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**Lead pollution in subtropical ecosystems on the SE Gulf of California Coast: A study
of Concentrations and Isotopic Composition**

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Abstract

Lead pollution was investigated in environmental matrices and biological indicators collected from two typical subtropical coastal ecosystems in the southeast Gulf of California, Mexico. Lead concentrations and isotopic compositions ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$) were measured using high resolution inductively-coupled plasma mass spectrometry (HR-ICP-MS) and thermal ionization mass spectrometry (TIMS), respectively. Lead in surface estuary sediments ($10.0\text{--}34.2\text{ }\mu\text{g g}^{-1}$) and particulate Pb ($25.0\text{--}128.7\text{ }\mu\text{g g}^{-1}$, >98% of total Pb) in the water column were significantly higher than levels in natural bedrock soils ($15.1\pm 8.3\text{ }\mu\text{g g}^{-1}$) and river runoff ($1.9\pm 1.4\text{ }\mu\text{g g}^{-1}$). Aquatic plants had Pb concentrations between 2.5 and $7.2\text{ }\mu\text{g g}^{-1}$, while those in macroalgae ranged from 3 to $5\text{ }\mu\text{g g}^{-1}$. The ranges of mean Pb concentrations in the aquatic animals studied (ranges in $\mu\text{g g}^{-1}$) were as follows: zooplankton 32 ± 3 , mussels $2.3\text{--}3.9$, oysters $1.9\text{--}7.9$, snail $2.0\text{--}7.7$, barnacles $0.1\text{--}18.5$, fish $1.4\text{--}8.9$, crab $6.3\text{--}40.2$ and polychaetae $8.5\text{--}16.7$. Pb values in 20-40% of oyster and fish samples and in all samples of crab exceeded acceptable levels for a food source for human consumption. Pb isotope ratios $^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$ in biota ranged from 1.188 to 1.206 and 2.448 to 2.470, respectively. A plot of $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{207}\text{Pb}$ for the environmental and biological samples collected from two study areas indicates that they contain lead from ores mined in Mexico and used in the past to produce leaded gasoline in use until 1997, natural Pb weathered from the Sierra Madre Occidental mother rock, and the later influence of inputs from a more radiogenic source related to industrial activity in the United States. Statistical software IsoSource results revealed that the Pb contained in environmental matrices and biomonitors is mostly derived from gasoline (20-90%) and US emissions (10-40%).

48 **Author Keywords:** Pb pollution, sources and isotopic ratios; biological indicators; Gulf of
California.

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1. Introduction

The subtropical Gulf of California Ecoregion (GCE), located on the northwest coast of Mexico, provides habitat for a wide diversity of plant and animal species, many of them rare and endangered (Hendrickxs et al., 2002; www.worldwildlife.org). In recent decades, many associated marine ecosystems and/or their catchments have been used for diverse anthropogenic activities in this region, including agriculture, urban development, tourism, fishing, industry, mineral extraction, shipping, and shrimp farming. Consequently, the urban and suburban coastal ecosystems in the GCE have become reservoirs for diverse pollutants such as pesticides, nutrients and metals.

Pb has no known essential role in living organisms, and is toxic at even low concentrations. Because Pb persists in the environment, concentrations of this metal may progressively increase in water, sediments or in biological tissues to levels above natural background. Elevated metal concentrations in aquatic systems may pose health risks to marine life (e.g. primary producers, fish and filter feeders) and consumers of those organisms, including humans (Bryan and Langston, 1992). Previous studies have found elevated concentrations of Pb in the sediments and organisms in coastal environments in the GCE (Ruelas-Inzunza et al., 2000; Green-Ruiz and Pérez-Osuna, 2001; Pérez-Osuna et al., 2002; 2003; Soto-Jiménez et al., 2001; 2003; Frías-Espericueta et al., 2008).

The primary objectives of this study evaluating Pb pollution in the GCE, were: (1) to determine the degree of environmental Pb contamination and the potential risk of seafood consumption; and (2) to identify the major sources of lead. This study was carried out on a wide range of environmental matrices (water, particulate matter, and sediments) and aquatic biota (primary producers, primary, secondary and tertiary consumers) from two

representative ecosystems. High-precision instruments were used to analyze Pb concentrations and isotopic ratios ($^{206}\text{Pb}/^{207}\text{Pb}$, $^{208}\text{Pb}/^{207}\text{Pb}$) in all samples. IsoSource software was used to model the feasible source contributions of environmental Pb. This is the first comprehensive survey of lead contamination in Mexico to include state-of-the-art techniques and instrumentation to measure concentrations and isotopic compositions of lead encountered in samples from the natural environment.

2. Methods

2.1. Study area

The Chiricahueto marsh and Urías estuary are representatives, respectively, of rural and urban subtropical coastal ecosystems in the Gulf of California Ecoregion of NW Mexico (Fig.1). Designated as priority marine areas by the Mexican government because of their ecological and economic importance, these ecosystems provide habitat for a wide variety of plants and animals, including rare and endangered species, as well as commercially valuable fish and invertebrates. Both regions have been impacted by anthropogenic activities including agriculture, aquaculture, mining, tourism, shipping and industry.

Chiricahueto marsh (23 km² area, <0.5 m depth) is located at the interface between the Altata Ensenada Pabellón (AEP) lagoon and the agricultural watershed headwater within the Culiacán valley. The marsh has functioned for over 50 years as a natural filter, trapping eroded soil particles, fertilizers, and pesticides from agricultural soils and from discharges of untreated sewage and storm water from Culiacán City.

Bounded by two breakwaters, the Mazatlán harbor lies within the Urías estuary (16 km² area, 1-10 m depth). This harbor is the main port on the Mexican Pacific coast and

Mazatlán is one of the main tourist centers in México. Impacts include harbor activities (waste from docked boats and ships, and their repair and maintenance), electric power generation, seafood processing, shrimp farming, and runoff of storm water and untreated sewage effluents during heavy rainfall.

2.2. Sampling

2.2.1. Environmental samples

Trace-metal clean sampling techniques were used to minimize potential sample contamination (Flegal and Smith, 1995). Surface water from five sampling stations in Chiricahueto marsh and six in Urías estuary was sampled on several field trips between November 2002 and February 2003 (drought season). Duplicate samples from a depth of 0.1 m below the surface were collected in 2 L bottles, placed in a cooler and transported to the laboratory for analysis. Suspended particulate matter (SPM) was collected by filtering 200-1000 ml from each water sample through a trace metal pre-cleaned and pre-combusted (500°C, 4 hr) glass fiber filter (GF/F) with a low-pressure vacuum pump. Filtered and unfiltered water samples were aliquoted into acid-cleaned polyethylene (LDPE) bottles. The particulates on the filters ($>0.45\ \mu\text{m}$) were air-dried at 55-60°C. Total SPM was determined by comparing filter weights before and after filtration of a known amount of water. Surface sediments (0-2 cm depth) from selected sampling sites in both study areas were also collected.

2.2.2. Biological samples

Biomonitors living in the studied ecosystems and selected for this study included biota from different trophic levels including primary producers, primary consumers and secondary consumers. Organisms were collected from the sampling stations in Chiricahueto marsh and Urías Estuary according to their distribution at the time of the field trips carried out between November 2002 and February 2003. A total of 87 composite samples of aquatic organisms were collected. Not all species were present or present in sufficient numbers at all stations in both studied ecosystems. Approximately 1,018 specimens of macro-organisms, macroalgae, and plants were collected, representing a total of 15 species. An undetermined number of specimens of plankton was collected. The organisms were selected for their direct or indirect response to at least one particular Pb source. Most of these satisfy all the basic requirements of biomonitors: they are sedentary, easy to identify and to collect, accumulate metals to a satisfactory degree, and are widely distributed on the Pacific coast of Mexico and in the GCE. More details on most of these species regarding biological context, propensity to accumulate metals, and inherent seasonal variability are given by Ruelas-Inzunza et al. (2000), Soto-Jiménez et al. (2001), Páez-Osuna et al., (1999; 2000; 2002), Mendez (2002) and cited references.

Biological species included two species of macroalgae (*Ulva lactuca* and *Gracilaria vermiculophylla*); three angiosperm species (*Batis maritima*, *Rhizophora mangle* and *Thypha angustifolia*); mixed zooplankton (dominated by 80-90% copepods); an herbivore gastropod mollusk (*Littoraria aberrans*); three filter-feeding species including oyster (*Crassostrea corteziensis*), mussel (*Mytella strigata*) and barnacle (*Fistulobalanus dentivarians*); one crab (*Callinectes arcuatus*); a species of Polychaeta (*Streblospio benedicti*); and one commercially important species of fish (*Mugil cephalus*).

SPM collected from filtering of the water column is considered 'seston' in this study. Seston is comprised principally of living or dead phytoplankton, mangrove detritus, macroalgae and associated invertebrate fauna, and inorganic particulate matter including silt grains. Three replicates, each consisting of 3-5 whole macroalgae was chosen from each site where available. Leaves from mangrove trees (15-20 of the second-youngest leaves from 3-5 plants), saltwort and cattail (2-3 whole plants) were also collected. Zooplankton was collected at each water sampling station using 270 μm mesh conical nets. The net was towed slowly (2 knots) for approximately 10 min. Fish larvae were collected from the net along with the zooplankton. Adult fish samples were collected with a gill net by local fishermen. One species of snail, two mollusks and two crustacean species associated with mangrove roots were collected by hand. Polychaetes organisms were separated from sediment samples obtained with a 0.1 m^2 grab and carefully sieved through a 0.5 mm mesh. All samples of biota were stored in sealed doubled plastic bags at 4–6°C immediately after collection.

In the laboratory, the samples were first rinsed with potable water to remove sediment and salt particles, and then rinsed with Milli-Q water. The samples of phytoplankton in the nets were cleansed with MilliQ water and filtered through GF/F filters with a 0.45 μm pore size using a vacuum pump. Mollusks were placed in seawater from the sampling site with aeration for 24-h depuration periods, rinsed in de-ionized water and dissected to isolate the edible tissues (including liquor). Composites of 20 to 50 individuals of similar size (depending on the species) were made for each sampling station. Fish specimens were dissected for muscle, with two to three specimens comprising each pooled

sample. All biota and environmental samples were stored frozen at -20°C , lyophilized at -45°C for 3 days, and then pulverized to a homogeneous powder using an agate mortar.

2.3. Analysis of lead concentrations and isotopic composition

All of the environmental and biological samples were processed and analyzed in a HEPA (Class 1000) filtered-air, trace metal clean laboratory, using high-purity (e.g., 2x sub-boiling quartz distilled acids) reagents and high-purity ($18.3\text{ M}\Omega\text{ cm}$) water. Water samples were acidified to pH 1.5 in the laboratory using 6N HCl sub-boiling quartz distilled and stored for at least 1 month. Before analysis the water samples were exposed to UV light for 1 hour to break down all of the inorganic complexes and some of the organic complexes present in the water (Ndung'u et al., 2003). Solid aliquot samples (250-500 mg of powder) were digested using concentrated aqua regia ($\text{HNO}_3\text{:HCl}$, 1:3 v/v) decanted into Teflon vessels (30 mL), and refluxed at 130°C overnight on a Mod Block unit. Digested samples were evaporated to dryness, redissolved in 10 mL of 1N HNO_3 , and diluted in 5 mL of 1N HNO_3 .

Pb concentrations were measured with a Finnigan MAT Element® magnetic sector high-resolution inductively coupled plasma-source mass spectrometer (ICPMS). A bismuth tracer (^{209}Bi) was added as an internal standard to correct for instrumental drift. Blanks and international standard reference materials (NRCC SLEW-2 estuarine water, NRCC MESS-2 marine sediment, NBS NIST 1547 of Peach Leaves and NIST 1566 of Oyster tissue) were included in each digestion batch to verify the accuracy of the extraction method. The results obtained for these reference materials are given in Table 1. The agreement with certified

values is better than 10% for Pb in sediments and water, and better than 6% for Pb in biological tissues.

Isotopic compositions of Pb in environmental and biological samples were measured with a VG Sector 54® thermal-ionization mass spectrometer (TIMS). Because the proportion of Pb in the SPM constituted the most abundant fraction of the total lead (>95%) in the unfiltered water samples, the isotopic composition was not determined in the dissolved fraction. Digested aliquots (0.5 mL) were purified in extractions using Teflon® microcolumns loaded with AG1-X8 75–150 mesh anion exchange resin, flushed with HCl, and eluted with HBr, using established procedures (Flegal et al., 1987). To load Pb, 2 µl of an over-saturated silica-gel solution was loaded onto an Re filament. The sample was dissolved in 2 µl H₃PO₄ and added to the incompletely dried silica gel. The filament was then briefly heated to a dull red color before being loaded into the mass spectrometer. Lead isotopes ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb were measured simultaneously using 4 Faraday collectors in a static mode. A standard reference material (NIST SRM 981, common lead) was used to check for instrumental performance and to determine the mass fractionation factor that needed to be applied for each sample. Lead blanks during the course of the study were less than 0.1% of the amount of lead measured in each sample. A mass fractionation correction based on the standard run (NIST SRM 981) was applied to all samples. Maximum analytical uncertainties for ± 2 standard error of the mean are as follows: ²⁰⁶Pb/²⁰⁷Pb < 0.0005, and for ²⁰⁸Pb/²⁰⁷Pb < 0.0003).

3.4. Statistical analyses

All data were presented as mean $\pm$ SD. One-way analysis of variance followed by Tukey's HSD test was performed for Pb concentrations and isotopic composition ratios of Pb considering sampling sites and studied species. Because the analyses of concentration and isotopic compositions of Pb were realized in composite samples, the normal distribution was assumed in our data according to the Central Limit Theorem (Zar, 1999). The level of significance in all statistical tests was 0.05. Statistica 7.0 (Statsoft inc., Tulsa, USA) was used for all the statistical analyses.

3. Results and discussion

3.1. Pb concentrations

Resulting Pb concentrations and isotopic composition for the environmental and biological samples from Chiricahueto marsh and Urías estuary, representative of the southeast GCE, are listed in Tables 2 and 3, respectively. Dissolved Pb concentrations from both sites ($2.2 \pm 1.6 \mu\text{g L}^{-1}$ and $1.9 \pm 1.4 \mu\text{g L}^{-1}$) were comparable. A comparison with data available in the literature (Bryan and Langston, 1992; Sadiq, 1992; Coung et al., 2008) revealed that the Pb dissolved concentrations in this study are significantly more elevated than those reported in surficial seawater ($0.01\text{--}0.14 \mu\text{g L}^{-1}$) and other coastal and estuarine waters from non-polluted areas around the world ($0.02\text{--}0.88 \mu\text{g L}^{-1}$). However, the dissolved Pb levels in Chiricahueto marsh and Urías estuary are 3-4 times lower than the Criterion Continuous Concentration ($\text{CCC}=8.1 \mu\text{g L}^{-1}$) given in the National Recommended Water Quality Criteria (USEPA, 2006) which represents the level to which an aquatic community can be exposed indefinitely without an unacceptable effect.

The Pb in the SPM or seston was significantly higher ($p < 0.05$) in Chiricahueto marsh than in Urías estuary (95.3 ± 33.4 and $49.0 \pm 24.0 \mu\text{g g}^{-1}$, respectively). Most of the Pb (>98%) is associated with the SPM. High spatial variability in Pb concentrations in seston was observed among stations from both ecosystems with generally higher levels recorded in the areas characterized by the convergence of tributaries discharging runoff and effluents (Fig. 1). Pb contents in the seston and dissolved in the water are a major source of Pb for organisms at many trophic levels (Ward et al., 1982; Simkiss and Taylor, 1989).

Pb in the surface sediments from both sites showed comparable concentrations, from 24.1 ± 10.6 and $17.4 \pm 7.3 \mu\text{g g}^{-1}$, respectively. Similarly to seston, there were considerable spatial differences in the Pb levels in sediments, with generally higher levels recorded in stations adjacent to the urban areas receiving local effluents, and with favorable conditions for the sedimentation of materials and the scavenging of metals. These values are slightly enriched considering the regional background Pb value ($10 \mu\text{g g}^{-1}$, Soto-Jiménez et al., 2003) and average composition of the crust ($15 \mu\text{g g}^{-1}$, Martin and Meybeck, 1979), but no higher than the sediment quality guideline values for effects range-median (ERM) of $46.1 \mu\text{g g}^{-1}$ (Long et al., 1990).

In addition to the environmental matrices, organism monitors occupying different trophic levels, such as primary producers and primary, secondary and tertiary consumers with different feeding strategies (e.g. grazing, burrowing, filter-feeding, suspension and deposit-feeding, predators and scavengers) were selected for their direct or indirect response to at least one particular Pb source. The measured Pb content in macroalgae samples, which reflects the surface uptake of dissolved Pb in the water column (Fisher et al, 1987; Phillips, 1990; Haritonidis and Malea, 1999), averaged 3.0 ± 0.7 and $2.0 \pm 0.7 \mu\text{g g}^{-1}$

for *U. lactuca* and 5.1 ± 3.3 and $4.0 \pm 0.7 \mu\text{g g}^{-1}$ for *G. vermiculophylla* from Chiricahueto marsh and Urías estuary, respectively. The highest values of metal in seaweeds were found in Chiricahueto marsh which is receiving municipal sewage and agriculture effluents. Previous studies of macroalgae suggest that interspecies metal accumulation may be similar among species from the same locations (Páez-Osuna et al., 2000; Huerta-Díaz et al., 2007). Thus, the differences in Pb accumulation between macroalgae from both sites indicate higher bioavailability in Chiricahueto marsh than in Urías Estuary ($p < 0.05$).

The angiosperm species used as indicators of Pb in air, water, and sediments showed high variability in Pb concentrations, ranging from 1.2 to $10.7 \mu\text{g g}^{-1}$. Inter-species comparisons of angiosperms revealed that *B. maritima* ($7.2 \pm 3.5 \mu\text{g g}^{-1}$) had the highest leaf Pb concentrations followed by *T. angustifolia* ($3.7 \pm 2.5 \mu\text{g g}^{-1}$) and then by *R. mangle* ($2.5 \pm 2.2 \mu\text{g g}^{-1}$). The significantly greater accumulation of Pb by *B. maritima* could be due to the physiological strategies of this plant species for tolerating high salinity levels characterized by very low transpiration through the plant (Lovelock and Ball, 2002). This may indirectly contribute to the accumulation of Pb and other metals. However, Pb concentrations in the different plant species are also dependent on location, environmental conditions, and bioavailability of the metal in the water and in the sediment. By comparing Pb concentration means in *R. mangle*, we found no significant difference ($p < 0.05$) between mangroves from Urías Estuary ($2.5 \pm 2.2 \mu\text{g g}^{-1}$) and Chiricahueto marsh ($3.8 \pm 1.8 \mu\text{g g}^{-1}$).

Another set of Pb biomonitors was that of aquatic animals exposed to Pb in solution and through ingestion of particulate material. These included zooplankton (dominated by copepods) with Pb concentrations averaging $7.6 \pm 4.5 \mu\text{g g}^{-1}$ for those from Chiricahueto marsh and $2.0 \pm 0.7 \mu\text{g g}^{-1}$ in Urías estuary. Phytoplankton in seston can scavenge and

concentrate Pb and other trace elements very appreciably from the seawater (Fisher 1986),
 278 representing the main source of Pb for the zooplankton (Ward et al., 1982).

Pb concentrations in the snail *L. aberrans*, an herbivore gastropod, averaged 3.0 ± 1.0
 280 and $6.3 \pm 1.4 \mu\text{g g}^{-1}$ in Chiricahueto marsh and Urias estuary, respectively. In Urias estuary,
 mean Pb levels were $3.1 \pm 0.8 \mu\text{g g}^{-1}$ in the mussel *M. strigata*, $4.9 \pm 3.0 \mu\text{g g}^{-1}$ in the oyster
 282 *C. corteziensis* and $8.5 \pm 10.0 \mu\text{g g}^{-1}$ in the barnacle *F. dentivarians*. These organisms are
 exposed to lead both in solution and through ingestion of organic and inorganic particulate
 284 material (Luoma and Bryan 1981; Bryan and Langston 1992). The polychaete *S. benedicti*,
 a secondary consumer that lives in the mud-submerged roots of mangroves, had Pb
 286 concentrations that varied between 8.2 and $16.7 \mu\text{g g}^{-1}$. This organism is a deposit-feeding
 detritivore, i.e. eats suspended particles and fresh deposited material on the surface (Dauer
 288 et al., 1981; Carrasco, 1986), and thus responds to Pb present in solution, in suspension,
 and/or in deposited sediments (Rainbow and Phillips, 1993).

290 The crabs *Callinectes* sp. show the highest concentration of Pb ($23.0 \pm 17.0 \mu\text{g g}^{-1}$) in
 Urias estuary. The blue crabs are opportunistic consumers with a versatile feeding nature
 292 (Hoeinghaus and Davis, 2007). For example, they may alter their feeding behavior in favor
 of detritus when living prey (e.g. bivalves, small fish) are less abundant (Bucci et al. 2007).
 294 In this study, the high Pb values are probably the result of a diet based in the consumption
 of detritus in sediments and bivalves. Finally, one species of demersal carnivorous fish that
 296 feeds preferentially on smaller fish and crustaceans had average concentrations of 3.3 ± 1.9
 and $5.7 \pm 3.2 \mu\text{g g}^{-1}$ for Urias estuary and Chiricahueto marsh, respectively. For fish the
 298 primarily sources of metal are their food (primary producer and/or prey), Pb dissolved in
 the water, and incidental ingestion of sediment (Heath, 1987; Campbell et al., 1988).

Given the human health implications of consuming seafood containing Pb, the concentrations (expressed as $\mu\text{g g}^{-1}$ wet weight) found in mussels (0.4 to 0.8 $\mu\text{g g}^{-1}$), oysters (0.3 to 1.6 $\mu\text{g g}^{-1}$), crabs (1.2 to 8.0 $\mu\text{g g}^{-1}$), and fish (0.3 to 1.8 $\mu\text{g g}^{-1}$), in our study, were compared with limits established by the Mexican government (1.0 $\mu\text{g/g}$; Secretaría de Salud, 1995), the European Community (1.5 $\mu\text{g g}^{-1}$ for bivalves, 0.5 $\mu\text{g g}^{-1}$ for crustaceans, 0.2-0.4 $\mu\text{g g}^{-1}$ for fish; EC, 2001), the U.S. Food and Drug Administration (1.7 $\mu\text{g g}^{-1}$ for bivalves, 1.5 $\mu\text{g g}^{-1}$ for crustaceans and 1.3 $\mu\text{g g}^{-1}$ for fish; FDA, 1993) and the World Health Organization (0.3 $\mu\text{g g}^{-1}$; WHO, 1972). Most samples of shellfish and fish in this study exceeded the WHO Pb guideline value. None of the mussel samples and about 20-40% of the oysters exceeded the Pb limits for bivalves established by México, the EC and the USFDA. Approximately 20-30% of the fish samples had Pb levels higher than the legislated limit in Mexico and the action level established by the USFDA. Over 85% exceeded the safety limits set by the EC. Finally, Pb concentrations in crabs exceeded all of these guidelines.

3.2. Stable Pb isotope compositions

The isotopic compositions of Pb ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$) in seston from Chiricahueto marsh and Urías estuary show ratio averages of 1.194 and 2.453, and 1.197 and 2.456, respectively. Pb isotopic ratios of the sediments were comparable in Chiricahueto marsh (1.200 ± 0.005 and 2.456 ± 0.009) and Urías Estuary (1.202 ± 0.004 and 2.464 ± 0.006) as well. There were no significant differences between sites ($p < 0.05$). The isotopic composition of Pb in the aquatic organisms averaged from 1.192 to 1.209, and 2.452 to 2.470, respectively. The sampled plant leaves had a $^{206}\text{Pb}/^{207}\text{Pb}$ ratio of 1.194-

1.206, with the highest values for *B. maritima* and the mangrove *R. mangle*, and the lowest
 324 for macroalgae *U. lactuca* and *G. vermiculophylla*. Ratios in the animal tissues varied
 from 1.199 to 1.204 in the following descending order: fish > crab > shellfish. On
 326 comparing Pb isotopic composition of the particulate Pb in the water column and in
 sediments with the isotopic ratios determined for the aquatic organisms, no significant
 328 differences were found ($p < 0.01$).

330 3.3. Pb sources

Figure 2 schematizes the main identified sources of Pb for the coastal lagoons in the
 332 GCE. These include: (i) Pb as a natural component of bedrock in the Sierra Madre
 Occidental (SMO) (1.188 ± 0.005 for $^{206}\text{Pb}/^{207}\text{Pb}$ and 2.455 ± 0.008 for $^{206}\text{Pb}/^{208}\text{Pb}$; Cameron
 334 et al., 1992), (ii) Pb from Mexican Pb ores used in the tetraethyl added to the leaded
 gasoline used between the 1940's to 1997 (1.195 ± 0.002 and 2.471 ± 0.003 , respectively;
 336 Cummins et al., 1979), and (iii) the influence of a non-regional source derived from U.S.
 aerosols from industrial emissions (1.21 ± 0.02 and 2.455 ± 0.02 ; Bollhöfer and Rosman,
 338 2001). The isotopic compositions of Pb found in environmental matrices and in
 biomonitors are also included in Figure 2. The results indicate that a large proportion of the
 340 Pb derives from the natural bedrock from the SMO with a secondary source the leaded
 gasoline. However, there is a statistically significant scatter in the data, with several
 342 biological samples off the simple two-component mixing line, indicating that a third end
 member with higher $^{208}\text{Pb}/^{207}\text{Pb}$ ratios is present. This end-member is related to the US
 344 industrial emissions. This member was previously observed in Pb accumulated in dated
 sediment cores collected in the Urías and Culiacán estuaries in the GCE (Soto-Jimenez et
 346 al., 2006).

When plotted on a $^{206}\text{Pb}/^{207}\text{Pb}$ vs. lead concentration diagram (Fig. 3), the biological samples plot between two lines with three vertices representing the three end-members.. Most of the biological samples from both studied ecosystems plotted within the corresponding area for Mexican Pb ores. A few biological samples lie between industrial Pb emissions from Mexico and from the United States. This confirms that despite the use of leaded gasoline having ended in 1997, Pb from these past emissions still remains as a major contaminant of urban areas and coastal ecosystems in the southeastern GCE.

A ternary mixing model was used to conduct the estimation of the sources of the environmental Pb. The IsoSource software package was used to run mixing equations (Phillips and Gregg, 2003). For this purpose we consider the averaged $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios for three end-members: a) natural Pb (1.188 and 2.455, respectively), b) Mexican lead ores (1.201 and 2.475), and c) U.S. industrial lead (1.21 and 2.46, Mississippi type lead). Based on the IsoSource results (averaged contributions), the Pb in seston from Chiricahueto and Urías estuaries is 42-66% derived from anthropogenic sources (16-32% is Pb from past automobile emissions and 26-36% is Pb from US industrial emissions). The majority of Pb accumulated in the sediments is also derived from tetraethyl Pb added to Mexican gasoline (25-56%) and from US industrial emissions (30-40% of total Pb).

Isotopic modeling indicates that the macroalgae received contributions of Pb from natural (50-57%) and anthropogenic sources (29-37% from US industrial emissions and 4-12% from leaded gasoline). Because the macroalgae reflect the dissolved Pb fraction of the water column (Fisher et al, 1987), the stable Pb isotope composition of dissolved Pb must be the same as in the macroalgae ($^{206}\text{Pb}/^{207}\text{Pb}=1.192-1.197$ and $^{208}\text{Pb}/^{207}\text{Pb}= 2.452-2.456$). Pb contained in angiosperms is mainly derived from leaded gasoline, as is 60-70% of total Pb in saltwort and 25-56% of total lead in mangrove and cattail leaves. The rest of

the Pb is contributed by natural sources (16-34%) and US emissions (8 to 30%). Results for aquatic animals indicate that the Pb in samples of zooplankton, fish and bivalve mollusks species is derived from leaded gasoline (40-70% of total Pb) and U.S. emissions (10-20%), with only 10-30% derived from natural sources. Pb in crab samples with highest concentrations was >90% associate with leaded gasoline.

4. Conclusions

This work reports the first results from Mexico focused on tracing the origins of Pb in the southeastern Gulf of California ecoregion through stable Pb isotopes in biological samples. Results revealed differences in Pb concentrations between different species of biomonitors, obviously related to different feeding strategies toxicokinetics of Pb. All concentrations measured in crabs and certain values of Pb in edible fish fillets (20-30%) and oyster (20-40%) were above the limits set in national and international standards. At least two routes of Pb uptake by organisms in coastal ecosystems can be identified. One is uptake of particulate and dissolved Pb from the water column by most of the sampled organisms including macroalgae, shellfish, crabs, and fish. The other is uptake of available Pb from sediments by angiosperms such as mangroves and halophytes.

The similarity in the isotopic composition values for aquatic organisms from different trophic levels indicates that they are exposed to Pb from the same sources. According to the isotopic ratios of the Pb encountered in this study, most of the Pb in biological and environmental samples has an anthropogenic origin, primarily from the use of leaded gasoline between the 1940's and 1997 (>25% of total Pb) and from US industrial emissions (10-20%). In addition, the similar isotopic compositions of Pb suggested that bio-

transference of assimilated Pb occurs. However, there was no evidence of bio-magnification.

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Table 1. Lead analysis of standard reference materials.

Reference material	Certified	This study
NRCC SLEW-3 Estuarine Water (n = 5), $\mu\text{g L}^{-1}$	0.009 ± 0.001	0.008 ± 0.001
NRCC MESS-3 Marine Sediment (n = 6), $\mu\text{g g}^{-1}$	21.1 ± 0.7	19.1 ± 0.9
NIST 1547 of Peach Leaves (n = 4), $\mu\text{g g}^{-1}$	0.87 ± 0.03	0.82 ± 0.05
NIST 1566b of Oyster Tissue (n = 4), $\mu\text{g g}^{-1}$	0.31 ± 0.01	0.32 ± 0.02

Table 2. Lead concentration ($\mu\text{g g}^{-1}$ except dissolved lead in $\mu\text{g L}^{-1}$) and isotopic

composition ($\pm$ S.D.) in environmental matrices and biota from Chiricahueto marsh.

	n	Pb ($\mu\text{g g}^{-1}$)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
Environmental matrices				
Seawater	15	2.2(1.6)	N.D.	N.D.
SPM or seston	15	95.3(33.4)	1.194(0.005)	2.457 (0.004)
Surface sediment (0-2 cm)	15	24(10)	1.200(0.005)	2.456(0.009)
Primary producers				
Macroalgae (<i>Gracilaria vermiculophylla</i>)	60	5(3)	1.196(0.003)	2.453(0.005)
Macroalgae (<i>Ulva lactuca</i>)	6	3.0(0.7)	1.192(0.004)	2.453(0.003)
Mangrove (<i>Rizophora mangle</i>)	24	3.8(1.8)	1.202(0.007)	2.463(0.006)
Cattail (<i>Thypha angustifolia</i>)	36	3.7(2.5)	1.194(0.004)	2.465(0.005)
Saltworth (<i>Batis maritima</i>)	36	7.2(3.5)	1.208(0.005)	2.465(0.004)
Primary consumers				
Zooplankton (Copepods)	6	7.6(4.5)	1.201(0.002)	2.456(0.003)
Snail (<i>Littoraria aberrans</i>)	75	3(1)	1.199(0.002)	2.453(0.002)
Juvenile fish (<i>Mugil cephalus</i>)	14	5.7(3.2)	1.204(0.005)	2.461(0.007)
N.D. Non determined				

Table 3. Lead concentration ($\mu\text{g g}^{-1}$ except dissolved lead in $\mu\text{g L}^{-1}$) and isotopic536 composition ($\pm$ S.D.) in environmental matrices and biota from Urias estuary.

	n	Pb ($\mu\text{g g}^{-1}$)	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
Environmental matrices				
Seawater	18	1.9(1.4)	N.D.	N.D.
SPM or seston	18	49.0(24.0)	1.197(0.007)	2.458(0.007)
Surface sediment	18	17(7)	1.202(0.004)	2.464(0.006)
Primary producers				
Macroalgae (<i>Gracilaria vermiculophylla</i>)	6	3.9(0.7)	1.197(0.003)	2.456(0.007)
Macroalgae (<i>Ulva lactuca</i>)	18	3.0(0.7)	1.197(0.002)	2.456(0.004)
Mangrove (<i>Rhizophora mangle</i>)	30	2.5(2.2)	1.198(0.004)	2.463(0.007)
Primary consumers				
Zooplankton (copepods)	8	32(3)	1.197(0.007)	2.457(0.006)
Snail (<i>Littoraria aberrans</i>)	94	6.3(1.4)	1.199(0.002)	2.466(0.003)
Oyster (<i>Crassostrea corteziensis</i>)	152	4.9(3)	1.200(0.002)	2.466(0.003)
Mussel (<i>Mytella strigata</i>)	244	3.1(0.8)	1.198(0.005)	2.465(0.001)
Barnacle (<i>Fistulobalanus dentivarans</i>)	160	8.5(10)	1.200(0.006)	2.458(0.007)
Polychaete (<i>Streblospio benedicti</i>)	36	12.6(4.1)	1.197(0.002)	2.461(0.006)
Crab (<i>Callinectes arcuatus</i>)	18	23(17)	1.201(0.002)	2.470(0.004)

Secondary consumers

Fish (<i>Mugil cephalus</i>)	21	3.3(1.9)	1.201(0.001)	2.464(0.008)
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N.D. Non determined

Legends

Figure 1. Study area in the Gulf of California ecoregion: Chiricahueto marsh near the city of Culiacán and Urías estuary near the city of Mazatlán in northwestern Mexico.

Figure 2. Lead isotopic compositions ($^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{208}\text{Pb}/^{206}\text{Pb}$) (a) environmental and biological monitors collected from Chiricahueto marsh and from Urías estuary near the cities of Culiacán and Mazatlán, respectively, in northwestern Mexico along with those of (b) natural lead sources in Mexico (i.e., upper crust from Sierra Madre Occidental, NW Mexico), (c) Mexican lead ores, and (d) Pb derived from United States industrial emissions (see text for references).

Figure 3. Scatter plot of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios versus Pb concentration of environment and biological samples collected from Chiricahueto marsh and Urías estuary. The colored bars indicate the isotopic ratio ranges for the identified sources of Pb: natural Pb bedrock Mexican Pb ores (blue) and the United States emissions (yellow).

Fig. 1. Soto-Jimenez et al.

Fig. 2. Soto-Jimenez et al.

Fig. 3. Soto-Jimenez et al.