968). The northern portion of the Concepción peninsula is characterized by El Gavilán and Guadalupe Mn deposits, which consist of Mn oxides (pyrulosite, coronadite, and romanechite), along with dolomite, quartz and barite (Camprubí *et al.,* 2008). The granulometry of surface sediments of the bay has been described by Rodríguez-Meza *et al*. (2009) and González-Yajimovich *et al*. (2010). The general geochemical study determined the existence of different associations between sediment components and elements. For example, $CaCO_3$ was associated with Ca, Cd, and Pb (which were probably incorporated during the formation of shells), and C_{org} was associated with several trace elements (Cd, Br, Cu, Hg, Ni, and Zn; likely due to aggregate formations), and finally Ba, Cs, Cu, Fe, Hf,

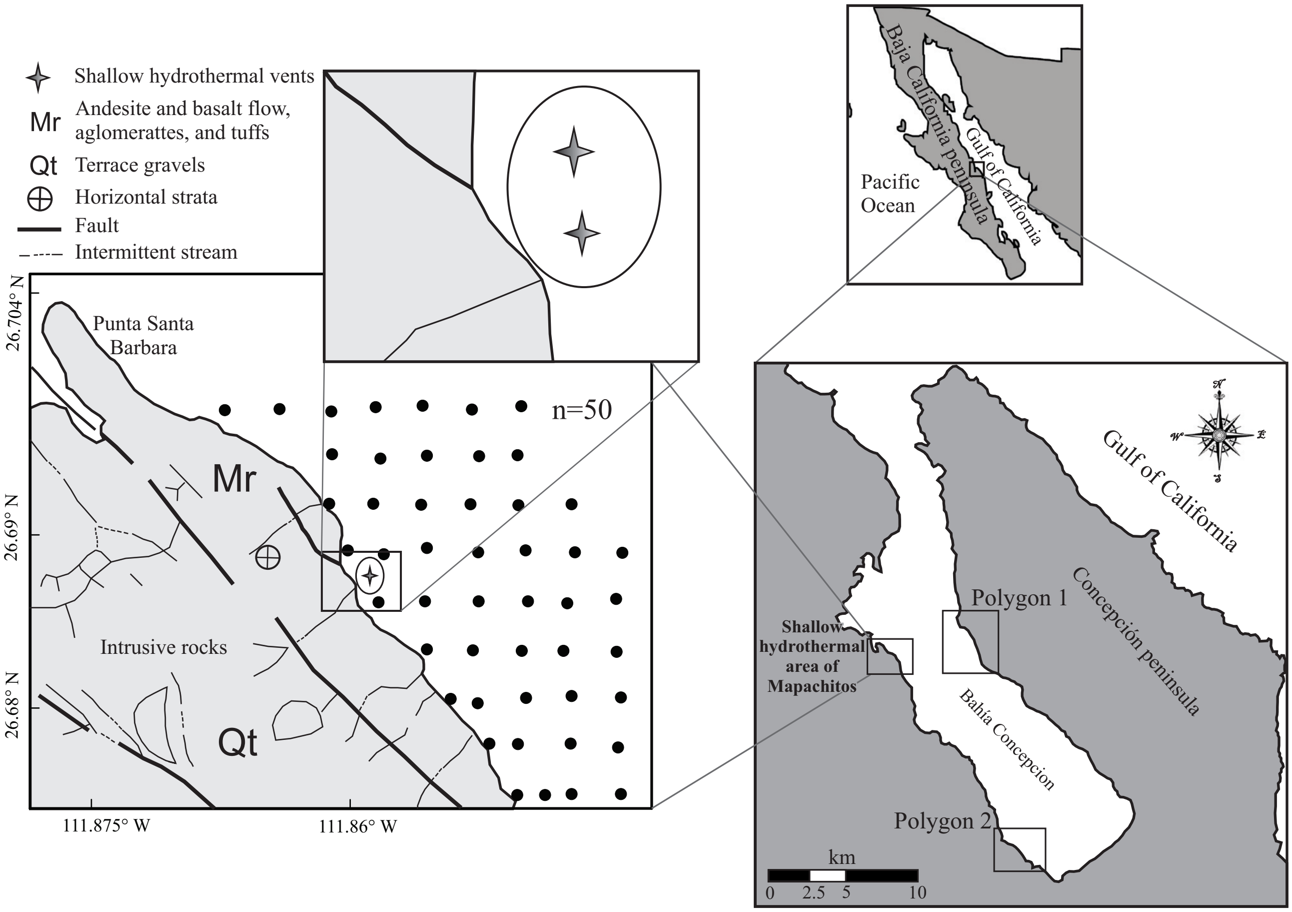

Figure 1. Location of the study area and sampling stations of Mapachitos in bahía Concepción (geologic details taken from McFall, 1968).

lantanides, Rb, Th, U, and Zn were found to be associated with terrigenous sources (Rodríguez-Meza *et al.,* 2009). The water column in bahía Concepción is characterized by stratification in summer but it is well mixed during the other seasons. Sometimes anoxic and hypoxic conditions can appear during periods of strong stratification and high biological productivity (Lechuga-Devezé *et al.,* 2000).

The shallow submarine hydrothermal vent area at Mapachitos, south of cape Santa Bárbara, along the northwest coast of bahía Concepción (Figure 1) has been recently discovered (Forrest *et al.,* 2005). Its appearance and intensity are controlled by the northwest-southeast fractures that cut the volcanic rocks of the Requesón Formation (Comondú Group), revealing altered aureoles, secondary opal, and quartz aggregates (McFall, 1968; Camprubí *et al.,* 2008). The vent system is located near the western coast of the bay between 5 and 15 m water depth with N_2 and CO_2 gas bubbling and minor amounts of CH_4, Ar, He, H_2, C_2H_6, and C_3H_8 (Forrest *et al.,* 2005). This area is situated along a 700 m scarped coast line (Canet and Prol-Ledesma, 2006). The hydrothermal fluids (with temperatures of 60-85°C) are enriched in dissolved As, B, Ba, Ca, Cs, Fe, Hg, HCO_3^-, I, Li, Mn, Si, and Sr (Prol-Ledesma *et al.*, 2004). The chemical and isotopic composition of hydrothermal fluid is explained by the interaction between seawater and thermal-meteoric water end members (Prol-Ledesma *et al.,* 2004; Villanueva-Estrada *et al*., 2005; Villanueva-Estrada *et al.,* 2010). The hydrothermal deposits are formed at marine shallow-water hydrothermal vents by a variety of precipitates, found in veins, breccias, crusts, and stockworks. These deposits consist of Mn-oxides (pyrolusite, coronadite, and romanechite), dolomite, quartz, barite, and opal, as well as stromatolites of Fe oxyhydroxides (characterized by their enrichment in As, Hg, and Sb which is probably due to sorption onto Fe-Mn oxides substrates; Canet *et al.,* 2005). The last evidence of hydrothermal activity in Mapachitos was the high concentration (up to 5000 Bq m^{-3}) of the radioactive gas ^{222}Rn detected in surface seawater over the vents. This concentration was 2-3 orders of magnitude higher than in the seawater of bahía Concepción, not influenced by groundwater, geothermal, nor hydrothermal discharges (Santos *et al*., 2011).

The geochemical and ecological consequences of hydrothermal processes of the Mapachitos vent on the surrounding marine environment are almost unknown, with exception of the increased abundance of the phytoplankton, in particular cyanophyte cells at the point, where hydrothermal fluid discharged in october 2006 (the most abundant species were *Nostoc pruniforme* and *Trichodesmiuni erythraum*; Estradas-Romero *et al*., 2009). The objective of this study was to evaluate the degree of influence of the Mapachitos marine shallow-water hydrothermal vents on the chemical composition of surface sediments in bahía Concepción in the western portion of the Gulf of California.

MATERIALS AND METHODS

Sampling and analysis

Fifty surface sediment samples were collected by scuba divers or by Van Veen grabs in front of the Mapachitos vent site. The location of sampling stations is shown in Figure 1. The collected samples were frozen at -4 °C until they were processed. Subsamples of sediments were dried at 60°C and homogenized in an agate mortar. The contents of As and Hg were determined by atomic absorption spectrophotometry after the generation of As hydride or elementary mercury, respectively (Leal-Acosta *et al*., 2010). The concentration of Al, Ba, Ca, Cd, Co, Cs, Cu, Fe, Li, Mn, Mo, Ni, Rb, Ti, U, V, and Zn in the sediment samples were determined by the combination of ICP-AES and ICP-MS methods after total digestion with concentrated strong acids (HNO_3, HCl, $HClO_4$, and HF) at 130 °C. Sulphur content in sediments was determined also by ICP-AES in solution obtained by decomposition of sediments by alkali fusion with lithium metaborate, then dissolved in 1 M nitric acid (Wei and Haraguchi, 1999). The percent recovery was assessed using certified standard reference materials (PACS-2, MESS-3, and NIST-1646a; Table 1). The accuracy of the analyses for major elements (Fe, Al, and Ti) and trace elements (As, Pb, and Zn) was acceptable (Table 1). The inorganic and organic carbon contents in the sediments were measured by coulometry and infrared spectrophotometric techniques, respectively (Ostermann *et al*., 1990; Goñi *et al*., 2001). The accuracy of the analysis of inorganic and organic carbon was better than 2%. The statistical treatment of data (Principal Component Analysis) was carried out with the program STATISTIC® to determine the possible relationship between elements. The spatial distributions of elements, $CaCO_3$ and C_{org} contents in surface sediments were drawn using SURFER 8.0® software (Surface Mapping System, Golden Software, Inc. 2002) (Rodríguez-Meza *et al*., 2009). The enrichment factors (EFs) for elements were calculated using the Earth's crustal average (Taylor, 1964) with Al as the normalizing element (Salomons and Förstner, 1984):

$$EF = \frac{\left(\frac{El}{Al}\right)_{sample}}{\left(\frac{El}{Al}\right)_{crust}} \tag{1}$$

where EF is the enrichment factor

$\left(\frac{El}{Al}\right)_{Sample}$ is the ratio between trace element and aluminum content in a sediment sample, and

$\left(\frac{El}{Al}\right)_{Crust}$ is the ratio between trace element and aluminum average abundance in the continental crust (Taylor, 1964).

RESULTS

The chemical composition of surface sediments in the vent region of Mapachitos is presented in Table 2, and for the sediments of surrounding area in Table 3. The concentrations of chemical elements (Tables 2 and 3)

Table 1. Measured values, certificated values and % recovery for elements using marine sediments reference materials (MESS-3, PACS-2 and NIST 1646a).

Element	MESS-3			PACS-2			NIST 1646a		
	Measured	Certificated	% recovery	Measured	Certificated	% recovery	Measured	Certificate	% recovery
Al	8.59	8.59	100	6.9	6.62	104	2.8	2.297	122
Ca	1.41	1.47	96	2.18	1.96	111	0.63	0.519	121
Fe	4.4	4.34	101	4.7	4.09	115	2.5	2.008	125
Ti	0.41	0.44	93	0.431	0.443	97	0.484	0.456	106
As	20.8	21.2	98	28.6	26.2	109	8.4	6.23	135
Co	13.6	14.4	95	12.6	11.5	110	5.17	(5)*	103
Cr	108	105	103	115	90.7	127	54.3	40.9	133
Mn	340	324	105	491	440	112	286	234.5	122
Ni	47.3	46.9	101	45.1	39.5	114	25.2	(23)*	110
Pb	22.4	21.1	106	165	183	90	11.5	11.7	98
Sr	136	129	105	260	276	94	73.8	(68)*	109
U	3.7	(4)*	92.5	2.1	(3)*	70	2.03	(2)*	109
V	229	243	94	144	133	108	49.3	44.84	110
Zn	136	159	86	357	364	98	47.5	48.9	97

* Means non-certified average value.

were compared with the average concentrations of surface sediments of two other coastal regions (polygons 1 and 2, Figure 1) in bahía Concepción (Tables 4 and 5), and also to the average abundances in the continental crust (Taylor, 1964).

The concentration of major components (C_{org}, carbonates, and sulphur) in the surrounding area of the hydrothermal vents was inverse between C_{org} and carbonates in sediments. The samples with high percent to carbonates (Figure 2) had low contents of C_{org} (Figure 3). For both components the marine shallow-water hydrothermal area had low contents. The sulphur had a similar spatial distribution as C_{org} probably due to reduction conditions in some stations. The Al and Fe contents, opposite to C_{org} and carbonates, were higher within the vent region and lower in the surrounding area (Figure 4).

The composition of sediments collected in the hydrothermal area is slightly different of those from the adjacent region with respect to trace elements. The As average content in the surface sediments of all areas analyzed in bahía Concepción (Tables 2 to 5), and by Rodríguez-Meza *et al*. (2009) are higher than the continental crustal average (1.8 mg kg^{-1}; Taylor, 1964). The As concentration in the sediments collected from the hydrothermal vents were 115 times higher than the continental average value (Taylor, 1964), and decreases in the sediments of the adjacent zone (Figure 5a). The As average content in the sediments of the polygon 1 and polygon 2 are higher than in the sediments of the area surrounding the vents (Tables 5 and 6), probably because of lower contribution of the calcareous materials in the polygons 1 and polygon 2 sediments. However the enrichment factor for As of the sediments of the area surrounding the vents displays high enrichement because EF calculations eliminate dilution effects of biogenic carbonates.

For mercury, the results were similar. Although the average Hg concentration in sediments of vent area is high (30575 μg kg^{-1}, Table 2), the sediments of adjacent area have low concentrations of this element (range 8-431 μg kg^{-1} and 52 μg kg^{-1} in average, Table 3; Figure 5b).

Barium, Cs, Cu, Mn, Ni, Rb, U and Zn also have slightly higher contents in the sediments collected at the sites of the hydrothermal discharges, than in the sediments of the surrounding area (Tables 2 and 3; Figure 6a). The Ba and Mn accumulation is a common phenomenon for the sediments of the hydrothermal zones. The sediments of hydrothermal vents in Mapachitos have up to 1350 mg kg^{-1} of Mn, while the sediments of the adjacent area and of other two reference areas have lower Mn concentrations (143 mg kg^{-1} in average, Table 3; Figure 6b). This is probably due to the occurrence of most of trace elements in the dissolved fraction in Mapachitos hydrothermal fluids and water column of the adjacent zone. Another factor is the high carbonate concentration in the sediments of the adjacent area (with an

Table 2. Geochemical composition of surficial sediments collected directly in shallow hydrothermal vents (n=5).

Component or element	Min	Max	Average	S. D.	Average abundances in Earth's crust[1]
%					
Ca	5	9	6	2	4.2
$CaCO_3$	0.6	131	33	56	-
C_{org}	0.06	1	0.3	0.4	-
Fe	1	6	4	2	5.6
mg kg^{-1}					
As	14	207	83	92	1.8
Ba	759	1350	606	540	425
Co	6	18	3.8	1.7	25
Cs	1.5	17	9	6	3
Cu	7	54	22	19	55
Hg	60	143062	30575	62974	80
Mn	146	508	350	159	950
Ni	18	63	37	17	75
Rb	7	43	29	19	90
Sc	8	24	17	6	22
U	1	5	3	2	2.7
Zn	22	65	41	18	70

[1] Taylor, 1964

Table 3. Geochemical composition of surficial sediments collected in the surrounding area of marine shallow-water hydrothermal vents (n=50).

Component or element	Min.	Max.	Average	S. D.	Average abundances in Earth's crust[1]
%					
Al	0.1	8	2	1.8	8.23
Ca	8	39	29	7	4.2
$CaCO_3$	13	88	64	18	-
C_{org}	0.05	3.3	1.1	0.8	-
Fe	0.2	4	1	0.2	5.6
S	0.2	1.2	0.4	0.2	-
mg kg^{-1}					
As	0.9	9.2	3.7	2.2	1.8
Ba	11	609	136	108	425
Cd	0.1	4.1	0.1	0.9	0.2
Co	0.5	16.7	3.7	2.9	25
Cs	0.1	2.1	0.7	0.5	3
Cu	1	34	10	7	55
Hg	8	431	52	63	80
Li	3	20	10	4	20
Mn	24	532	143	94	950
Mo	0.2	11.8	2.7	2.5	1.5
Ni	9	49	19	8	75
Rb	0.6	28	7	6	90
Ti	0.01	0.38	0.1	0.1	0.57
U	0.4	3.7	1.7	0.8	2.7
V	4	122	27	18	85
Zn	3	67	20	14	70

[1]Taylor, 1964

Table 4. Geochemical composition of surficial sediments collected in polygon 1 (adjacent to Concepción peninsula) (n=27).

Element	Min	Max	Average	S. D.	Average abundances in Earth's crust[1]
Al	0.6	10	5	2	8.23
As	2	59	18	14	1.8
Ba	58	573	358	134	425
Ca	10	36	19	7	4.2
Cd	0.1	2	0.6	0.6	0.2
Co	2	17	9	4	25
Cs	0.3	6	2.6	1.5	3
Cu	5	91	28	19	55
Fe	0.4	4.4	2.6	1	5.6
Li	4	28	17	6	20
Mn	75	645	362	141	950
Mo	0.2	4.2	1.2	7	1.5
Ni	12	36	19	7	75
Rb	3	44	21	9	90
Ti	0.1	0.8	0.4	0.3	0.57
U	1	3	2	0.5	2.7
V	9	137	62	31	85
Zn	5	65	39	16	70

[1] Taylor, 1964

Table 5. Geochemical composition of surficial sediments collected in polygon 2 (south of bahía Concepción) (n=22).

Element	Min	Max	Average	S. D.	Average abundances in Earth's crust[1]	Unit
Al	0.8	10	5	2	8.23	%
As	0.3	11	4	3	1.8	mg kg^{-1}
Ca	5	34	18	8	4.2	%
Ba	70	924	460	231	425	mg kg^{-1}
Cd	0.1	2.1	0.4	0.5	0.2	mg kg^{-1}
Co	2	21	12	5	25	mg kg^{-1}
Cs	0.1	1	0.5	0.2	3	mg kg^{-1}
Cu	6	55	25	12	55	mg kg^{-1}
Fe	0.8	4.6	2.8	1	5.6	%
Li	6	55	25	12	20	mg kg^{-1}
Mn	107	674	331	143	950	mg kg^{-1}
Mo	0.1	4.6	1.3	1.4	1.5	mg kg^{-1}
Ni	20	107	61	22	75	mg kg^{-1}
Rb	3	29	16	7	90	mg kg^{-1}
Ti	0.05	5	0.3	0.1	0.57	mg kg^{-1}
U	1	6	2	1	2.7	mg kg^{-1}
V	7	105	61	26	85	mg kg^{-1}
Zn	11	75	40	16	70	mg kg^{-1}

[1] Taylor, 1964

average content of 64%; Table 3). The simple dilution effect by carbonates is eliminated by calculating the enrichment factor (EF) of the elements in the sediments.

DISCUSSION

Major components in surface sediments of the Mapachitos vent region

Major element concentrations may provide general information on the processes that control the mineralogical and chemical composition of oceanic sediments (Chester, 2003). The concentrations of major components such as biogenic $CaCO_3$, C_{org}, and terrigenous elements (Al, Fe, and Ti) in sediments collected at the sites of the hydrothermal discharges and in the sediments of the adjacent area are shown in Tables 2 and 3, respectively. The results show that surface sediments in the study area are composed primarily of mixed calcareous bioclast and rock fragments. The average $CaCO_3$ content (64%) in the sediments of the area adjacent to Mapachitos is higher than in sediments of the hydrothermal sites (33%), as well as for the average content of bahía Concepción (41%; Rodríguez-Meza *et al.,* 2009). The presence of shell debris depends on the fertility of the area, which controls primary productivity (Chester, 2003). The C_{org} content in the sediments is typical for nearshore sediments (Chester, 2003). The average content of this component was very low in sediments of hydrothermal area (0.3%; Table 2). The average C_{org} content of sediments of the area adjacent to the vent sites was 1.1%, with a maximum of 3.3%. Similar contents of C_{org} were found in surface sediments of bahía Concepción, with values above 2% in the central part of the bay (Rodríguez-Meza *et al.,* 2009) and the upper Gulf of California (Shumilin *et al*., 2002). The spatial distribution of C_{org} showed major accumulation in the central part of study area (Figure 2). As previously mentioned, both $CaCO_3$ and C_{org}, depend on primary productivity. Although bahía Concepción is an oligotrophic environment, during some seasons mesotrophic conditions predominate, and thus there is an increase in phytoplankton biomass (López-Cortés *et al.*, 2003). Therefore, the primary productivity may be an important source of organic carbon to the water column and sediments. Moreover, the reported hypoxic and anoxic conditions could indicate high fluxes of C_{org} in the study area (Lechuga-Devezé *et al.*, 2000).

The elements Al, Fe, and Ti are considered to be of terrigenous origin due to their high abundance in the Earth's crust (Taylor, 1964). The maximum values of these elements in the sediments from the vent region exceed their average crust abundances (Table 2, Figure 3). The reactions between basalt and seawater are an important source of Fe in low temperature hydrothermal regions. Other elements such as Al and Ti show low interactions of that type (Honnerez, 1981). Canet *et al.* (2005), however, also reported precipitated Al_2O_3 and TiO_2 near the vents. It is likely that the maximum concentrations of Al and Ti in the sediments of the hydrothermal vent region of this study are due to the leaching of the Al^{3+} and Ti^{4+} hydratated cations from the rocks of the hydrothermal channel to the acidic fluids with

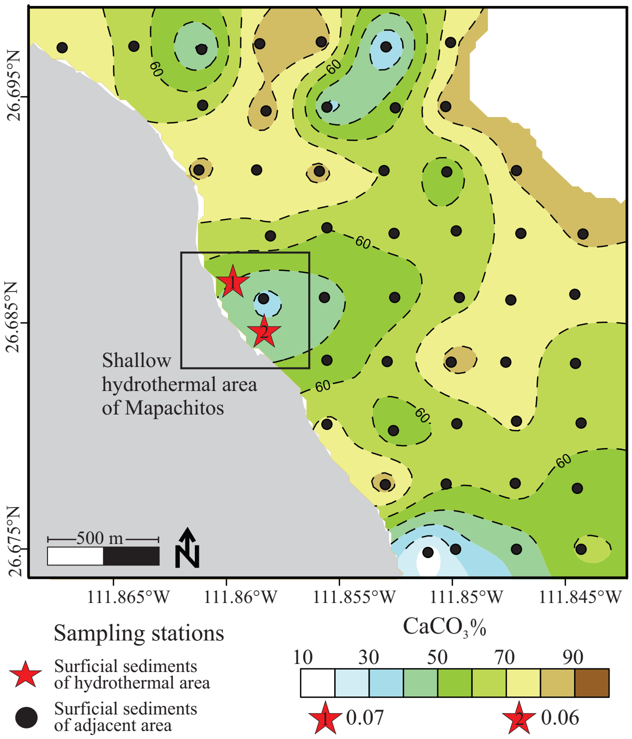

Figure 2. The spatial distribution of the content of $CaCO_3$ (%) in surface sediments of Mapachitos.

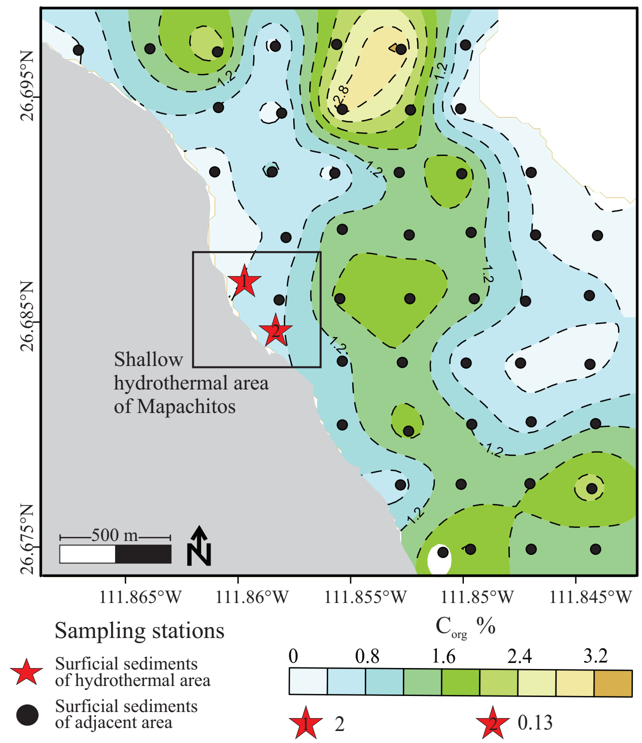

Figure 3. The spatial distribution of organic carbon content (%) in surficial sediments of Mapachitos.

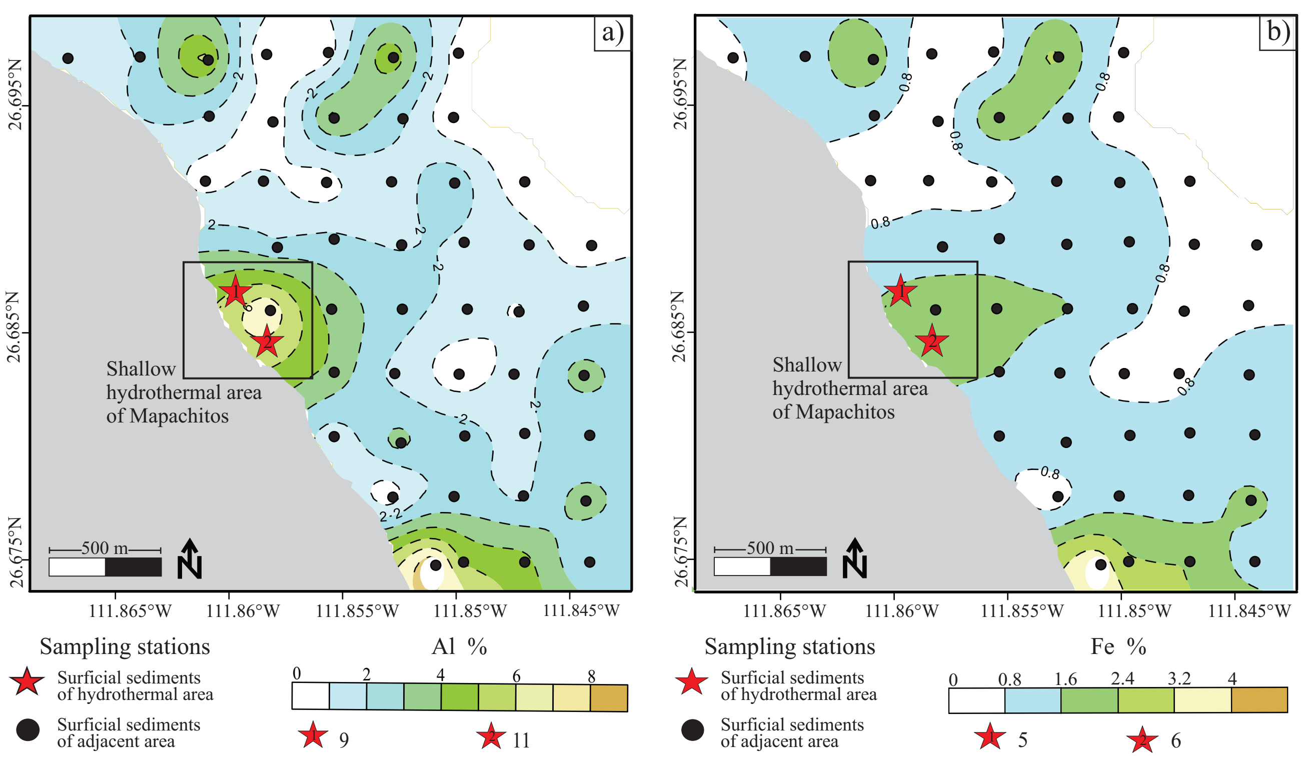

Figure 4. The spatial distribution of Al (A) and Fe (B) content (%) in surficial sediments of Mapachitos.

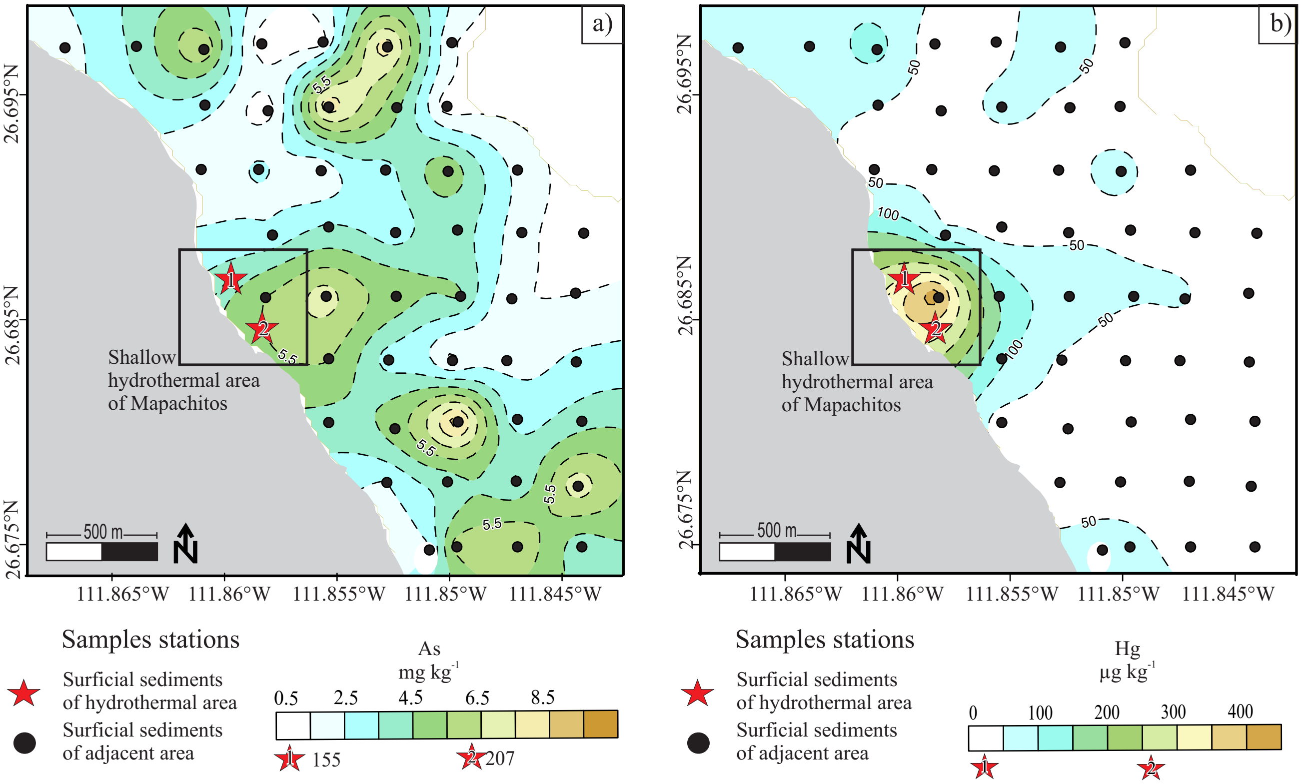

Figure 5. Spatial distribution of the concentration of As (mg kg-1) (a) and Hg (µg kg-1) (b) in surficial sediments of Mapachitos.

subsequent hydrolysis and precipitation of them during the contact of fluids with seawater. The Fe content (5.5%) in sediments near to vents matches with the composition of the precipitates, which were characterized as poorly crystallized Fe-oxyhydroxide and ferrihydrite aggregates with an elevated amount of As, probably accumulated through adsorption (Canet *et al.*, 2005). It is common to find minerals rich in Fe in hydrothermal environments. For example, in Champagne Hot Springs (Dominica, Lesser Antilles) McCarthy *et al.* (2005) reported sediments with a Fe content up to 38.8% with Fe-rich minerals such as hydrous ferric oxides and ferrihydrite. In Tutum bay (Ambite island, Papua New Guinea) precipitated Fe (as Fe_2O_3) of hydrothermal origin also exhibited an elevated content in the sediments (44 to 45%; Price and Pichler *et al.*, 2005). By comparing Mapachitos with these cases, it can be seen that the precipitates formed in the sediments of Mapachitos are of less importance than those formed in Tutum bay.

Sediments in the area adjacent to Mapachitos have Fe content similar to the average in bahía Concepción (3%; Rodríguez-Meza *et al.*, 2009), with a 3.3% average content for the samples collected in Mapachitos. It is possible that the Fe in the sediments adjacent to the vent site is derived from terrestrial erosion and fluvial input. The episodic fluvial contributions, however, are generally low due to the fact that bahía Concepción is located in an arid zone with low precipitation (Mendoza-Salgado *et al.*, 2006), though the influence of sporadic hurricanes may be considered an important source of terrigenous Fe (Silverberg *et al.*, 2007).

Trace elements in surface sediments

The concentrations of trace elements in the surface sediments of the Mapachitos vent site are shown in Table 2. These values are compared with the average concentrations for the surface sediments of bahía Concepción reported by Rodríguez Meza *et al.* (2009) and average crustal abundances (Taylor, 1964). It has been shown by Elderfield (1976) that low temperature weathering of basalt may be a source of Fe and Mn to sea water; in support of this finding, the “wall crust” sampled at the geothermal source in Santipac bight (north of Mapachitos) shows high concentrations of As (635 mg kg^{-1}), Hg (60.3 mg kg^{-1}) and Mn (10.35 %) (Leal-Acosta *et al*., 2010). It is likely that a similar situation is occurring at the Mapachitos vent site.

Arsenic and mercury

The potentially toxic elements As and Hg have been widely studied due to their effects on the marine biota (Clark, 2001). The vent sediments of Mapachitos have a maximum As concentration of 207 mg kg^{-1}, much higher than 1.8 mg kg^{-1} for As average abundance in continental crust (Taylor, 1964). Arsenic frequently exhibits high concentrations in sediments and precipitates in shallow hy-

Table 6. Results of Principal Components Analysis (PCA) applied to chemical composition of sediments of study area

Element	Factor 1	Factor 2	Factor 3
Hg	-0.434	0.442	**0.732**
As	**-0.794**	-0.329	0.283
Li	**-0.964**	-0.075	-0.091
Al	**-0.931**	0.330	0.084
Ca	**0.941**	-0.104	0.049
Cd	**-0.717**	**-0.625**	0.150
V	**-0.964**	0.213	-0.086
Mn	**-0.927**	0.295	-0.170
Fe	**-0.977**	0.182	-0.104
Ni	**-0.976**	0.055	-0.153
Cs	**-0.946**	-0.118	0.204
Cr	**-0.903**	0.158	-0.097
Pb	**-0.981**	0.082	-0.121
Sb	-0.487	0.390	**0.740**
Se	**-0.655**	-0.143	0.037
Co	**-0.923**	0.312	-0.213
Zn	**-0.897**	0.026	-0.134
Rb	**-0.981**	0.052	-0.096
Mo	**-0.743**	**-0.628**	0.123
Ba	**-0.908**	0.398	-0.094
Cu	**-0.973**	-0.036	-0.101
U	**-0.795**	-0.472	0.161
Ti	**-0.975**	0.178	-0.115
S	**-0.751**	**-0.631**	0.062
C_{org}	**-0.851**	-0.447	-0.039
$CaCO_3$	**0.988**	-0.103	-0.0002
Expl. Var	19.840	2.723	1.492
Prp. Totl	0.763	0.103	0.0574

drothermal areas, primarily in Fe oxyhydroxide precipitates (Pichler and Veizer, 1999; Rancourt *et al*., 2001). Generally, As associates with the hydrous ferric oxide fraction. It was shown by traditional sequential leaching technique that 98.6% of As was in this fraction in vent precipitate, and in average of 93.3% in surface sediments of adjacent areas (Price and Pichler, 2005).

In Mapachitos, however, the Fe-rich precipitates are poorly formed as ferrihydrite aggregates with high concentrations of As, which are likely incorporated by adsorption (Canet *et al.,* 2005). It is possible that due to the absence of abundant authigenic Fe-oxyhydroxides, arsenic remains in dissolved form in seawater after it is discharged within the hydrothermal fluids (Prol-Ledesma *et al*., 2004; Leal-Acosta *et al*., 2013). The concentration of dissolved As in vent fluids was 10.4 µmol kg^{-1} compared to the concentration typically found in seawater (0.023 µmol kg^{-1}; Chester, 2003). This can be a reason for high As concentrations up to 640 mg kg^{-1} in the seaweeds *Sargassum sinicola* collected near the vents in Mapachitos (Leal-Acosta *et al*., 2013), because it is well known that the macroalgae accumulate only dissolved trace elements from the seawater. The absence of low contribution of As particulate has as a consequence the low concentration range of As (0.9 – 9.2 mg kg^{-1}) in sediments of the area adjacent to the vent site.

Price and Pichler (2005) showed that in sediments collected in Tutum bay relatively far from a vent site (250 m) the As concentration decrease considerably (from 33200

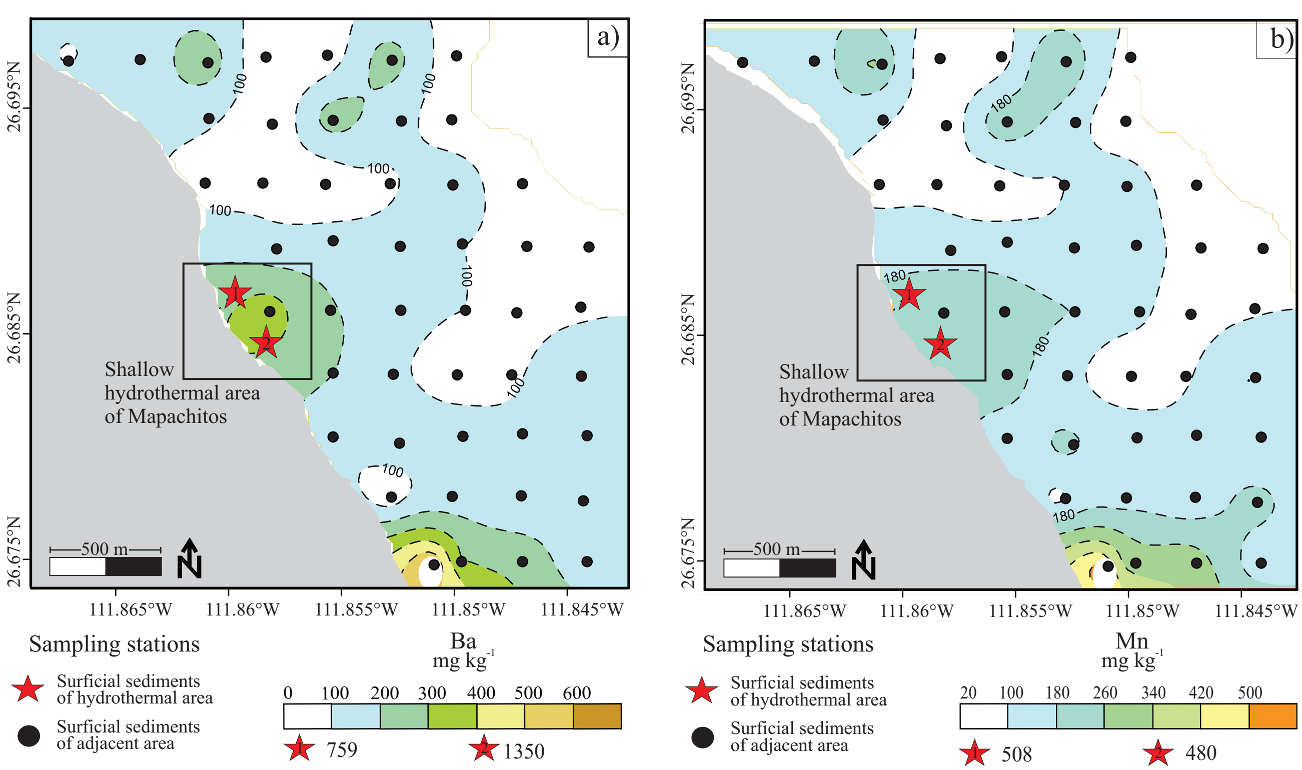

Figure 6. The spatial distribution of the Ba (a) and Mn (b) concentrations (mg kg^{-1}) in surficial sediments of Mapachitos.

mg kg^{-1} at the vent site to 44 mg kg^{-1} on a station away from the vent site).

Mercury also exhibited high concentrations (with a maximum value of 143 mg kg^{-1}) in sediments at the vent site. Canet *et al*. (2005) attributed high Hg concentrations with mineralized cinnabar in the absence of Cl; however, high Hg concentrations do not exclude the possibility of corderoite ($Hg_3S_2Cl_2$) incorporation into mineralized aggregates (Canet *et al.,* 2005). Even the adjacent sediments have a high Hg range (8 – 431 µg kg^{-1}). The affinity of Hg to associate with organic particles such as humic substances has been well documented (Clark, 2001). However, in our study the correlation between C_{org} and Hg is very low (r^2=0.05). In bahía Concepción geothermal processes are an important source of Hg to the environment. The geothermal sediments in Santispac bight have as much as 25.2 mg kg^{-1} of Hg in the sediments of the principal geothermal source (Leal-Acosta *et al*., 2010).

Redox sensitive elements

Dissolved manganese is a well recognized indicator of hydrothermal processes because it is highly enriched in the hydrothermal fluids (Baker *et al.,* 1995). In high temperature, low pH, and reduced hydrothermal fluids, Mn remains in dissolved form, as it occurs at the Juan de Fuca ridge region, where the hydrothermal plume is distributed over 40 km^2 (McConachy and Scott, 1987). In shallow submarine hydrothermal vents the conditions are different: the fluid temperature in Mapachitos is 60ºC and the pH value is about 6.8 (Prol-Ledesma *et al.,* 2004). These conditions should favor the precipitation of Mn oxyhydroxide aggregates (Canet *et al.,* 2005). However, the maximum concentrations of Mn found in the sediments at the vent site and adjacent area, are more than 39 times lower compared with the Earth's crust average abundance (Table 3; Taylor, 1964). The manganese deposits of the Conception peninsula (Camprubí *et al.,* 2008; McFall, 1968) and the fluvial discharge from the peninsula could contribute to Mn accumulation in the surficial sediments. However, this is not the case in the Mapachitos area: the analysis of Mapachitos hydrothermal fluid reveals concentration of Mn up to 648 times higher than the seawater value: 43.14 to 64.8 µM of Mn in hydrothemal fluid versus 0.10 µM of Mn in the sea water (Prol-Ledesma *et al.,* 2004). Manganese remains dissolved likely due to the specific hydrothermal conditions or because of low oxygen concentration in the water of the bay, at least near the venting area (Lechuga-Devezé *et al.,* 2000).

The maximum values of V in the surface sediments of Mapachitos are also found in the sediments collected near the vent site. The pH of hydrothermal fluids is slightly acidic and the environment seawater is probably low in oxygen. The behavior of V, which is inverse to that of Mn, is characterized by the occurrence of the particulate phase of V, which in redox conditions generally forms insoluble aggregates. Nameroff *et al.* (2002) showed the enrichment of V in surface sediments of the Mazatlán shelf, when the O_2 concentration decreases below 10 µM and the sediments became depleted in Mn. Other indicators of redox conditions are U and Mo. Uranium concentration in the study sediments did not exceed the average abundance of the continental crust. However, the Mo concentration was about eight times above its reference value (Taylor, 1964). Both U and Mo have similar spatial distributions as C_{org} and S. The reductive conditions probably allow the formation of authigenic sulfide minerals and precipitation of these elements (Morford and Emerson, 1999). Cadmium spatial distribution is similar to that of organic carbon, which could be explained by the fact that it is a micronutrient for phytoplankton (Bruland *et al.,* 1978). It was demonstrated that bahía Concepción is a pristine environment and the organic carbon source primarily results from the high biological productivity of this marine ecosystem (López-Cortes *et al*., 2003).

Enrichment Factors

The average EF values are shown in Figure 7. It should be noted that the majority of the elements are conservative (do not show any notable enrichment). This is probably a result of the terrigenous input of eroded coastal rocks transported to the study area by wave action, episodic rain discharge, wind transport, and redistributed by tidal and residual currents (Rodríguez-Meza *et al.,* 2009). Due to the high abundance of biogenic calcareous material

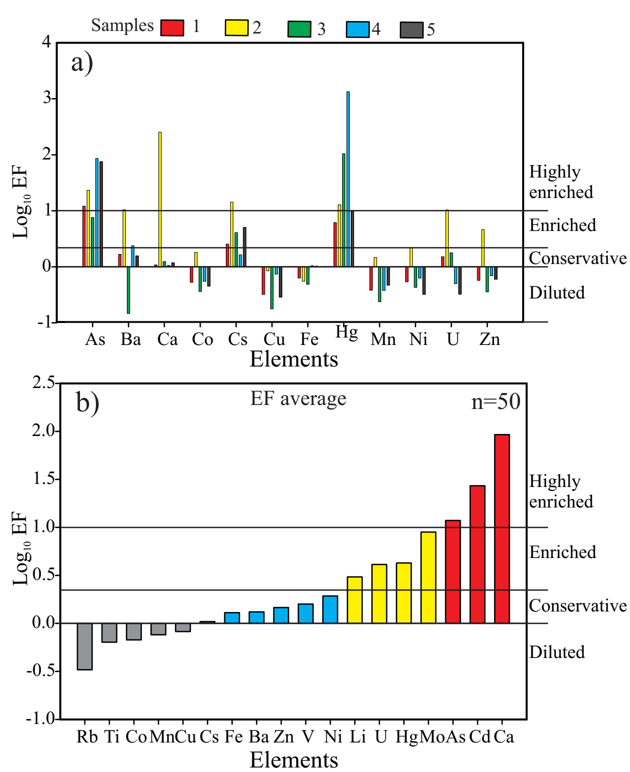

Figure 7. Enrichment factor values by samples collected in vent site (a) and average EF by sediments collected in surrounding area (b).

(primarily rhodolith and shell fragments), according to enrichment factor, Ca was highly enriched (Figure 2b). Three other elements are also enriched: Li, Mo, and U. Molybdenum and U are redox sensitive elements that in reducing conditions have a high affinity towards other particles, including insoluble sulfides of chalcophilic elements (Chester, 2003). Lithium spatial distribution is highly similar to other terrigenous elements (including Al and Ti) and exhibits an inverse distribution to carbonates. Cadmium is also highly enriched in the sediments of Mapachitos. Its high concentration is presumably associated to biologic sources due to the fact, as previously mentioned, that it is a micronutrient for phytoplankton. Moreover, the spatial distribution of Cd was similar to that of C_{org} and S. This is an indication that it is possible that redox processes affect cadmium behavior in Mapachitos surficial sediments. The high EF value for As and Hg was likely caused by hydrothermal sources, since the maximum EF values for both elements were detected near the vent area. Furthermore, the hydrothermal fluid of Mapachitos showed elevated concentrations of dissolved As and Hg (Villanueva-Estrada *et al*., 2010). This can be observed also in the spatial distribution of EF values for As and Hg for the sediments of the study area (Figure 8). The enrichment of As, Ca, and Cd in surface sediments of Mapachitos is probably characteristic for the sediments of the rest of the bay (Rodríguez-Meza *et al.*, 2009). These high values are associated with adjacent deposits which contain minerals rich in manganese oxides with some trace elements (As, Ba, Sr, and V; Camprubí *et al.,* 2008).

Associations of elements in the sediments near the Mapachitos hydrothermal vent site

The statistical treatment of the geochemical data by Principal Components Analysis (PCA) allowed the identification of associations among elements according to their geochemical behavior and potential sources (Rodríguez-Meza *et al*., 2009). The results showed that three factors explain 91% of variance (Table 6). The first factor is important for the terrigenous elements (As, Al, Ba, Ce, Cs, Co, Cu, Fe, Mn, Ni, Rb, Ti, V, and Zn) with high negative scores, and for Ca, $CaCO_3$, and C_{org} with high positive scores. These components explain about 70% of the data variance. This also indicates that terrigenous material supply governs the geochemical composition of sediments in Mapachitos and that the biogenic calcareous material only dilutes them. The second factor displays high positive scores for Mo, U, and S. Since these elements are redox sensitive, this association is likely related to reduction processes, coinciding with the possible formation of authigenic insoluble molybdenum sulfides (Crusius and Thompson, 2000). However, this is a low intensity process in the study area, because the second

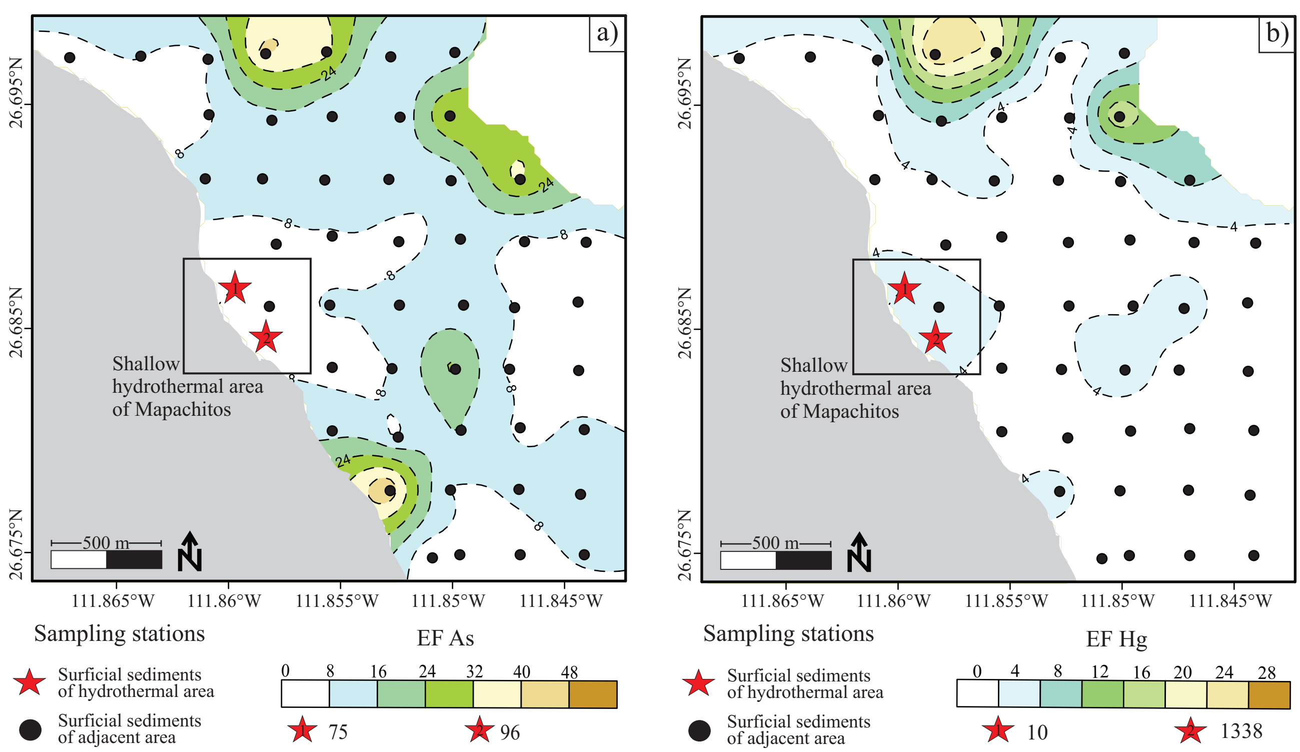

Figure 8. The spatial distribution of EF of As (a), and EF of Hg (b) in surficial sediments of Mapachitos.

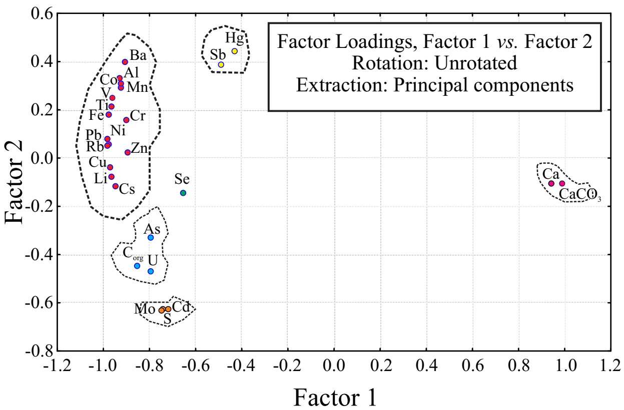

Figure 9. The associations between elements in the surficial sediments of Mapachitos according to Principal Components Analysis (PCA).

factor explains only 15% of the data variance. The third factor corresponds only to 5% of variance and probably represents the hydrothermal influence, which is important for Hg and Sb. The high concentration of both elements is seen only in the vent area, and their distribution is precisely located within the vent site and adjacent zone. The groups of elements are showed graphically in Figure 9.

CONCLUSIONS

The chemical composition of surface sediments in the Mapachitos vent site indicates that they represent primarily the mixture of terrigenous materials of coastal erosion and biogenic calcareous materials, with elevated organic carbon contents in deeper areas. The high concentrations of Cd in sediments could be a product of a biological productivity, due to the fact that this element is a micronutrient for phytoplankton. The statistical results allow the determination of five associations between elements (terrigenous, redox sensitive, biogenic, and micronutrient of hydrothermal origin). The comparison of trace element concentrations in the sediments with Earth's crustal average concentrations showed that only Hg and As concentrations in the sediments near underwater hydrothermal site greatly exceeded their average concentrations in the sediments of the bay and average crustal abundances. The concentrations of Hg and As also showed that a certain dilution by $CaCO_3$ occurs, decreasing the relative concentrations of trace elements. Enrichment factor values showed that the majority of elements are conservative in the surface sediments of Mapachitos. On the contrary, As, Ca, Cd, and Hg are highly enriched indicating that different processes control their geochemical behavior and accumulation in the sediments of the study area. Although hydrothermal As and Hg could represent environmental risk for adjacent marine ecosystem, their high concentration in the sediments is only seen in the vent area, while the other elements (*e.g.* Al, Ba, Fe and Mn) show low hydrothermal influence or its absence.

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