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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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24

**Abstract**

26 Lead pollution was investigated in environmental matrices and biological indicators  
collected from two typical subtropical coastal ecosystems in the southeast Gulf of  
28 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  
30 spectrometry (HR-ICP-MS) and thermal ionization mass spectrometry (TIMS),  
respectively. Lead in surface estuary sediments ( $10.0\text{-}34.2\ \mu\text{g g}^{-1}$ ) and particulate Pb ( $25.0\text{-}$   
32  $128.7\ \mu\text{g g}^{-1}$ , >98% of total Pb) in the water column were significantly higher than levels in  
natural bedrock soils ( $15.1\pm 8.3\ \mu\text{g g}^{-1}$ ) and river runoff ( $1.9\pm 1.4\ \mu\text{g g}^{-1}$ ). Aquatic plants had  
34 Pb concentrations between  $2.5$  and  $7.2\ \mu\text{g g}^{-1}$ , while those in macroalgae ranged from  $3$  to  $5$   
 $\mu\text{g g}^{-1}$ . The ranges of mean Pb concentrations in the aquatic animals studied (ranges in  $\mu\text{g}$   
36  $\text{g}^{-1}$ ) were as follows: zooplankton  $32\pm 3$ , 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-  
38 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  
40 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  
42 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  
44 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  
46 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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## 50 1. Introduction

52 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,  
54 many associated marine ecosystems and/or their catchments have been used for diverse  
anthropogenic activities in this region, including agriculture, urban development, tourism,  
56 fishing, industry, mineral extraction, shipping, and shrimp farming. Consequently, the  
urban and suburban coastal ecosystems in the GCE have become reservoirs for diverse  
58 pollutants such as pesticides, nutrients and metals.

Pb has no known essential role in living organisms, and is toxic at even low  
60 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  
62 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  
64 organisms, including humans (Bryan and Langston, 1992). Previous studies have found  
elevated concentrations of Pb in the sediments and organisms in coastal environments in  
66 the GCE (Ruelas-Inzunza et al., 2000; Green-Ruiz and Páez-Osuna, 2001; Páez-Osuna et  
al., 2002; 2003; Soto-Jiménez et al., 2001; 2003; Frías-Espericueta et al., 2008).

68 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  
70 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)  
72 and aquatic biota (primary producers, primary, secondary and tertiary consumers) from two

representative ecosystems. High-precision instruments were used to analyze Pb  
74 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  
76 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  
78 lead encountered in samples from the natural environment.

## 80 **2. Methods**

### 2.1. Study area

82 The Chiricahueto marsh and Urías estuary are representatives, respectively, of rural  
and urban subtropical coastal ecosystems in the Gulf of California Ecoregion of NW  
84 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  
86 variety of plants and animals, including rare and endangered species, as well as  
commercially valuable fish and invertebrates. Both regions have been impacted by  
88 anthropogenic activities including agriculture, aquaculture, mining, tourism, shipping and  
industry.

90 Chiricahueto marsh (23 km<sup>2</sup> area, <0.5 m depth) is located at the interface between  
the Altata Ensenada Pabellón (AEP) lagoon and the agricultural watershed headwater  
92 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  
94 discharges of untreated sewage and storm water from Culiacán City.

Bounded by two breakwaters, the Mazatlán harbor lies within the Urías estuary (16  
96 km<sup>2</sup> 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  
98 (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  
100 sewage effluents during heavy rainfall.

## 102 2.2. Sampling

### 2.2.1. Environmental samples

104 Trace-metal clean sampling techniques were used to minimize potential sample  
contamination (Flegal and Smith, 1995). Surface water from five sampling stations in  
106 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  
108 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  
110 200-1000 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  
112 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  
114 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  
116 were also collected.

### 118 2.2.2. Biological samples



Biomonitors living in the studied ecosystems and selected for this study included  
120 biota from different trophic levels including primary producers, primary consumers and  
secondary consumers. Organisms were collected from the sampling stations in Chiricahueto  
122 marsh and Urías Estuary according 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  
124 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-  
126 organisms, macroalgae, and plants were collected, representing a total of 15 species. An  
undetermined number of specimens of plankton was collected. The organisms were  
128 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  
130 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  
132 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;  
134 2000; 2002), Mendez (2002) and cited references.

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

142 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,  
144 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  
146 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  
148 was collected at each water sampling station using 270  $\mu\text{m}$  mesh conical nets. The net was  
towed slowly (2 knots) for approximately 10 min. Fish larvae were collected from the net  
150 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  
152 mangrove roots were collected by hand. Polychaetes organisms were separated from  
sediment samples obtained with a 0.1  $\text{m}^2$  grab and carefully sieved through a 0.5 mm mesh.  
154 All samples of biota were stored in sealed doubled plastic bags at 4–6°C immediately after  
collection.

156 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  
158 phytoplankton in the nets were cleansed with MilliQ water and filtered through GF/F filters  
with a 0.45  $\mu\text{m}$  pore size using a vacuum pump. Mollusks were placed in seawater from the  
160 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  
162 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

164 sample. All biota and environmental samples were stored frozen at  $-20^{\circ}\text{C}$ , lyophilized at  
165  $-45^{\circ}\text{C}$  for 3 days, and then pulverized to a homogeneous powder using an agate mortar.

166

### 2.3. Analysis of lead concentrations and isotopic composition

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

Pb concentrations were measured with a Finnigan MAT Element® magnetic sector  
180 high-resolution inductively coupled plasma-source mass spectrometer (ICPMS). A bismuth  
181 tracer ( $^{209}\text{Bi}$ ) was added as an internal standard to correct for instrumental drift. Blanks and  
182 international standard reference materials (NRCC SLEW-2 estuarine water, NRCC MESS-  
183 2 marine sediment, NBS NIST 1547 of Peach Leaves and NIST 1566 of Oyster tissue) were  
184 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

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

188 Isotopic compositions of Pb in environmental and biological samples were  
measured with a VG Sector 54® thermal-ionization mass spectrometer (TIMS). Because  
190 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  
192 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,  
194 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  
196 dissolved in 2 µl H<sub>3</sub>PO<sub>4</sub> 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  
198 isotopes 204, 206, 207, and 208 were measured simultaneously using 4 Faraday collectors  
in a static mode. A standard reference material (NIST SRM 981, common lead) was used to  
200 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  
202 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  
204 analytical uncertainties for ± 2 standard error of the mean are as follows: <sup>206</sup>Pb/<sup>207</sup>Pb <  
0.0005, and for <sup>208</sup>Pb/<sup>207</sup>Pb < 0.0003).

206

### 3.4. Statistical analyses

208 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  
210 considering sampling sites and studied species. Because the analyses of concentration and  
isotopic compositions of Pb were realized in composite samples, the normal distribution  
212 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  
214 used for all the statistical analyses.

### 216 **3. Results and discussion**

#### **3.1. Pb concentrations**

218 Resulting Pb concentrations and isotopic composition for the environmental and  
biological samples from Chiricahueto marsh and Urías estuary, representative of the  
220 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  
222 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  
224 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  
226 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  
228 Water Quality Criteria (USEPA, 2006) which represents the level to which an aquatic  
community can be exposed indefinitely without an unacceptable effect.

230

The Pb in the SPM or seston was significantly higher ( $p < 0.05$ ) in Chiricahueto  
232 marsh than in Urías estuary ( $95.3 \pm 33.4$  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  
234 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  
236 (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,  
238 from  $24.1 \pm 10.6$  and  $17.4 \pm 7.3 \mu\text{g g}^{-1}$ , respectively. Similarly to seston, there were  
240 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  
242 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-  
244 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  
246 (ERM) of  $46.1 \mu\text{g g}^{-1}$  (Long et al., 1990).

In addition to the environmental matrices, organism monitors occupying different  
248 trophic levels, such as primary producers and primary, secondary and tertiary consumers  
with different feeding strategies (e.g. grazing, burrowing, filter-feeding, suspension and  
250 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  
252 samples, which reflects the surface uptake of dissolved Pb in the water column (Fisher et al,  
1987; Phillips, 1990; Haritonidis and Malea, 1999), averaged  $3.0 \pm 0.7$  and  $2.0 \pm 0.7 \mu\text{g g}^{-1}$

254 for *U. lactuca* and  $5.1\pm 3.3$  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  
256 in Chiricahueto marsh which is receiving municipal sewage and agriculture effluents.  
Previous studies of macroalgae suggest that interspecies metal accumulation may be  
258 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  
260 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  
262 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  
264 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  
266 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  
268 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  
270 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  
272 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  
274 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  
276 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  $3.0 \pm 1.0$   
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  $3.3 \pm 1.9$   
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).



300 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  $\mu\text{g g}^{-1}$ ),  
302 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  
304 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  
306 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  
308 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  
310 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%  
312 exceeded the safety limits set by the EC. Finally, Pb concentrations in crabs exceeded all of  
these guidelines.

314

### 3.2. Stable Pb isotope compositions

316 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  
318 and 2.456, respectively. Pb isotopic ratios of the sediments were comparable in  
Chiricahueto marsh (1.200 $\pm$ 0.005 and 2.456 $\pm$ 0.009) and Urías Estuary (1.202 $\pm$ 0.004 and  
320 2.464 $\pm$ 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  
322 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) ( $1.188 \pm 0.005$  for  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $2.455 \pm 0.008$  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 ( $1.195 \pm 0.002$  and  $2.471 \pm 0.003$ , respectively;  
336 Cummins et al., 1979), and (iii) the influence of a non-regional source derived from U.S.  
aerosols from industrial emissions ( $1.21 \pm 0.02$  and  $2.455 \pm 0.02$ ; 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  
348 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  
350 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  
352 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.

354 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  
356 (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)  
358 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  
360 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  
362 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).

364 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-  
366 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  
368 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%  
370 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  
372 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%),  
374 with only 10-30% derived from natural sources. Pb in crab samples with highest  
concentrations was >90% associate with leaded gasoline.

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#### 4. Conclusions

378 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  
380 samples. Results revealed differences in Pb concentrations between different species of  
biomonitors, obviously related to different feeding strategies toxicokinetics of Pb. All  
382 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  
384 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  
386 organisms including macroalgae, shellfish, crabs, and fish. The other is uptake of  
available Pb from sediments by angiosperms such as mangroves and halophytes.

388 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.  
390 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  
392 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-

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

396

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512 Table 1. Lead analysis of standard reference materials.

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

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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)
Saltwort ( <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				

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Table 3. 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 Urias estuary.

	n	Pb ( $\mu\text{g g}^{-1}$ )	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{208}\text{Pb}/^{207}\text{Pb}$
<b>Environmental matrices</b>				
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)
<b>Primary producers</b>				
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)
<b>Primary consumers</b>				
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 dentivaricans</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

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542 Legends

Figure 1. Study area in the Gulf of California ecoregion: Chiricahueto marsh near the city  
544 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  
546 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  
548 (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  
550 (see text for references).

Figure 3. Scatter plot of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios versus Pb concentration of environment and  
552 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  
554 Mexican Pb ores (blue) and the United States emissions (yellow).

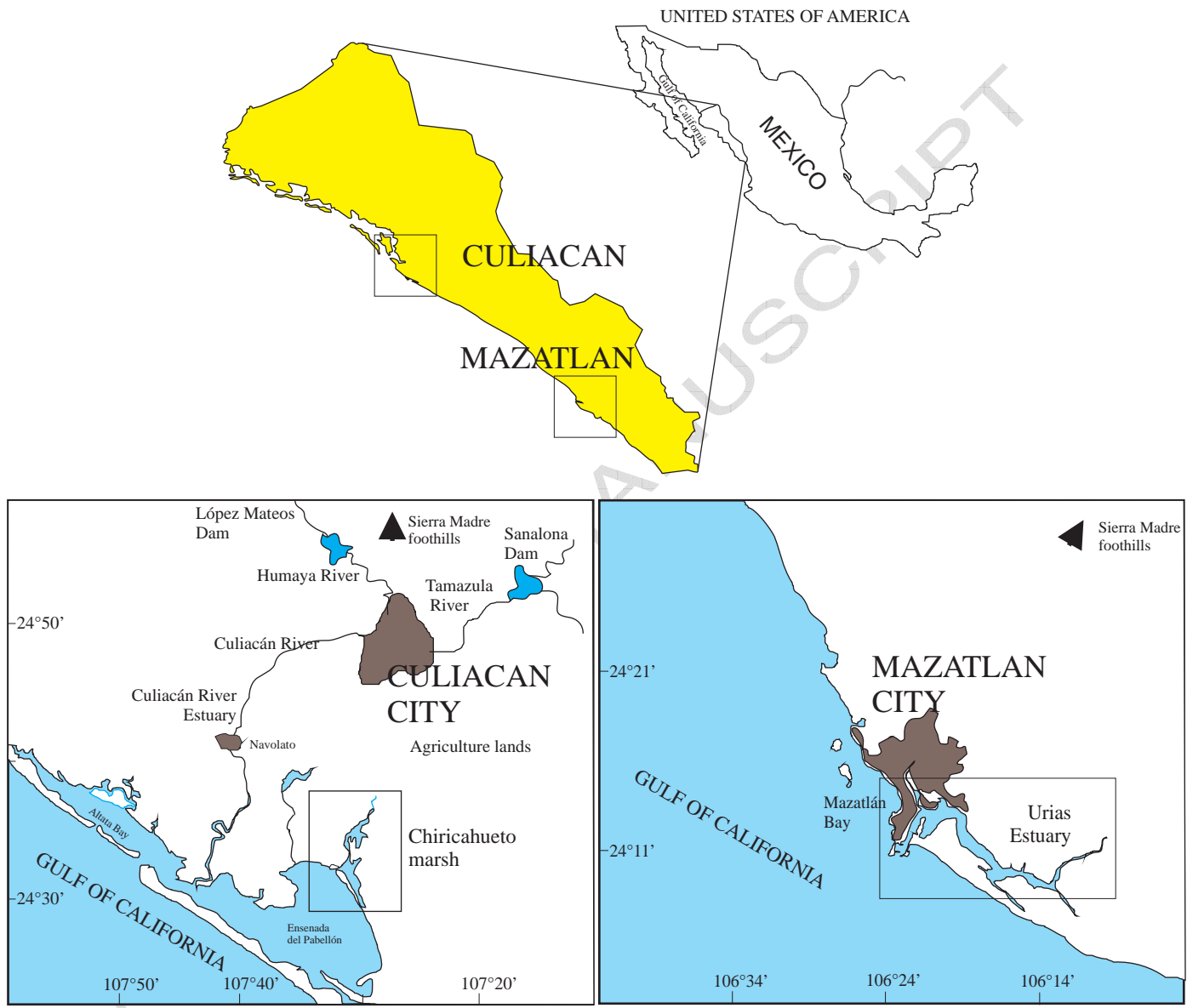


Fig. 1. Soto-Jimenez et al.

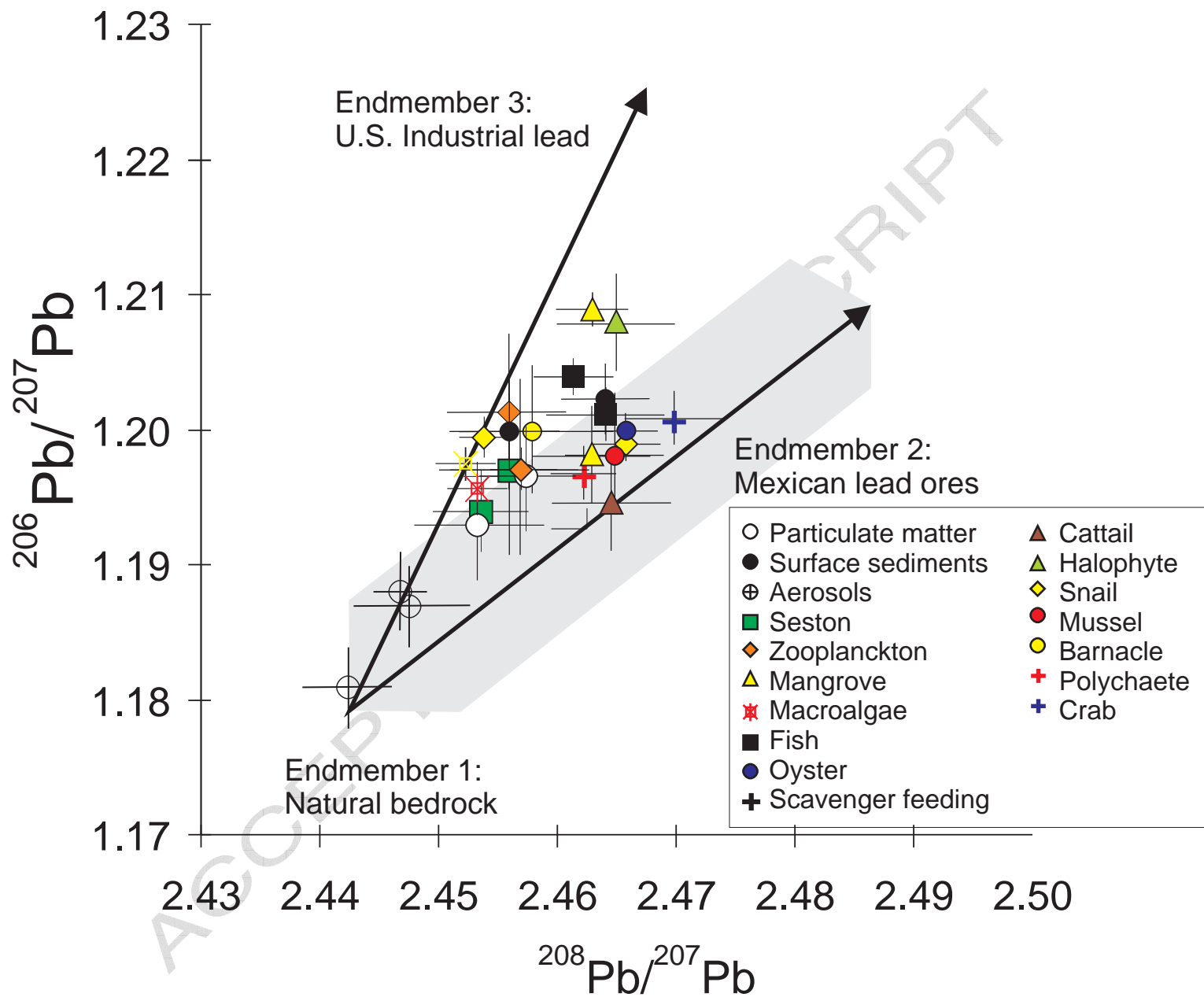


Fig. 2. Soto-Jimenez et al.

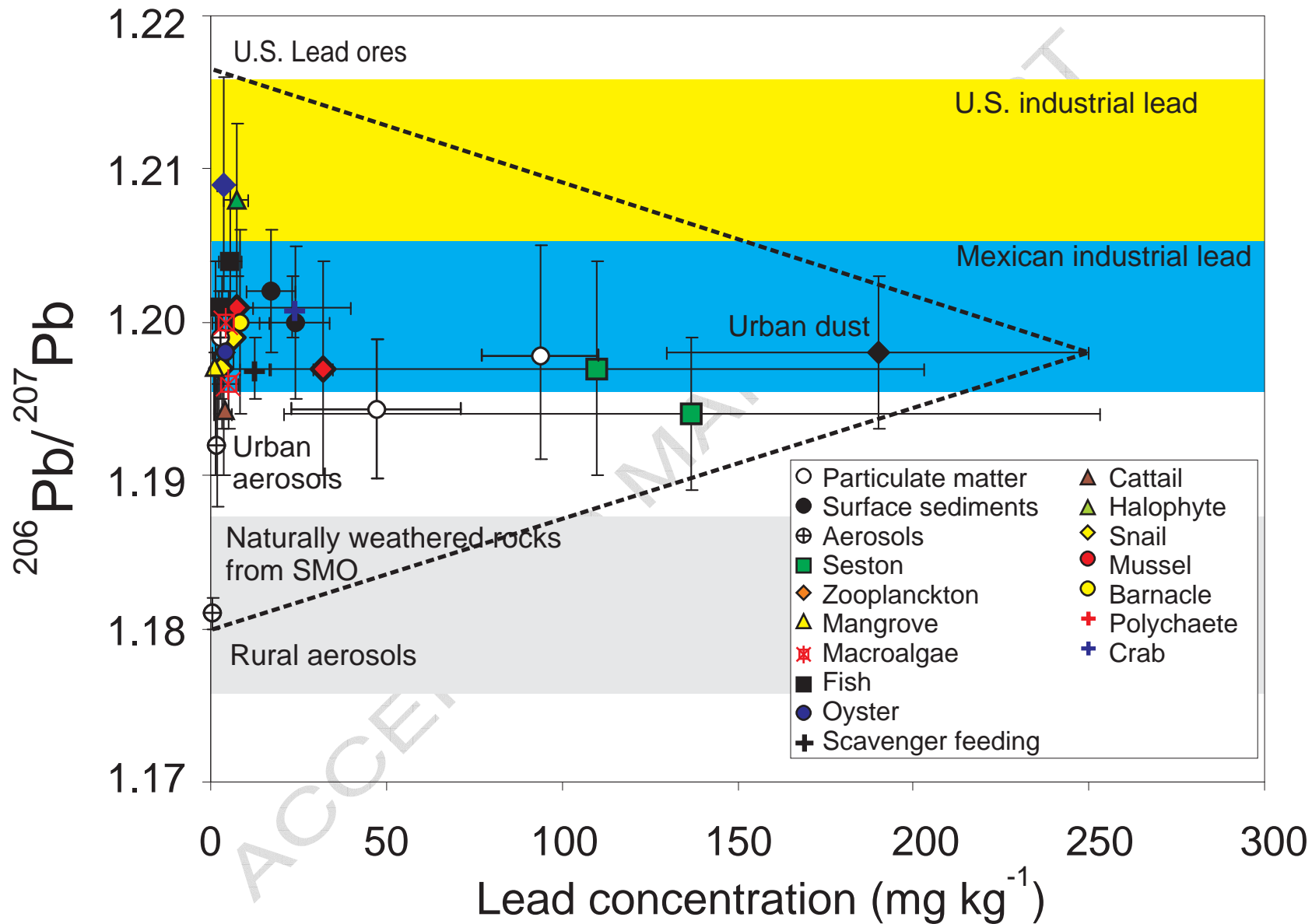


Fig. 3. Soto-Jimenez et al.