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Environmental Assessment of Aromatic Hydrocarbons-Contaminated Sediments of the Mexican Salina Cruz Bay

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Abstract Concentrations of total aromatic hydrocarbons and extractable organic matter in the water column and sediment were determined in samples collected in the course of the last 20 years from the Salina Cruz Harbor, México, to assess the degree of organic contamination. In sediments, organic compounds accumulate in shallow areas mostly associated with extractable organic matter and fine fractions. Calculated geocumulation index and enrichment factors suggest that contamination could be derived from anthropogenic activities attributed to harbor and ship scrapping activities, as well as transboundary source. Concentration of total aromatic hydrocarbons (as chrysene equivalents) ranged from 0.01 to 534 μg l^{-1} in water, and from 0.10 to 2,160 μg g^{-1} in sediments. Total aromatic concentration of 5 μg g^{-1} is proposed as background concentration.

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1 Introduction

The study of trace organic contaminants in coastal marine environments and especially in estuarine systems is of great importance since these areas are biologically productive and receive considerable pollutant inputs from land-based sources via river runoff and sewage outfalls. Therefore, estuaries act as a transit zone in which contaminants are transported from rivers to oceans (Karichknoff et al. 1979; Kot-Wasik et al. 2004; Means et al. 1980).

Chronic spillages from land-based facilities, vessels, effluent discharges, and accidental spills introduce large amounts of petroleum hydrocarbons to urbanized coastal areas. Depending on the partitioning properties of hydrocarbons, a large fraction adsorbs to suspended particles and accumulates in underlying sediments which becomes long term reservoirs and secondary sources.

The Salina Cruz Bay located at the Ventosa Bay, State of Oaxaca, has undergone considerable development, and consequently urbanization, industrialization. Ship scrapping industry and oil processing in the area has become potential source of contamination to the marine environment.

The Bay receives continental runoff from the Ventosa Estuary System – which runs perpendicular to the coast- and freshwater from the Tehuantepec River flowing into the Ventosa Bay. Municipal waste discharges are also an important source of petroleum hydrocarbons which has been estimated to account roughly for 5% of the total global input per year in other regions of the world (Barrick 1982; Eganhouse and Kaplan 1982; Latimer and Quinn 1996).

Organic pollution from anthropogenic sources to aquatic environments has been an area of great concern. In terms of "unpolluted" intertidal and estuarine sediments, concentrations generally range from sub- μg g^{-1} to approximately 10 μg g^{-1} (Bouloubassi and Saliot 1993; Volkman et al. 1992).

For example, Tolosa et al. (2005) found concentration levels <15 μg g^{-1}, as chrysene equivalents, for bottom sediments of the Gulf of Oman, that were proposed to reflect background levels in this region.

To calculate approximately the severity of oil contamination, a number of indicators have been proposed, among them: (a) high concentrations (>100 μg g^{-1}) of total hydrocarbons; (b) C_{21}–C_{35}*n*-alkanes having no odd over even predominance; (c) complex distributions; (d) an unresolved complex mixture which produces a raised baseline in the gas-chromatogram of the hydrocarbon fraction; (e) biomarkers (Volkman et al. 1992).

Massoud et al. (1996) recognized chronic moderately (50–89 μg g^{-1}) and heavily hydrocarbons polluted areas (266–1,448 μg g^{-1}) in bottom sediments of the Arabian Gulf, concluding that the grain-size distribution and the hydrocarbons content were positively correlated.

Readman et al. (2002) reported concentrations of petroleum hydrocarbons from surface sediment in the Black Sea (2–310 μg g^{-1}) comparable to those encountered in the Mediterranean, but lower than those found by others in highly contaminated areas such as Saudi Arabia Gulf (11–6,900 μg g^{-1}) or Taiwan (869–10,300 μg g^{-1}) (Jeng and Han 1994; Readman et al. 1996).

In the literature scarce information exists concerning the impact of the anthropogenic activities around the coastal waterways and estuarine environments of the Gulf of Tehuantepec.

Botello et al. (1998) reported for the Salina Cruz Bay levels of total polycyclic aromatic hydrocarbons (PAH) of 3.21 μg g^{-1} in the inner port sediments, while in the outer harbor, the concentrations were in the order of 0.22 μg g^{-1}. Moreover, García-Ruelas et al. (2004) reported PAH concentrations in sediments along the coasts of Mexican Pacific within a range of values between 0.2 and 55.3 μg g^{-1}.

High lead enrichment factor in sediment collected during the last two decades at the Salina Cruz Bay was reported in a previous work (González-Macías et al. 2006). Geoaccumulation and enrichment factors for Cr, Cu, Fe, Ni, V, and Zn showed values similar to those found worldwide for sites with analogous industrial activities (Readman et al. 2002).

The major objective of the current study was to estimate the spatial patterns and historical trends in organic contamination of the surface sediments from the inner shelf and coastal areas of the Salina Cruz Harbor. For that purpose, evaluation of total aromatic hydrocarbon (TAH) and extractable organic matter (EOM) in the water column and sediment was assessed for samples collected by our group in the course of the last 20 years.

Normalization was performed for background contributions, with the aim of differentiate any potential site contaminant releases from background sources (both naturally occurring and anthropogenic).

2 Materials and Methods

2.1 Study area

The Salina Cruz (SC) Bay is located at the North side of the Tehuantepec Golf in the Mexican Pacific Ocean (16°06′–16°11′ N and 95°15′–95°07′ W). A high-energy oceanographic condition prevails in the area which generates dispersal of the different inputs (Trasviña et al. 1995). The study area, 30 km along the coast, includes the Salina Cruz city (population 230,000), and harbor.

Figure 1 displays the bathymetry of the Bay, and a schematic diagram of the sample sites at La Ventosa Estuary System, and the Tehuantepec River. The main surface current pattern (indicated by arrows in the Figure) runs east to west. Two seasonal climatic conditions are well defined: rainy from May–September and dry windy seasons from October to April (Chelton et al. 2000).

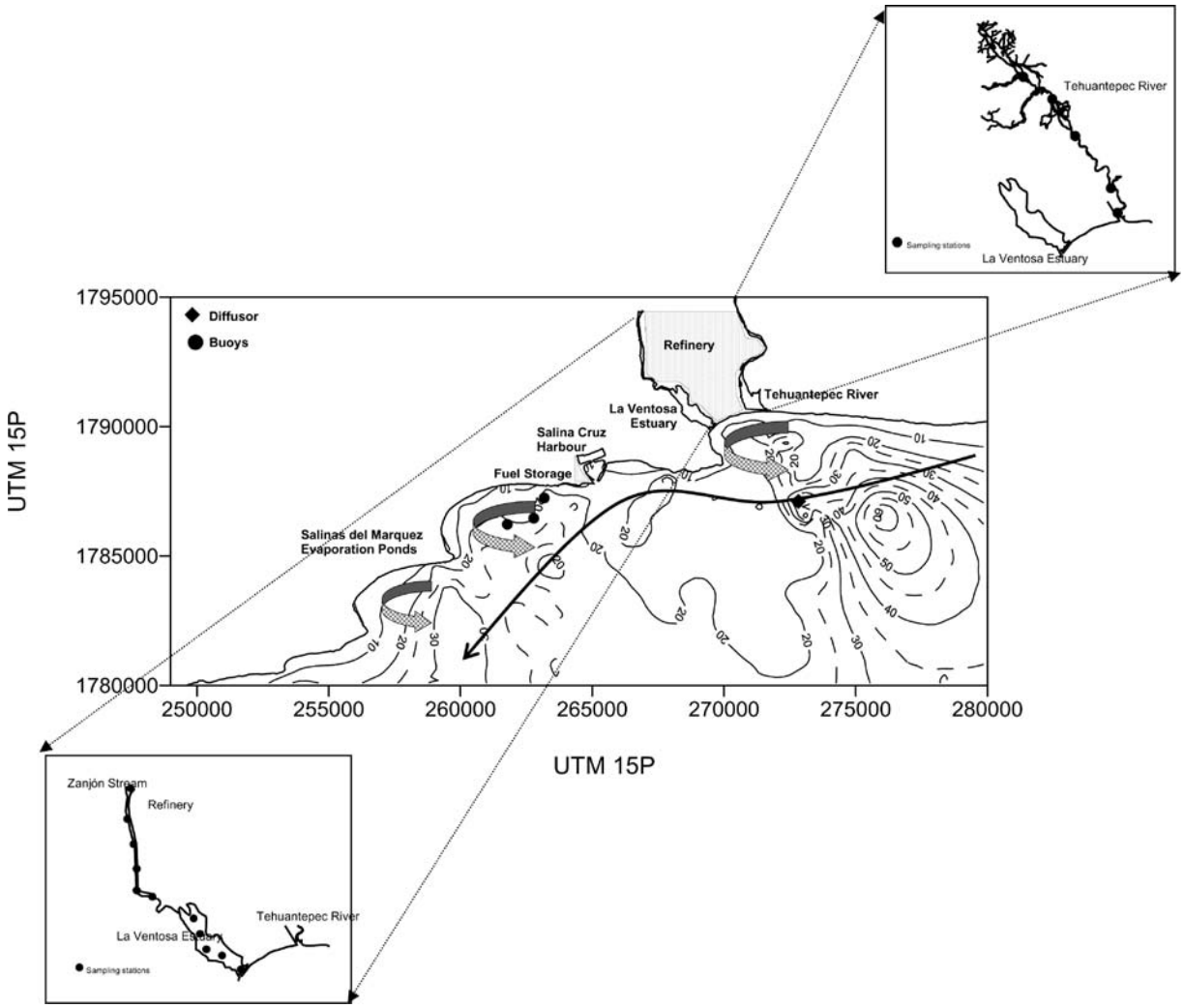


Fig. 1 Map of bathymetry of Salina Cruz Bay and schematic representation of sampling stations in continental water bodies

One of the six major oil processing facilities in the country is located 5 km NE from the harbor with and off-shore outfalls diffusor that discharges the treated sewage effluents to the Bay. The large oil refinery supplies most oil and by-products required by the Pacific Coastal region of Mexico.

Three buoys are located for oil exports in the outer harbor, and the Salinas de Marquez evaporation ponds are sited at 5 km SW of the harbor. The Tehuantepec River release approximately 1,400 million m^3 $year^{-1}$ of water to the Bay, while the La Ventosa Estuarine System discharges are not constant and arise mostly during the rainy seasons.

A total of 365 samples were collected at 24 sites between October 1982, and September 2002 at different seasons of the year, aboard chartered oceanographic vessel. A global positioning system, Micro logic ML-150, was used to locate the sites. Between December 1995 and May 2002 sites sampled, using small boats, accomplished 241 stations from La Ventosa Estuarine System and Tehuantepec River (coded as "Continental").

The location of sites and the number of collected samples for each event at the Ventosa Bay is shown in Table 1. The analytical detection limit (DL) and the number below the DL for sediments and water samples collected in the Salina Cruz Bay are shown in Table 2.

With regards to Continental water bodies, summary data of sediment sampling points are presented in Table 3, combined with the number of samples below the DL. The materials represent the full range of

Table 1 Salina Cruz Bay: sampling period data matrix composition

Sampling event	Date	Season	Geographical limits		
			UTM[a] northing	UTM easting	Number of samples
1	Oct-1982	dry/windy	1,783,063–1,788,875	261,570–273,263	24
2	Dec-1982	dry/windy	1,783,063–1,788,875	261,570–273,263	24
3	Apr-1983	dry/windy	1,783,063–1,788,875	261,570–273,263	24
4	May-1984	rainy	1,779,753–1,788,806	253,817–284,524	24
5	May-1985	rainy	1,784,118–1,788,630	262,397–271,895	3
6	Jul-1985	rainy	1,783,254–1,788,630	262,655–271,895	3
7	Oct-1985	dry/windy	1,782,755–1,783,017	261,820–272,132	3
8	Mar-1988	dry/windy	1,782,260–1,788,639	261,699–272,229	24
9	Jul-1988	rainy	1,782,260–1,788,639	261,699–272,229	24
10	Sep-1988	rainy	1,782,253–1,788,639	261,699–272,229	24
11	Mar-1989	dry/windy	1,782,260–1,788,639	261,699–272,229	24
12	Aug-1990	rainy	1,780,656–1,788,092	259,034–273,727	19
13	Dec-1995	dry/windy	1,784,479–1,790,709	271,079–276,903	18
14	Jul-1997	rainy	1,782,290–1,789,499	262,214–272,821	11
15	Dec-1997	dry/windy	1,783,322–1,787,818	262,214–272,821	2
16	Feb-1998	dry/windy	1,783,322–1,789,470	263,705–272,821	6
17	May-1998	rainy	1,787,133–1,789,954	269,826–274,472	10
18	Jun-1999	rainy	1,783,771–1,787,921	259,487–267,998	9
19	Sep-1999	rainy	1,783,771–1,787,921	259,487–267,998	9
20	Aug-2000	rainy	1,783,708–1,790,158	259,575–273,304	17
21	Aug-2001	rainy	1,779,824–1,790,158	249,579–273,304	21
22	Dec-2001	dry/windy	1,779,824–1,790,158	249,579–273,304	21
23	May-2002	rainy	1,788,699–1,789,833	263,999–264,805	7
24	Sept-2002	rainy	1,779,824–1,790,158	249,579–273,304	14
Total					365

[a] Universal Transverse Mercator Zone 15P

sediment textures, i.e., from fine-grained mud to coarse-grained sand.

2.2 Sampling

A total of 326 one gallon water samples were collected from −50 cm depth in each site using pre-cleaned amber glass bottles with screw cap narrow neck and aluminum foil lid liners. The extraction was performed on site and samples transported back to the laboratory on ice, and stored at 4°C before analysis. A delay between sampling and extraction of greater than 4 h required sampling preservation by the addition of 5 ml HCl.

Samples of surface sediment (10–15 cm depth) from the continental shelf of the SC Bay were collected using a Smith-McIntyre grab. At each site, the top 1–5 cm of surface sediment was carefully removed with a stainless steel spoon. Sediments were homogenized into a stainless steal bowl, and 250 g. later transferred into acid soak/solvents precleaned amber frozen glass jars with aluminum foil-lined lids.

Total suspended solids in water were measured by calculating the difference between the initial and final weight of a standard glass-fiber filter after filtration of a 250 ml well-mixed water sub-sample (APHA 1995).

Grain analysis was performed to establish the particle size distribution of the sediment, which can contribute in defining the origin and deposition environment. Sediments grain size was estimated by a combination of wet sieving (2 mm–63 μm) and pipette analysis (<63 μm) (Folk 1974).

2.3 Extraction

Water samples were extracted three times into 30 ml of spectrophotometer grade carbon tetrachloride, using fresh solvent, and combining all solvent into the volumetric flask. The combined extracts were filtered trough glass fiber wool, transferred to an acid-soak

Table 2 Salina Cruz Bay: number of samples analyzed (*n*SA), detection limits (DL), and number of samples below limit (<DL)

Sampling event	Water variables			Sediment variables					
	Suspended solids (water)	EOM (*w*)[a] DL< 1.0 (μg l^{-1})	TAH (*w*) DL< 0.01 (μg l^{-1})	EOM (*s*)[b] DL< 1.0 (μg g^{-1})	TAH (*s*) DL< 0.1 (μg g^{-1})	Sand %> 63 μm< 2 mm	Silt %	% Clay	[c]Fines (% <63 μm)
	*n*SA	*n*SA	*n*SA/< DL	*n*SA	*n*SA/< DL	*n*SA	*n*SA	*n*SA	*n*SA
1	24	–	–	24	24	24	24	24	24
2	24	23	24	23	23/1	19	19	19	19
3	24	–	24	24	24	–	–	–	–
4	24	24	24	24	24	24	24	–	24
5	3	3	3	3	3	2	2	2	2
6	3	3	3	2	2	2	2	2	2
7	3	2	2	3	3	3	3	3	3
8	–	24	23/1	10	10	–	–	–	–
9	–	24	24	10	9/1	24	24	24	24
10	–	24	24	10	10	24	24	24	24
11	–	24	24	10	10	–	–	–	–
12	–	19	19	19	19	–	–	–	–
13	18	9	9	10	10	–	–	–	–
14	11	11	11	11	11	–	–	–	–
15	2	–	–	1	1/1	–	–	–	–
16	6	6	6	6	6	5	5	5	5
17	10	10	9	9	–	–	–	–	–
18	9	9	9	9	9	9	9	9	9
19	9	9	9	9	3/6	9	9	9	9
20	–	17	17	17	12/5	17	17	17	17
21	21	21	21	21	20/1	21	21	21	21
22	20	20	20	21	17/4	21	21	21	21
23	7	7	7	7	7	7	7	7	7
24	14	14	14	14	14	14	14	14	14
Total Data	232	303	326	297	271	225	225	201	225
Total <DL			1		19				

[a] *w* water

[b] *s* sediments

[c] Silt+clay fractions

precleaned amber glass, and stored at 4°C until analysis. Previous to analysis, extracts were reduced to 2 ml by rotary evaporation under soft flowing nitrogen gas at ambient temperature.

Frozen sediments were dried at 40°C to constant weight, and 50 g of the dry material was digested under reflux with 100 ml of methanol and 3 g of KOH. The non-saponificable fraction was obtained by extracting twice with 25 ml of spectrophotometer grade hexane. The combined extracts were dried with anhydrous sodium sulfate, and reduced to 2 ml by rotary evaporation under soft flowing nitrogen gas at ambient temperature.

2.4 Analysis

Instruments calibrations were performed against pure reference standards; blank samples were analyzed with each sample batch and positive peaks were negligible.

Total EOM was quantified by infrared spectrometry in a FT-IR Thermo Electron Corporation Nicolet Model 710, or a Perkin Elmer UNICAM Model SP-2000, base on the United States Environmental Protection Agency (USEPA) Method 418.1 (Chesler et al. 1976; USEPA 1978, 1996). The acid sulfur pre-treatment was excluded in order to recover all material soluble in CCl_4 (lipids, chlorinated hydrocarbons,

Table 3 Continental water bodies: sampling period data matrix composition: number of samples analyzed (*n*SA), detection limits (DL), and number of samples below limit (*n*<DL)

Sampling event	Date	Season	Geographical limits		*n*SA	Sediment variables					
						Organic *n*SA (*n*<DL)$^{-1}$		Sediment grain size			
			UTM[a] easting	UTM northing		EOM DL<1.0 (μg g^{-1})	TAH DL<0.1 (μg g^{-1})	Sand % >63 μm <2 mm	Silt %	Clay %	[b]Fines % < 63 μm
La Ventosa Estuary											
1	Dec-1995	dry/windy	267,964–269,091	1,790,191–1,791,656	16	6	6/0	–	–	–	–
2	Mar-1996	dry/windy	268,124–269,091	1,790,307–1,791,531	6	6	6/0	–	–	–	–
3	Jul-1997	rainy	266,891–269,091	1,790,307–1,795,708	11	11	11/0	11	11	11	11
4	Nov-1997	dry/windy	266,891–269,091	1,790,307–1,795,708	11	7	7/0	7	7	7	7
5	Feb-1998	dry/windy	266,891–269,091	1,790,307–1,795,708	11	11	10/1	11	11	11	11
6	May-1998	rainy	266,891–269,091	1,790,307–1,795,708	11	8	10/0	10	10	10	10
7	Aug-1998	rainy	266,891–269,091	1,790,307–1,795,708	11	10	10/0	10	10	10	10
8	Aug-2000	rainy	266,891–269,091	1,790,307–1,795,708	11	11	11/0	11	11	11	11
9	Aug-2001	rainy	267,431–269,737	1,789.562–1,793,397	11	11	11/2	11	11	11	11
10	Nov-2001	dry/windy	267,431–267,794	1,791,211–1,793,397	6	6	6/0	6	6	6	6
11	Dec-2001	dry/windy	268,267–269,737	1,789,562–1,790,991	5	5	5/0	5	5	5	5
12	Feb-2002	dry/windy	267,431–269,737	1,789,562–1,793,397	12	12	12/1	–	–	–	–
Total Data					122	104	105	82	82	82	82
Total <DL							3				
Tehuantepec River											
1	Jul-1997	rainy	252,082–268,142	1,799,488–1,815,641	17	17	17/0	17	17	17	17
2	Nov-1997	dry/windy	252,082–268,142	1,799,488–1,815,641	17	17	4/0	5	5	5	5
3	Feb-1998	dry/windy	252,082–268,142	1,799,488–1,815,641	19	17	17/0	16	16	16	16
4	May-1998	rainy	252,082–268,142	1,799,488–1,815,641	19	17	16/0	18	18	18	18
5	Aug-1998	rainy	252,082–268,142	1,799,488–1,815,641	19	17	17/0	17	17	17	17
6	Aug-2001	rainy	227,078–268,081	1,798,677–1,821,959	9	9	9/2	–	–	–	–
7	Dec-2001	dry/windy	227,078–268,081	1,798,677–1,821,959	9	–	–	–	–	–	–
8	May-2002	rainy	227,078–270,733	1,791,119–1,821,959	10	10	10/7	–	–	–	–

Table 3 (continued)

Sampling event	Date	Season	Geographical limits		*n*SA	Sediment variables					
						Organic *n*SA (*n*<DL)$^{-1}$		Sediment grain size			
			UTM[a] easting	UTM northing		EOM DL<1.0 (μg g^{-1})	TAH DL<0.1 (μg g^{-1})	Sand % >63 μm <2 mm	Silt %	Clay %	[b]Fines % < 63 μm
Total Data					119	104	90	73	73	73	73
Total <DL							9				

[a] Universal Transverse Mercator Zone 15P

[b] Silt+Clay Fractions

fatty acids, soaps, fats, waxes), accounting then for the organic and mineral extractable matter.

TAH was evaluated in sub samples of the extracts suspended again in spectrophotometer grade, methylene chloride by fluorescence spectroscopy in Perkin Elmer models MPF-44B, and LS-3B spectrofluorometers (Gordon and Keizer 1976). The sediment samples were maintained frozen until analysis, and for extraction, we followed the methods and recommendations suggested in UNESCO (1982, 1984), and Gold et al. (1987).

The "chrysene equivalent" concentration of TAH was calculated by comparison with the fluorescence of known concentrations of chrysene in hexane (Mzoughi et al. 2005). For EOM analysis, the standard was composed of a mixture of spectrophotometer grade *n*-hexadecane, isooctane, and chlorobenzene.

Appropriate blanks analyzed were always at or below the DL. The precision for multiple analysis, as expressed by the relative standard deviation, was usually <10% for TAH. Recovery rates were determined by spiking duplicate sediments samples with a mixture of standard solution. The relative recoveries of TAH into seawater ranged from 90 to 110%, and in sediments from 70 to 110%.

2.5 Statistical analysis

Statistical analysis of the data was performed with Statistica (1998), and Surfer-8 software to draw the spatial distribution of the TAH (Surfer 2002). SC

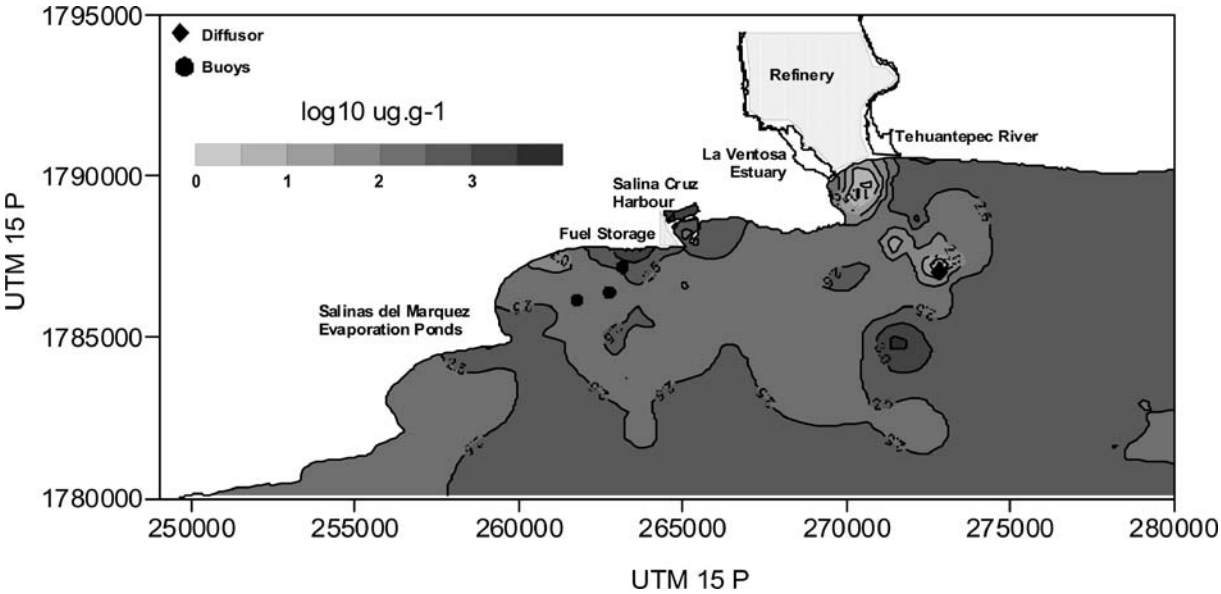


Fig. 2 Map of EOM distribution in surface sediments from Salina Cruz, Bay

Bay data matrix without outliers was employed to perform the *t* Student test, Pearson correlation coefficient, Tukey variance and scatter plots. Outliers are identified as those outside the range of ±2 standard deviations around the mean.

A similar procedure was followed for the raw data of the Continental water bodies (Tehuantepec River and La Ventosa Estuary). Outliers were not removed in order to select typical values to be use in normalization; enrichment factors, and geoaccumulation index calculations, thus the coded Global set is not represented.

Central tendency analysis of the SC Bay raw data was performed grouping the variables in three sets coded as: Dry, Rainy and Global. To evaluate if differences prevail among the data subset, Student's *t* test for independent samples with different variance was performed (Statistica 1998).

According to the Kolmogorov–Sminorv analysis, none of the resultant variables tested (without extreme values) were normally distributed (Massey 1951).

Moreover, Log Normal transformations were applied to correct for non constant variance and the non-normality of the data, ensuring that in the multiple regression test, normality is applied to the residuals, instead of the raw data. Extreme values were kept to evaluate quality of sediments.

The inference method appears to be well-suited to temperature and other environmental reconstructions (Holmström and Erästö 2001).

Therefore, the non-parametric SiZer method described by Chaudhuri and Marron (1999) was applied to assess the statistical significance of the reconstructed organic compounds variation along the time. SiZer enables meaningful statistical inference, while doing exploratory data analysis using statistical smoothing methods.

Consequently, a collection of scatter plot smoothers of the reconstructed TAH concentrations are considered, and inferences about the significance of the TAH trends made along time (Godtliebsen et al. 2003).

2.6 Normalization

In order to differentiate the TAH originating from human activities from those resulting from natural weathering, a 'normalization' technique is usually applied, i.e., the TAH concentrations are normalized to a textural or compositional characteristic of sediments (NFESC 2003).

The organic matter content of sediments, quantified by the concentration of total organic carbon (TOC), is thought to play an important role in the accumulation and release of different micro pollutants. Moreover, some studies of marine sediments have reported a progressive increase in TOC content concomitant with the decrease in grain-size (Karichknoff et al. 1979). Therefore, since grain size <63 μm, tend to co-vary with the EOM; the use of a single normalizer can often represent several underlying geochemical relationships.

First, Pearson coefficients were used to check if a positively correlation exists between normalizer and contaminants of concern. Later TAH were normalized to fine-grained fractions and EOM, and lastly scatter plots were draw to search correlations between the TAH, EOM, and fines fraction.

2.7 Enrichment factors (EF) and index of geoaccumulation (I_{geo})

When comparison of metals content in sediments is performed between different regions, normalization with respect to crusted average is usually applied to determine EF (Nolting et al. 1999; Taylor 1964). Therefore, a TAH enrichment factor was calculated as a quotient of the ratio of the normalizing element (i.e., EOM and percent of fine fractions) by the ratio found in the chosen baseline (i.e., Tehuantepec River continental water bodies which discharge to the Bay):

$$\mathrm{EF} = (\mathrm{TAH}/\mathrm{EOM})_{\text{sediments Bay.}} (\mathrm{TAH}/\mathrm{EOM})^{-1}_{\text{sediments Tehuantepec River.}}$$

According to the work of Zsefer et al. (1996), we associate EFs close to unity with TAH continental origin, while those less than 1.0 would suggests a possible mobilization or depletion of the hydrocarbons. If EF>1.0 is found, then TAH could be of anthropogenic origin, and EF greater than 10 should suggest TAH arising from non-continental runoff sources.

Indexes of TAH geo-accumulation were calculated modifying the Müller formula, originally described for metals (Müller 1979):

$$I_{\text{geo}} = \text{Log2}(M)_i\left[1.5(M)_r\right]^{-1}$$

Where, $(M)_i$=TAH concentration in sediments of the Bay; $(M)_r$=TAH concentration in samples of the Tehuantepec River.

EF and I_{geo} factors were estimated using the geometric means of the 50% EOM, TAH, and % fine grains(<63 μm) data, collected at the Tehuantepec River between 1995 and 2002.

2.8 Partition modeling

The TAH distribution between various phases is frequently described with the use of the distribution coefficient (K_{d}) as:

$$K_{\text{d}} = C_{\text{s}}\left(C_{\text{aq}}\right)^{-1}$$

Table 4 Salina Cruz Bay: organic content and suspended solids in water and grain size sediments

		Water			Sediment		
		Suspended solids	EOM (μg l^{-1})	[a]TAH (μg l^{-1})	Sand % >63 μm <2 mm	Silt%	[a]Clay%
Data with extreme values	Range	13–412	1.1–13300	0.01–534	5.59–99.22	0.14–92.60	0.51–52.23
	Mean	122.53	776.47	16.23	70.22	24.07	6.36
	Std. dev. (No. of samples)	74.94(232)	1735.61 (303)	51.95 (326)	23.17 (225)	21.34 (225)	6.91 (201)
	Coefficient variation %	61.16	223.53	320.03	32.99	88.67	108.66
	95 % Confidence interval	3.32	67.25	1.94	1.04	0.96	0.33
Global data without extreme values	Range	13–251	1.1–4226	0.01–120	24.55–99.22	0.14–66.36	0.51–20.00
	Mean	109.59	454.44	8.37	72.42	21.35	5.50
	Std. dev. (No. of samples)	48.17(221)	732.23 (289)	21.35 (315)	20.46 (217)	17.98 (214)	3.99 (196)
	Coefficient variation %	43.96	161.13	255.09	28.25	84.21	72.58
	95 % Confidence interval	2.19	29.05	0.81	0.94	0.83	0.19
Dry season	Range	41.40–244	7.60–2277	0.01–120	24.55–99.22	0.14–66.36	0.51–13.43
	Mean	101.70	376.14	15.80	70.26	24.46	3.52
	Std. dev. (No. of samples)	39.40(121)	440.82 (108)	29.95 (123)	22.35 (69)	19.77 (67)	1.92 (71)
	Coefficient variation %	38.74	117.20	189.53	31.81	80.83	54.58
	95 % Confidence interval	2.42	28.61	1.82	1.81	1.63	0.15
Rainy season	Range	13–251	1.1–4226	0.1–79.38	25.60–98.32	0.17–65.45	0.88–20.00
	Mean	119.15	501.17	3.61	73.42	19.93	6.63
	Std. dev. (No. of samples)	55.74(100)	858.18 (181)	10.87 (192)	19.51 (148)	16.98 (147)	4.41 (125)
	Coefficient variation 95%	46.79	171.24	301.22	26.57	85.20	66.60
	95 % Confidence interval	3.76	43.02	0.53	1.08	0.94	0.27

[a] *t* Student test; significant difference between seasons

Table 5 Salina Cruz Bay and Continental water bodies: surface sediments organics and fine grains content

		EOM (μg g^{-1})				TAH (μg g^{-1})				[c]Fines (%<63 μm)			
		Salina Cruz Bay	[a]Continental bodies	La Ventosa system	[a]Tehuantepec River	[a]Salina Cruz Bay	Continental bodies	La Ventosa System	Tehuantepec River	Salina Cruz Bay	Continental bodies	La Ventosa System	Tehuantepec River
Total data with extreme values	Range	1.54–10,105	28.65–30,401	28.65–30,401	33.31–1,665	0.10–2,160	0.11–3,094	0.14–3,094	0.11–196.54	0.78–94.41	0.55–94.09	0.75–94.09	0.55–66.59
	Geometric mean (data 50 %)		209.62	255.36	172.76		1.00	2.20	0.63		2.63	16.82	1.18
	Mean	563.90	978.03	[b]1,418.48	[b]469.06	52.84	90.92	[b]151.44	[b]15.46	29.76	26.61	[b]44.13	[b]6.93
	Std. dev. (No. of samples)	1,157.56 (297)	2,646.03 (194)	3,548.97 (104)	343.28 (90)	177.87 (271)	292.58 (182)	382.10 (101)	27.98 (81)	23.18 (225)	27.52 (155)	25.66 (82)	11.72 (73)
	Coefficient variation %	205.28	270.55	250.20	73.18	336.59	321.78	252.31	189.97	77.91	103.42	58.15	168.98
	95 % Confidence interval	45.30	128.14	234.73	24.41	7.29	14.63	25.64	2.10	1.04	1.49	1.91	0.93
Global data without extreme values	Range	1.54–2,553				0.10–365				0.78–75.45			
	Mean	348.73				31.79				27.55			
	Std. dev. (No. of samples)	394.29 (284)				61.73 (265)				20.47 (217)			
	Coefficient variation %	113.07				194.18				74.30			
	95 % Confidence interval	15.78				2.56				0.94			
Dry season	Range	22.80–2,553	28.65–11,803	26.85–11,803	294–1,356	0.12–365	0.11–3,094	0.15–3,094	0.11–197	0.78–75.45	0.55–85.84	2.14–85.84	0.55–26.21
	Geometric mean (data 50 %)		440.67	375.74	628.58		1.24	3.47	0.68		3.02	21.81	1.30

Table 5 (continued)

		EOM (μg g^{-1})				TAH (μg g^{-1})				[c]Fines (%<63 μm)			
		Salina Cruz Bay	[a]Continental bodies	La Ventosa system	[a]Tehuantepec River	[a]Salina Cruz Bay	Continental bodies	La Ventosa System	Tehuantepec River	Salina Cruz Bay	Continental bodies	La Ventosa System	Tehuantepec River
	Mean	318.56	1,126.65	1,310.25	768.19	40.47	139.47	[b]205.51	[b]16.82	29.75	27.24	[b]43.2	[b]5.2
	Std. dev. (No. of samples)	374.54 (126)	1,789.33 (62)	2,181.94 (41)	198.62 (21)	63.56 (126)	433.73 (60)	527.49(39)	44.76 (21)	22.37 (69)	27.70 (50)	26.17 (29)	6.49(21)
	Coefficient variation %	117.57	158.82	166.53	25.86	157.07	310.99	256.67	266.14	75.20	101.70	60.59	12.78
	95 % Confidence interval	22.51	153.27	229.84	29.23	3.82	37.77	56.97	6.59	1.82	2.64	3.28	0.96
Rainy season	Range	1.54–2,372	33.31–30,401	59.94–30,401	33.31–1,665	0.1–360	0.13–1,233	0.14–1,233	0.13–80.07	1.68–74.40	0.58–94.09	0.75–94.09	0.58–66.59
	Geometric mean (data 50 %)		171.52	220.72	142.78		0.92	1.70	0.62		2.47	17.61	1.18
	Mean	372.79	908.22	[b]1,488.92	[b]378.02	23.92	67.05	[b]117.43	[b]14.99	26.53	26.31	[b]44.63	[b]7.63
	Std. dev. (No. of samples)	408.94 (158)	2,967.98 (132)	4,223.74 (63)	426.47 (69)	59.16 (139)	185.94 (122)	250.93(62)	19.54 (60)	19.52 (148)	27.56 (105)	25.61 (53)	13.25 (52)
	Coefficient variation %	109.70	326.79	284.68	86.36	247.26	277.33	213.69	130.37	73.58	104.75	57.38	173.57
	95 % Confidence interval	21.94	174.24	358.92	26.51	3.38	11.35	21.49	1.70	1.08	1.81	2.37	1.24

[a] *t* Student test; significant difference between seasons

[b] *t* Student test; significant difference between sites

[c] Silt+clay fractions

Where, C_s=TAH concentration in the solid phase, C_{aq}=TAH concentration in the dissolved phase.

Sediment organic carbon content and fine fraction are important in controlling the accumulation and release of organic pollutants, therefore K_d coefficient was normalized with these two variables to provide a sediment organic carbon coefficient defined as:

$$K_{oc} = K_d(\mathrm{EOM})^{-1} \text{ or;}$$
$$K_{oc} = K_d(\%\ \text{grains} \leq 63\mu\mathrm{m})^{-1}$$

Table 6 Correlation coefficients between paired water (*w*) and sediment (*s*) variables in SC Bay

Paired variables	*r* (*x*,*y*)	r^2	*t*	*p*	*n*
General					
EOM w(μg l^{-1}) vs. Suspended solids *w*(ppm)	0.3799	0.1443	5.0463	0.0000	153
EOM *w*(μg l^{-1}) vs. TAH *w*(μg l^{-1})	0.2411	0.0581	4.1575	0.0000	282
EOM *w*(μg l^{-1}) vs. Clay (%)	−0.5537	0.3066	−8.4640	0.0000	164
TAH *w*(μg l^{-1}) vs. Suspended solids *w*(ppm)	−0.2691	0.0724	−3.6650	0.0003	174
TAH *w*(μg l^{-1}) vs. TAH *s*(μg g−1)	0.3633	0.1320	5.8619	0.0000	228
TAH *w*(μg l^{-1}) vs. Sand (%)	−0.1654	0.0274	−2.2941	0.0229	189
TAH *w*(μg l^{-1}) vs. Silt (%)	0.1910	0.0365	2.6466	0.0088	187
TAH *w*(μg l^{-1}) vs. Fine (%)	0.1669	0.0278	2.3145	0.0217	189
EOM *s*(μg g^{-1}) vs. TAH *s*(μg g^{-1})	0.2392	0.0572	3.9270	0.0001	256
EOM *s*(μg g^{-1}) vs. Sand (%)	−0.3324	0.1105	−4.7020	0.0000	180
EOM *s*(μg g^{-1}) vs. Silt (%)	0.3239	0.1049	4.5285	0.0000	177
EOM *s*(μg g^{-1}) vs. Clay (%)	0.2264	0.0513	2.9221	0.0040	160
EOM *s*(μg g^{-1}) vs. Fine (%)	0.3319	0.1102	4.6946	0.0000	180
TAH *s*(μg g^{-1}) vs. Suspended solids *w*(ppm)	−0.3407	0.1160	−4.9282	0.0000	187
TAH *s*(μg g^{-1}) vs. Sand (%)	−0.4488	0.2014	−6.5286	0.0000	171
TAH *s*(μg g^{-1}) vs. Silt (%)	0.4501	0.2026	6.4941	0.0000	168
TAH *s*(μg.g^{-1}) vs. Fine (%)	0.4489	0.2016	6.5315	0.0000	171
TAH Dry season					
TAH *w*(μg l^{-1}) vs. Suspended solids *w*(ppm)	−0.4923	0.2424	−4.8658	0.0000	76
TAH *w*(μg l^{-1}) vs. EOM *w*(μg l^{-1})	0.6141	0.3771	7.8580	0.0000	104
TAH *w*(μg l^{-1}) vs. EOM *s*(μg g^{-1})	−0.2548	0.0649	−2.4717	0.0154	90
TAH *w*(μg l^{-1}) vs. TAH *s*(μg g^{-1})	0.3126	0.0977	3.0867	0.0027	90
TAH *w*(μg l^{-1}) vs. Sand (%)	−0.3103	0.0963	−2.0900	0.0429	43
TAH *w*(μg l^{-1}) vs. Silt (%)	0.3531	0.1247	2.3872	0.0218	42
TAH *w*(μg l^{-1}) vs. Fine (%)	0.3103	0.0963	2.0901	0.0429	43
TAH *s*(μg g^{-1}) vs. Suspended solids *w*(ppm)	−0.3888	0.1512	−4.2833	0.0000	105
TAH *s*(μg g^{-1}) vs. EOM *s*(μg g^{-1})	0.4169	0.1738	5.0249	0.0000	122
TAH *s*(μg g^{-1}) vs. Sand (%)	−0.5362	0.2875	−4.9610	0.0000	63
TAH *s*(μg g^{-1}) vs. Silt (%)	0.5228	0.2733	4.7111	0.0000	61
TAH *s*(μg g^{-1}) vs. Clay (%)	0.2617	0.0685	2.1526	0.0352	65
TAH *s*(μg g^{-1}) vs. Fine (%)	0.5357	0.2870	4.9550	0.0000	63
TAH Rainy season					
TAH *w*(μg l^{-1}) vs. Suspended solids *w*(ppm)	−0.3480	0.1211	−3.6373	0.0004	98
TAH *w*(μg l^{-1}) vs. TAH *s*(μg g^{-1})	0.2936	0.0862	3.5812	0.0005	138
TAH *w*(μg l^{-1}) vs. Clay (%)	0.4218	0.1779	5.1383	0.0000	124
TAH *s*(μg g^{-1}) vs. Suspended solids *w*(ppm)	−0.3173	0.1007	−2.9930	0.0037	82
TAH *s*(μg g^{-1}) vs. EOM *w*(μg l^{-1})	−0.2003	0.0401	−2.3225	0.0218	131
TAH *s*(μg g^{-1}) vs. EOM *s*(μg g^{-1})	0.2269	0.0515	2.6769	0.0084	134
TAH *s*(μg g^{-1}) vs. Sand (%)	−0.4032	0.1626	−4.5362	0.0000	108
TAH *s*(μg g^{-1}) vs. Silt (%)	0.3983	0.1586	4.4496	0.0000	107
TAH *s*(μg g^{-1}) vs. Fine (%)	0.4029	0.1623	4.5319	0.0000	108

r^2 at 95% confidence level, significance at p=<0.05

w water; *s* sediment

Table 7 Correlation coefficients between paired sediment variables in Continental water bodies

Paired variables	r (x,y)	r^2	t	p	n	r (x,y)	r^2	t	p	n	r (x,y)	r^2	t	p	n
	Continental water bodies					La Ventosa Estuary System					Tehuantepec River				
General															
EOM s(μg g^{-1}) vs. TAH s(μg g^{-1})	0.6562	0.4307	11.6035	0.0000	180	0.6665	0.4442	8.8041	0.0000	99	0.5545	0.3075	5.9221	0.0000	81
EOM s(μg g^{-1}) vs. Silt (%)	0.2032	0.0413	2.5241	0.0127	150										
EOM s(μg g^{-1}) vs. Fine (%)	0.1795	0.0322	2.2204	0.0279	150										
TAH s(μg g^{-1}) vs. Silt (%)	0.2675	0.0716	3.3549	0.0010	148										
TAH s(μg g^{-1}) vs. Clay (%)	0.2483	0.0617	3.0973	0.0023	148										
TAH s(μg g^{-1}) vs. Fine (%)	0.2739	0.0750	3.4410	0.0008	148										
TAH Dry season															
TAH s(μg g^{-1}) vs. EOM s(μg g^{-1})	0.5206	0.2710	4.6437	0.0000	60	0.6322	0.3997	4.9631	0.0000	39	0.5509	0.3035	2.8771	0.0097	21
TAH s(μg g^{-1})vs. Silt (%)	0.3120	0.0973	2.2027	0.0328	47										
TAH s(μg g^{-1}) vs. Clay (%)	0.3321	0.1103	2.3617	0.0226	47										
TAH s(μg g^{-1}) vs. Fine (%)	0.3398	0.1154	2.4234	0.0195	47										
TAH Rainy season															
TAH s(μg g^{-1}) vs. EOM s(μg g^{-1})	0.7255	0.5264	11.4525	0.0000	120	0.6907	0.4771	7.2739	0.0000	60	0.7489	0.5609	8.6072	0.0000	60
TAH s(μg g^{-1})vs. Silt (%)	0.2487	0.0619	2.5548	0.0121	101										
TAH s(μg g^{-1}) vs. Clay (%)	0.2044	0.0418	2.0772	0.0404	101										
TAH s(μg g^{-1}) vs. Fine (%)	0.2433	0.0592	2.4960	0.0142	101										

r^2 at 95% C.I., significance at p=<0.05

3 Results and Discussion

3.1 Physical and chemical characterization

The historical accumulated data were used to produce a map portraying the EOM concentrations of the Salina Cruz Bay as shown in Fig. 2. The color codes used are intended to illustrate the distributional concentration patterns presented as $\log_{10}$ μg g^{-1}.

The observed pattern suggests that a high level of organic matter was deposited offshore, towards lower energy areas, where high proportion of fine sediments was previously reported (González-Macías et al. 2006), while in near shore the lower concentrations suggest that EOM might be related with continental run off.

The statistical analysis results of TAH, EOM and total suspended solids in water for the SC Bay,

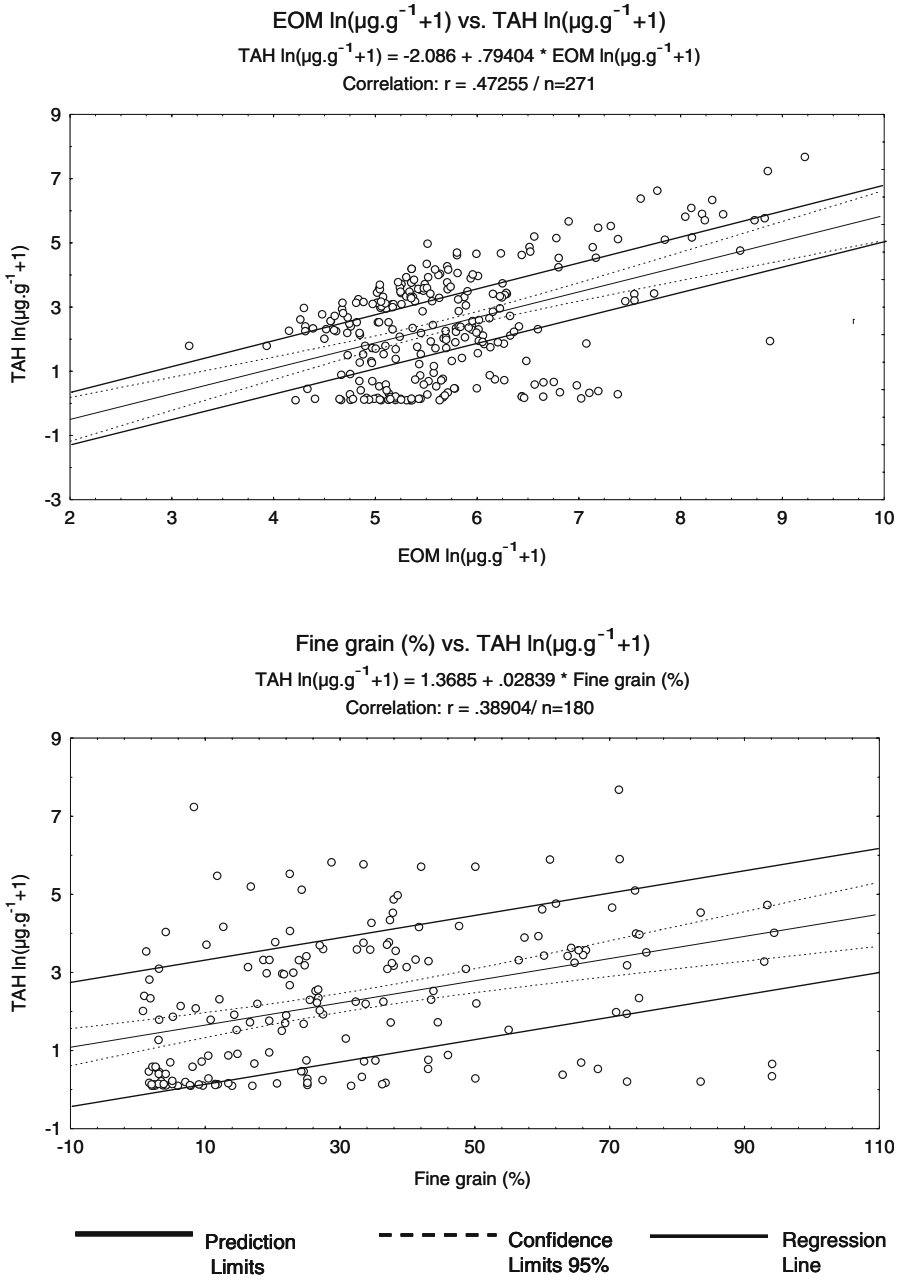


Fig. 3 Scatter plot showing relationship between concentration of *EOM* and *fine-grained fractions* (<63 μm) in surface sediments from Salina Cruz Bay

along with the original matrix including outliers, and global data set are shown in Table 4. Moreover, the Table includes sediments grain size distribution that prevails during the two dominant climatic periods in the Bay.

Mean average TAH values in water ranged from 0.01 to 120 μg l^{-1}. Student *t* test for independent samples, with different variance was tested for Dry (*D*) and Rainy (*R*) season sets.

The means are significantly different for TAH in water (t=35.8343, df=298, p=0.0000, nD=108, nR=192) and for the grain fractions: i.e. clay (t=−5.6264, df=194, p=0.0000, nD=71, nR=125).

Mean average values of TAH, EOM, and percentage fine grains distribution in sediments of the SC Bay and Continental water bodies are presented in Table 5 for the two dominant climatic periods of the area. TAH values from SC Bay vary between 0.10 to 2,160 μg g^{-1} while in Continental water bodies the mean average vary between 0.11 to 3,094 μg g^{-1}.

Student *t* test for independent samples showed significantly differences in TAH concentrations for SC Bay sediments between seasons (t=16.1520, df=316, p=0.0000, nD=126, nR=192), while no seasonal differences were found for TAH and fine fractions in Continental water bodies sets, although differences were found between La Ventosa Estuary system and the Tehuantepec River.

EOM values in sediments from Salina Cruz Bay vary from 1.54 to 10,105.0 μg g^{-1}, and from 28.65 to 30,401.0 μg g^{-1} in Continental water bodies. No differences were found during dry season for EOM between La Ventosa Estuary System (*V*) and Tehuantepec River (*T*) (t=−0.0798, df=60, p=0.9367, $n\boldsymbol{V}$=42, $n\boldsymbol{T}$=21), there were no seasonal differences either in Salina Cruz Bay.

There are EOM seasonal differences Dry (*D*) and Rainy (*R*) in Tehuantepec river (t =13.0877, df=57, p=0.0000, nD=21, nR=38) and Continental water bodies analyzed together (t=9.3658, df=161, p=0.0000, nD=62, nR=101).

EOM shows differences also between La Ventosa Estuary System and Tehuantepec River during rainy season (t=3.6884, df=192, p=0.0002, nV=104, nT=90) (t=5.9800, df=99, p=0.0000, nV=63, nT=38).

Significantly different coefficients between paired water and sediment variables were found in the SC Bay, see Table 6. TAH in water and sediments relate positive each other and both relate negative to suspended solids in water and sands.

TAH content in water relates with EOM in water and with the fine fractions of sediment while in sediments TAH content is related with EOM and fine particles. These patterns are present in both seasons, excluding the pair TAH in water vs. EOM in water, which is not followed during rainy season.

Table 7 shows grain sizes and TAH correlation coefficients obtained for significant paired variables from Continental water bodies. TAH relates positively with EOM, and fine grains, in both seasons when Continental body waters are considered together. If separate correlations for La Ventosa Estuary and the River are made, TAH correlates positive only with EOM in both seasons.

Briefly, EOM concentrations in Tehuantepec River are influenced by seasonal conditions with high values during dry season when water flow decreases. Pearson coefficients suggest that TAH are associated preferentially to EOM instead to fine particles, and don't settle down in the sediment.

TAH and fine grains in continental water bodies are not influenced by seasonal conditions, low concentrations of them are present in the River, accumulating in the sediments of the Bay during dry season. Regression analyses suggest that TAH in water and sediments compartments of Salina Cruz Bay are mostly associated to EOM and sediment fine fractions.

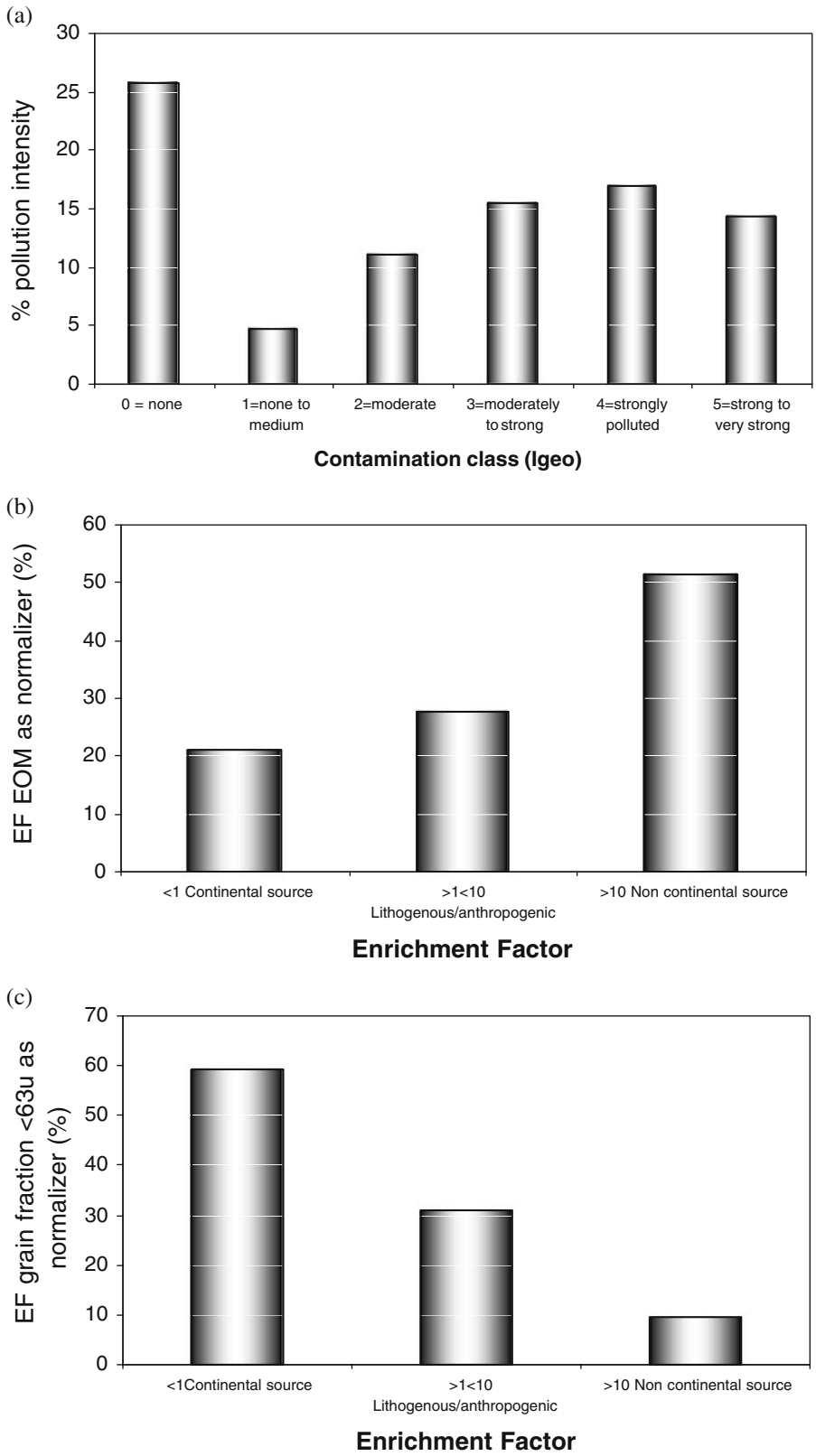
3.2 Normalization with EOM and fine-grained fraction <63 μm.

Scatter plots of TAH concentrations vs. EOM and fine-grained fractions, found in the sediments of SC Bay are shown in Fig. 3. Likewise, correlation values at the 95% probability level, defined as ± the standard error of estimate (n=>30), could constitute the naturally occurring background of the SC Bay. Samples where TAH plot is above background relationship have an additional source contribution not present in the background samples.

3.3 TAH enrichment factors and geo-accumulation index of the sediment

Figure 4a shows calculated I_{geo} factors while Fig. 4b and c illustrate the enrichment factors using EOM and grain fraction as normalizer respectively.

Fig. 4 **a** Geoaccumulation index (I_{geo}). Normalization results of enrichment factors: **b** using Tehuantepec River EOM, and **c** using fines fractions <63 μm



Approximately 70% of I_{geo} values range from moderately to strong contaminated classes. According to Müller (1979), concentrations of contaminants may be separated into ranges from 0 to 6 (0=none, 1=none to medium, 2=moderate, 3=moderately to strong, 4=strongly polluted, 5=strong to very strong, 6=very strong). The higher range expresses a total aromatic hydrocarbon concentration 100 times greater than that of the reference ambient.

Total aromatic hydrocarbons are depleted with respect to continental baseline in view that 21% of TAH data are below the baseline concentration (EF=<1) when normalized with respect to EOM (Fig. 4b) and 60% if fine grains size is employed (Fig. 4c). Thirty % of the data in Fig. 4b and c are above the baseline (EF=>1≤10) using either normalizer, pointed out to an enrichment of lithogenous or anthropogenic origin.

Pertaining to the non continental sources (EF≥10), 50% of the data shown in Fig. 4b are above the baseline concentration when EOM is the normalizer, and 10% of data are also above if normalized with respect to grain size fraction, Fig. 4c.

Organic carbon and grain size are employed in particular cases as geochemical normalizers. They will often shows strong relationships with site contaminants, and to varying degrees they covary together with sediment texture. This seems to be the case of the Salina Cruz, Bay site, but not of the Tehuantepec River, where the only significant positive relationship is observed between TAH and EOM (Tables 6 and 7).

View that both normalizers are positively correlated with TAH in the Bay (Table 6), and no seasonal differences influence the results with grain size fraction of the Tehuantepec River (Table 5), differences can be explained taking into account that each baseline represents unlike TAH sources, in accordance with Fig. 3 in which higher concentrations above the background using EOM as normalizer are found.

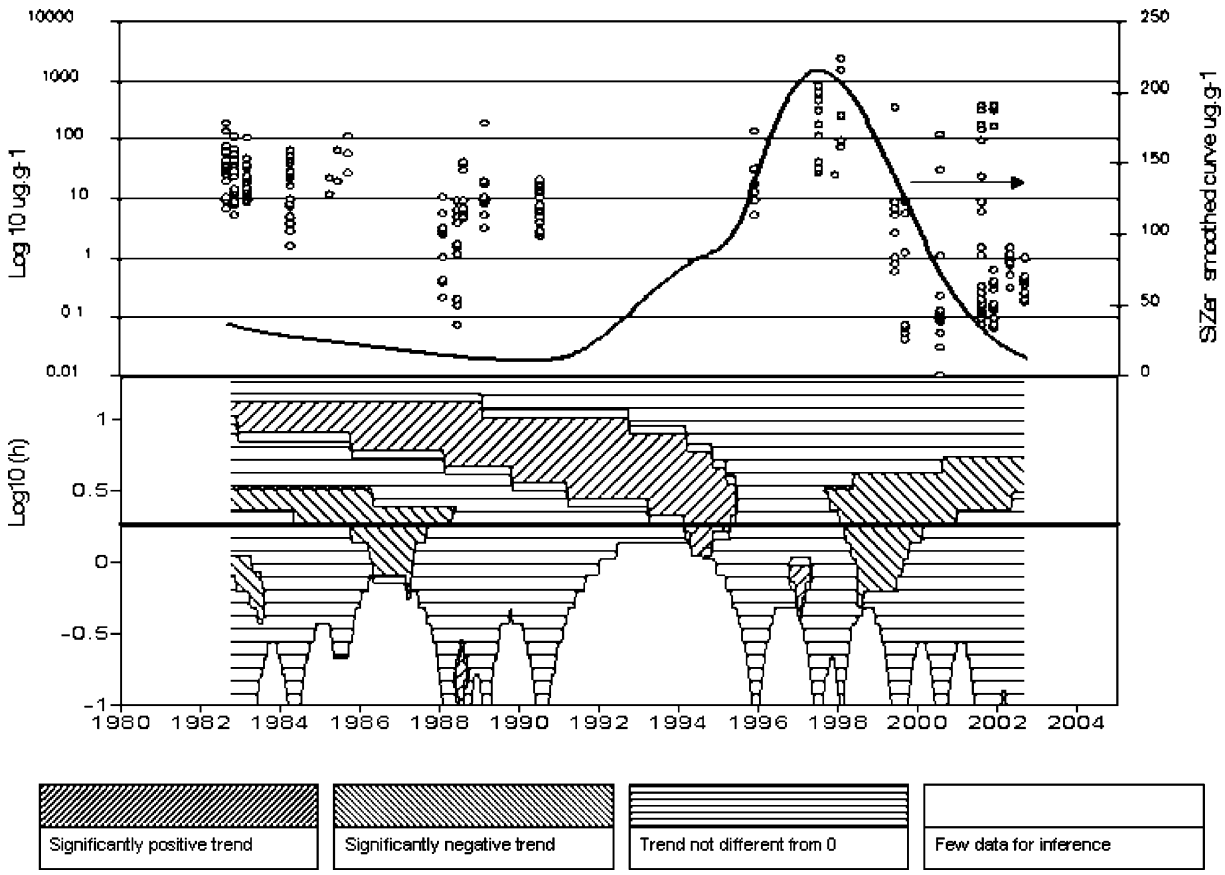


Fig. 5 Temporal trends of TAH concentrations in surface sediments from Salina Cruz Bay

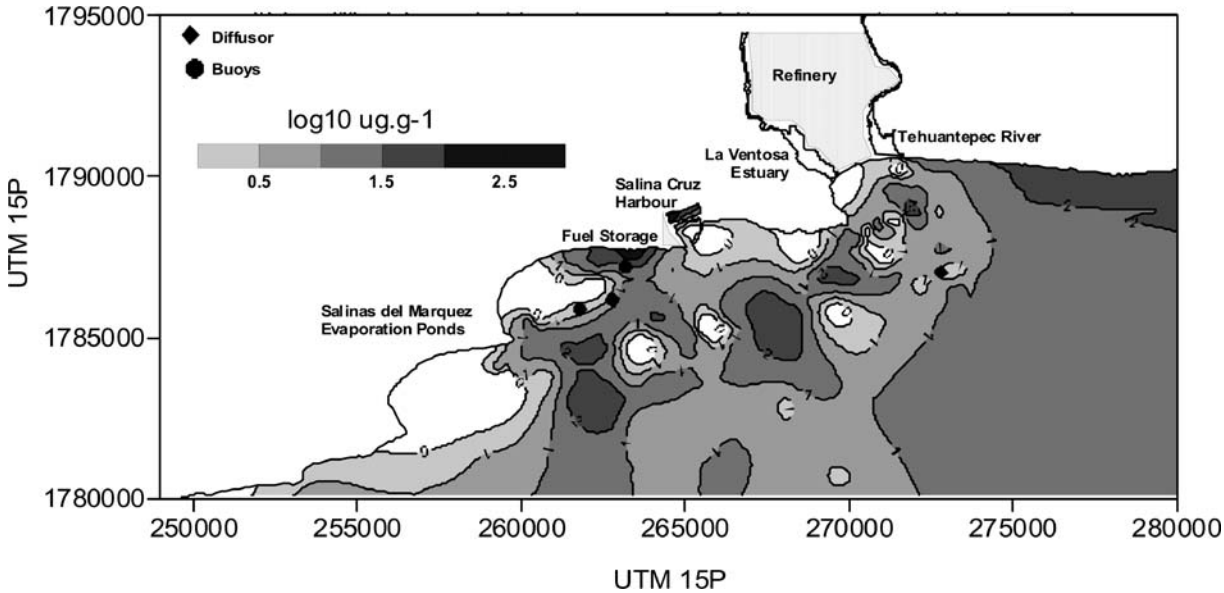


Fig. 6 Map of TAH (Log_{10} μg g^{-1}) distribution in surface sediments from Salina Cruz Bay

3.4 Temporal and spatial trends

The historical accumulated data portraying the TAH concentrations in sediments of the SC Bay is shown in Fig. 5. The lower part of the graph shows a SiZer plot which relates time and concentration trends while the upper part shows the inferred values of the smoothed line (continuous line, secondary *Y* scale) graphed along the raw data (dotted data, *Y* left scale).

In the plot, the entire point wise straight lines are shown. The bold lines illustrate the first inference straight line that uses all the data set to perform the time trend inference. The slope of the dashed lines is related with increasing or decreasing tendency as well as the magnitude and significance of the inference. Horizontal dashed lines indicate that for a specific timeframe, significant difference from 0 can not be ascertained for the smoothed line. The non-dashed areas indicate that few data are available to do inference.

TAH concentrations in surface sediments shows a decrease (negative slope at $\log_{10}(h)=0.25$) in the period 1984–1992, follows by an increase from 1992 to 1996 (dashed lines positive slope), and a significant decrease again from 1998 to 2002. Reconstruction of the temporal tendencies seems to indicate that TAH decrease continued to present days.

Experimental data were used to produce the map portraying SC Bay surface sediments concentrations presented in Fig. 6. The color codes intended to illustrate the distributional concentration pattern presented as $\log_{10}$ μg g^{-1}. TAH distribution follow same trend as the EOM pattern, showed in Fig. 2, the later is the main responsible for total aromatic hydrocarbon accumulation in sediments.

TAH concentrations range from 0.10 to 365 μg g^{-1}; the lowers values are found near shore and in the vicinity of the refinery diffusor, while the highest values are located east from the refinery diffusor,

Table 8 Surface sediments TAH concentrations. Related sites and events characteristics in Salina Cruz Bay

Site and events charateristics	Criteria	Harbour ship scrapping[a]
Oil industry diffusor	Area 3 km around diffusor/constant water treated discharges	0.0003
Oil industry spills	Samples taken after oil spills (June and September 1999)	0.0463
Harbour ship scrapping	Salina Cruz Harbour/Fuel Storage/Buoys	
Transboundary source	East Salina Cruz Bay area ,up stream diffusor UTM >274,000	
Salina Cruz Bay	West Salina Cruz Bay area, down stream diffusor	0.0012

[a] Tukey Honest Significant Difference test. Significant difference among sites and events at $p<0.0500$

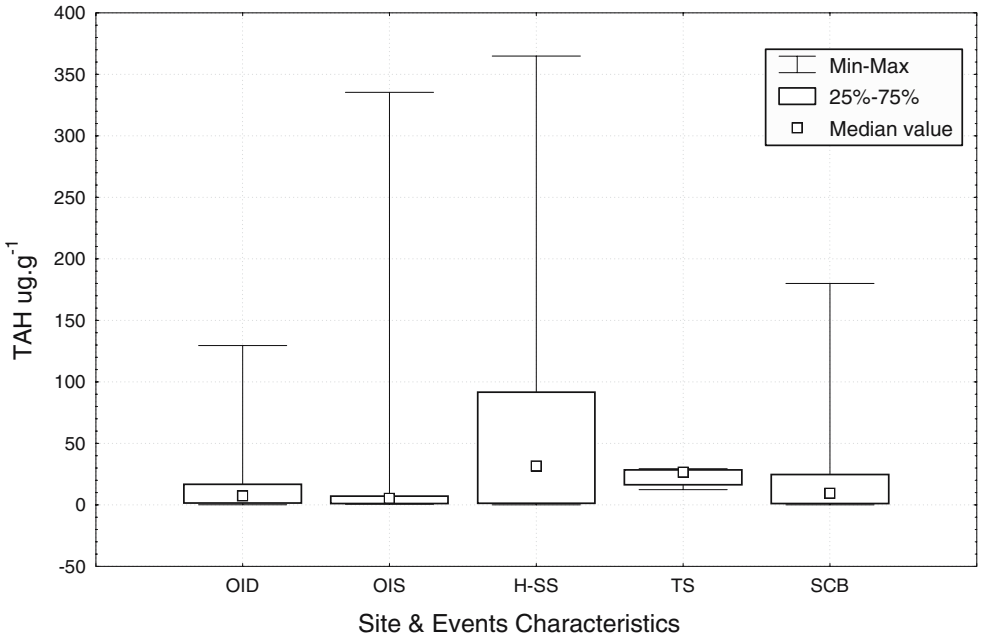


Fig. 7 Comparison of TAH values concentration for sites and events at Salina Cruz Bay

close to the fuels dispatch and at the evaporation ponds, suggesting that a transboundary source for TAH must influence the observed trends.

In attempt to relate the TAH spatial and temporal patterns with the sites activities and events that have taken place in the Bay, Table 8 shows sites related concentrations arranged in sets of data: three industrial related (oil industry diffusor *OID*, oil industry spills *OIS*, and harbor ship scrapping *H-SS*); a transboundary source *TS*, and the pattern of Salina Cruz Bay *SCB*. In the Table are indicated the criteria used for site differentiation. Tukey test showed that harbor ship

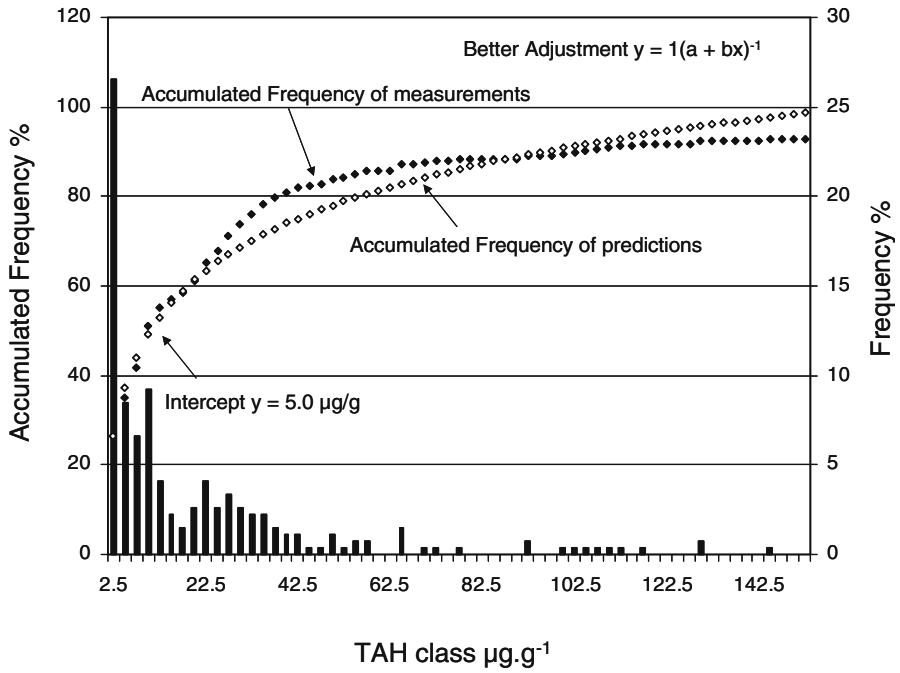


Fig. 8 Method for determining TAH natural background concentrations in surface sediments at Salina Cruz Bay

scrapping is different from the others events except for the transboundary source that seems to be alike harbor ship scraping activities. In Fig. 7 TAH values differences among sites and events are presented.

3.5 Background TAH concentration

Comparisons with sediments from pristine locations are difficult as sites are not easy to find, particularly with comparable grain size characteristics. We follow a background model in which the data were sorted in order of ascending concentrations, and the better curve adjusted model was run for it, the lowest concentration is assumed to represent the background level (Roach 2005).

A curve fitting system (Digital River 2005) was used for obtaining the better adjustment model for TAH accumulated frequency. The equation obtained $y=1(a+bx)^{-1}$ corresponds to a Yield Density Reciprocal Model in which there is a high incidence of sediments with low TAH concentrations.

In Fig. 8 the better adjustment model of the TAH accumulated frequency is compared with experimental measurements. The first interception between the two curves, which is related to the lowest concentration, predicts $Y=5.0$ μg g^{-1}, value which is proposed as the SC Bay background concentration for surface sediments. On notice also the presence of two modal distributions, the second one might be related with an additional source to the natural background.

The TAH water-sediment K_d for the entire period of study shows values that varied from 0.0676 to 38.7667, with 30% quotients close to 1.00. The results are no surprising given the dynamic nature and heterogeneity of the samples analyzed, but consistent with similar findings reported by other authors' (King et al. 2004). It is therefore clear that K_d along is not satisfactory to explain sediment-water distribution behavior that could not have reached geochemical equilibrium in a highly dynamic oceanic system such as SC Bay.

K_{oc} partition coefficients values fluctuate from 0.0003 to 0.2517 when EOM is used as normalize. The primary point here seems to be that all measures of partitioning of sediment with the overlying water have an uncertainty covering 3 to 4 orders of magnitude: they all strongly indicate the system is not in equilibrium which is not unexpected. If the data are normalized with respect to the fine fractions, the coefficient values varies between 0.0019 and 3.7698 with only 6% of the data present quotients above 1, therefore closer to phase's equilibrium.

In conclusion, TAH in water and sediments from Salina Cruz Bay are mostly associated to sediment EOM and fine fractions variables. Geocumulation index and enrichment factors show that TAH contamination could derive from industrial activities, atmospheric input, and domestic sewage contribution, all of them from continental runoff.

References

APHA. American Public Health Association, American Water Works Association, and Water Pollution and Control Federation, 1995, Standard Methods for the Examination of Water and Wastewater, 1995, Total Suspended Solids Dried at 103°–105°C, American Public Health Association, Method 2540D, Washington, D.C. 2-56.

Barrick, R. C. (1982). Flux of aliphatic and polycyclic aromatic hydrocarbons to Central Puget Sound from Seattle (Westpoint) primary sewage effluent. *Environmental Science and Technology, 16*, 682–692.

Botello, A. V., Villanueva, S. F., Diaz, G., & Escobar-Briones, E. (1998). Polycyclic Aromatic Hydrocarbons in Sediments from Salina Cruz Harbor and Coastal Areas, Oaxaca, Mexico. *Marine Pollution Bulletin, 36*, 554–558.

Bouloubassi, I., & Saliot, A. (1993). Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH). *Oceanologica Acta, 16*, 145–161.

Chaudhuri, P., & Marron, J. S. (1999). Sizer for Exploration of Structure in curves. *Journal of the American Statistical Association, 94*(447), 807–823.

Chelton, D. F., Freilich, M. H., & Esbensen, S. K. (2000). Satellite observations of the wind jets off the Pacific Coast of Central America. Part II: Regional Relationships and Dynamical Considerations Monthly Weathers Review, 128, 2019–2043.

Chesler, S. N., Cub, B. H., Hertz, H. S., May, W. W., Dyszel, M., & Enagonio, D. P. (1976). Trace hydrocarbons analysis. The National Bureau of Standards, Prince William Sound/North Easter Gulf of Alaska. Base line study, Washington, D.C.

Digital River, Inc. (2005). Curve Expert 1.3 Software, available at http://www.digitalriver.com.

Eganhouse, R. P., & Kaplan, I. R. (1982). Extractable organic matter in municipal wastewaters. 1. Petroleum hydrocarbons: Temporal variations and mass emission rates to the ocean. *Environmental Science and Technology, 16*, 180–186.

Folk, R. L. (1974). *The petrology of sedimentary rocks*. Austin, Texas: Hemphill.

García-Ruelas, C., Botello, A. V., Ponce-Vélez G., & Díaz-González G. (2004). Polycyclic aromatic hydrocarbons in coastal sediments from the subtropical Mexican Pacific. *Marine Pollution Bulletin, 49*, 514–519.

Godtliebsen, F., Olsen, L. R., & Winther, J-G. (2003). Recent developments in statistical time series analysis: Examples

of use in climate research. *Journal Geophysical Research, 30*(12), 1654–1657.

Gold, G., Acuña, J, & Morell, J. (1987). Manual CARIPOL/IOCARIBE para el análisis de hidrocarburos de petróleo en sedimentos y organismos marinos. Cartagena de Indias, Colombia.

González-Macías, C., Schifter, I., Lluch-Cota, D. B. Méndez-Rodríguez, L., & Hernández-Vázquez, S. (2006). Distribution, enrichment and accumulation of heavy metals in coastal sediments of Salina Cruz Bay, México. *Environmental Monitoring and Assessment, 118*, 1–3.

Gordon, D. C., & Keizer, P. D. (1976). *Estimation of petroleum hydrocarbons in sea water by fluorescence spectroscopy. Improved sampling and analytical methods. Technical Report No. 481*. Canada: Fisheries and Marine Service.

Holmström, L., & Erästö, P. (2001). *Using the SiZer method in Holocene temperature reconstruction. Research Reports A36, Rolf Nevanlinna Institute*. Finland: University of Helsinki.

Jeng, W. L., & Han, B. C. (1994). Sedimentary coprostanol in Kaohsiung harbor and the Tan-Shui estuary, Taiwan. *Marine Pollution Bulletin, 28*, 494–499.

Karichknoff, S. W., Brown, D. S., & Scott, T. A. (1979). Sorption of hydrophobic pollutants on natural sediments. *Water Research, 13*, 241–248.

King, A. J., Readman, J. W., & Zhou, J. L. (2004). Dynamic behavior of polycyclic hydrocarbons in Brighton marina, UK. *Marine Pollution Bulletin, 48*, 229–239.

Kot-Wasik, A., Dbska, J., & Namienik, J. (2004). Monitoring of organic pollutants in coastal waters of the Gulf of Gdansk, Southern Baltic. *Marine Pollution Bulletin, 49*, 264–276.

Latimer, J. S., & Quinn, J. G. (1996). Historical trends and current inputs of hydrophobic organic compounds in an urban estuary: The sedimentary record. *Environmental Science and Technology, 30*, 623–633.

Massey, Jr., F. J. (1951). The Kolmogorov–Smirnov test for goodness of fit. *Journal of the American Statistical Association, 46*, 68–78.

Massoud, M. S., Al-Abdali, F., Al-Ghadban, A. N., & Al-Sarawi, M. (1996). Botton Sediments of the Arabian Gulf-II.TPH and TOC contents as indicators of oil pollution and implications for the effect and fate of the Kuwait Oil Slick. *Environmental Pollution, 93*, 271–284.

Means, J. C., Wood, S. G., Hassett, J. I., & Banwart, W. L. (1980). Sorption of polynuclear aromatic hydrocarbons by sediments and soils. *Environmental Science and Technology, 14*, 1524–1528.

Müller, G. (1979). Schwermetalle in den sediments des Rheins-Veranderungen seitt 1971. *Umschan, 79*, 778–783.

Mzoughi, N., Dachraoui, M., & Villeneuve, J. P. (2005). Evaluation of aromatic hydrocarbons by spectrofluorometry in marine sediments and biological matrix: What reference should be considered? *Comptes Rendus Chimie, 8*, 97–102.

NFESC (2003). Final implementation guide for assessing and managing contaminated sediment at navy facilities. User's Guide UG-2053-ENV. Naval Facilities Engineering Command. Washington, DC 20374-5065.

Nolting, R. F., Ramkema, A., & Everaats, J. M. (1999). The geochemistry of Cu, Cd, Zn, Ni and Pb in sediment cores from the continental slope of the Banc d'Arguin (Mauritania). *Continental Shelf Research, 19*, 665–691.

Readman, J. W., Bartocci, J., Tolosa, I., Fowler, S. W., Oregioni, B., & Abdulraheem, M. Y. (1996). Recovery of the coastal marine environment in the Gulf following 1991 the war related oil spills. *Marine Pollution Bulletin, 32*, 493–498.

Readman, J. W., Fillmann, G., Tolosa, I., Bartocci, J. Villeneuve, J. P., Catinni, C., et al. (2002). Petroleum and PAH contamination of the Black Sea. *Marine Pollution Bulletin, 44*, 48–62.

Roach, A. C. (2005). Assessment of metals in sediments from Lake Macquarie, New South Wales, Australia, using normalization models and sediment quality guidelines. *Marine Environmental Research, 59*, 453–472.

Statistica (1998). Statistica for windows (Vol I). General Conventions General Conventions ands Statistics I (2nd ed.). StatSoft, Inc., Tulsa OK, USA.

Surfer® version 8.01 (2002). Golden Software, Inc., CO, USA.

Taylor, S. R. (1964). Abundance of chemical elements in the continental crust; a new table. *Geochimica Cosmochimica Acta, 28*, 1273–1285.

Tolosa, I., de Mora S. J., Fowler, S. W., Villeneuve, J. P., Bartocci, J., & Cattini, C. (2005). Aliphatic and aromatic hydrocarbons in marine biota and coastal sediments from the Gulf and the Gulf of Oman. *Marine Pollution Bulletin, 50*, 1619–1633.

Trasviña, A., Barton, E. D., Brown, J.,Velez, H. S., Kosro, P. M., & Smith, R. L. (1995). Offshore wind forcing in the Gulf of Tehuantepec, México. The asymmetric circulation. *Journal of Geophysical Research, 100*(20), 649–663.

United States Environmental Protection Agency (USEPA) (1978). *Test method for evaluating total recoverable petroleum hydrocarbon, method 418.1 (spectrophotometric, infrared)*. Washington, DC: U.S. Government Printing Office.

United States Environmental Protection Agency (USEPA) (1996). *Method 8440, total recoverable petroleum hydrocarbon by infrared spectrophotometry. SW-846 (3rd edn.). Revision-0*. Washington, DC: U.S.Government Printing Office.

UNESCO (1982). Comisión Oceanográfica Intergubernamental Determinación de los hidrocarburos de petróleo en los sedimentos. Manuales y Guías, 11, 1–35. Place de Fontenoy, París, Francia.

UNESCO (1984). Comisión Oceanográfica Intergubernamental Manual para la vigilancia del aceite y de los hidrocarburos del petróleo disueltos o dispersos en el agua del mar y en las playas. Procedimientos para el componente petróleo del sistema de vigilancia de la contaminación del mar (MARPOL-MON-P). Manuales y Guías, 13, 1–37. Place de Fontenoy, París, Francia.

Volkman, J. K., Holdswoeth, D. G., Neill, G. P., & Bavor, H. J. (1992). Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. *The Science of Total Environment, 112*, 203–219.

Zsefer, P., Glasby, G. P., Sefer, K., Pempkowiak, J., & Kaliszan, R. (1996). Heavy-metal pollution in superficial sediments from the southern Baltic Sea off Poland. *Journal of Environmental Science and Health, 31A*, 2723–2754.