# Nueces Bay Zinc in Sediment Profiling Assessment

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## Executive Summary

This project addressed two important questions and complements the ongoing Total Maximum Daily Load (TMDL) and Implementation Plan for zinc in Nueces Bay. This project (1) identified a legacy layer of zinc in the sediment of Nueces Bay and (2) determined that zinc sediment concentrations that are currently detected in the surficial layer are likely legacy but are also representative of the present zinc loading to Nueces Bay.

From 1941-1985 the American Smelting and Refining Company (ASARCO) was a high-grade zinc production facility located on the south side of Nueces Bay on approximately 108 acres. The ASARCO/ENCYCLE facility is located along the northern side of the Corpus Christi Inner Harbor (CCIH) and borders McBride Lane and Valero Refining to the east, and Up River Road and Dona Drive on the south (http://tceq.texas.gov/remediation/sites/encycle_facility/encycle).

This facility discharged contaminated effluent into Nueces Bay and the CCIH during its period of operation (TCEQ 2006, 2007, 2008, 2010). It is presumed that Nueces Bay received legacy zinc loadings through the Central Power and Light (CPL) electrical generating station that used CCIH water as once pass-through cooling water for facility operations until the operations ceased in December 2002 (Mrini et al. 2003). In 2004, Topaz Power Group purchased the CPL electric facility and began construction in 2008. The electric facility was renamed the Nueces Bay Energy Center (http://topazpowergroup.com/power-plants/nueces-bay-power-plant and became commercially operational and began discharging into Nueces Bay in 2010 (Permit No. WQ0001244-000).

The Texas Department of Safety and Health Services (DSHS) closed Nueces Bay to the harvesting of oysters in January 1995 under authority of Chapter 436 of the Texas Health and Safety Code (DSHS 2003; DSHS 2005). Following the 1995 oyster closure, Nueces Bay was put on the *Texas Water Quality Inventory and 303(d) List* for impaired oyster waters. The DSHS collected oysters from Nueces Bay in 2002 and again found elevated zinc levels in oysters ranging from 479-2300 mg/kg (CBBEP 2005). Since 2006, a TMDL has been implemented in Nueces Bay (Segment 2482) for zinc in oyster tissue not meeting the State of Texas acceptable level of <700 mg/kg. The TMDL established a total zinc criterion for surface water in Nueces Bay of 29 μg/L. For all other marine waters in the State of Texas the TCEQ established criteria is for dissolved zinc in water and is 87.2 μg/L. The TCEQ established zinc in sediment criteria is 410 mg/kg.

Nine TCEQ stations in Nueces Bay were sampled in June 2013. Mean water temperature was 28.93°C with station 14833 located near the NBEC having the warmest reading at 30.40°C. Mean salinity was 38.20 ppt with station 18866 located in back, or western portion of Nueces Bay having the highest salinity at 40.09 ppt. Mean pH of all stations sampled was 7.93 and mean DO % and mg/L were 90.94 and 5.65, respectively.

A legacy layer of zinc was identified in sediment cores in the southern part of Nueces Bay near the historical ASARCO/ENCYCLE and CPL discharge points (Fig. ES 1 and Fig. ES 2). Based on the minimum and maximum sediment profile zinc concentrations, it was determined that natural occurring zinc in sediment in Nueces Bay appears to be <124 mg/kg in the middle and northern parts of the bay. Based on the classification of Long et al. (1995) and MacDonald et al. (1996) this concentration is below the Threshold Effects Level (TEL). Stations 18619 and 14833 had zinc concentrations within the Effects Range Low (ERL) and Station 21484 exceeded the Effects Range Median (ERM) (see Table 4). Station 21484 is the only station sampled that appears to have undisturbed sediments and therefore is the focus for dating purposes.

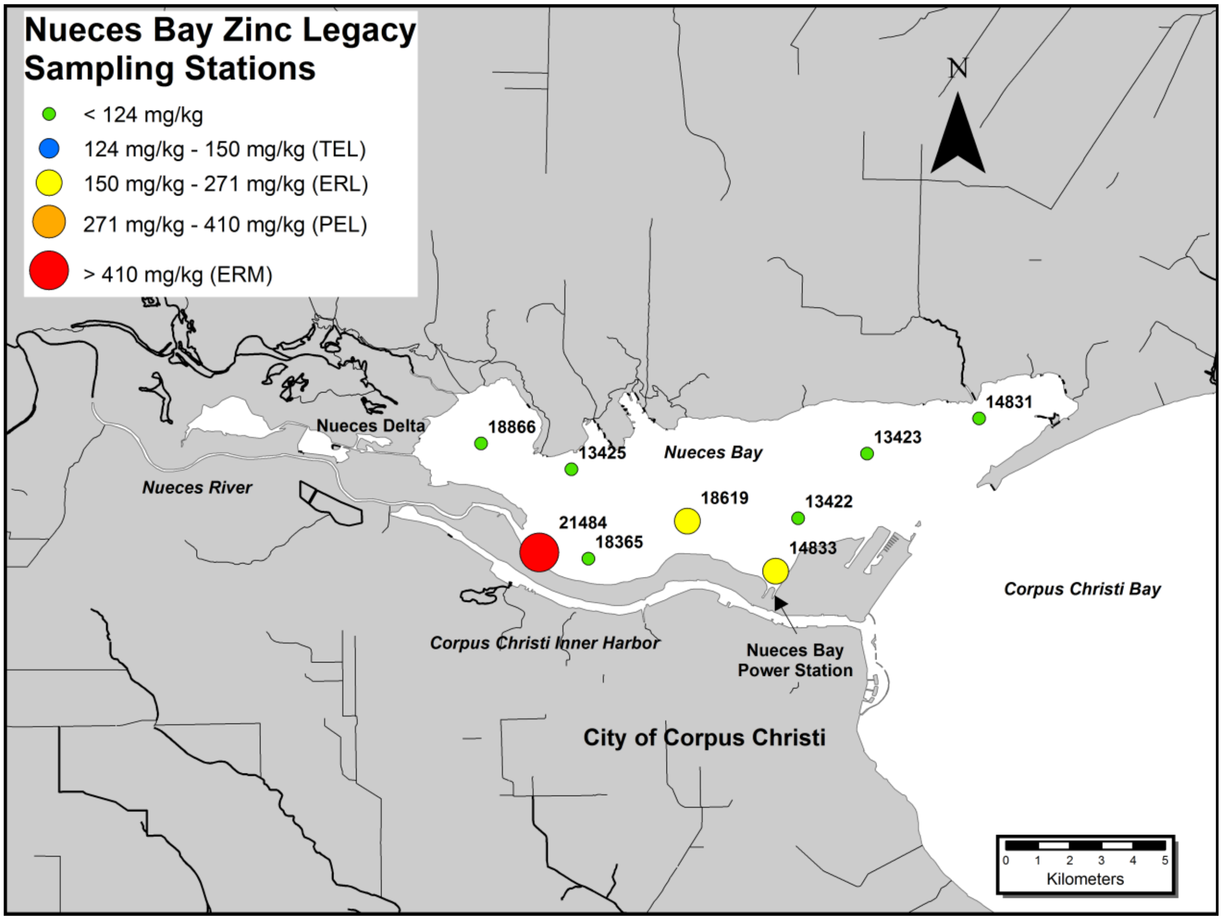


Figure ES 1. Maximum concentration of zinc in sediment (mg/kg) collected from Nueces Bay sediment profile assessment.

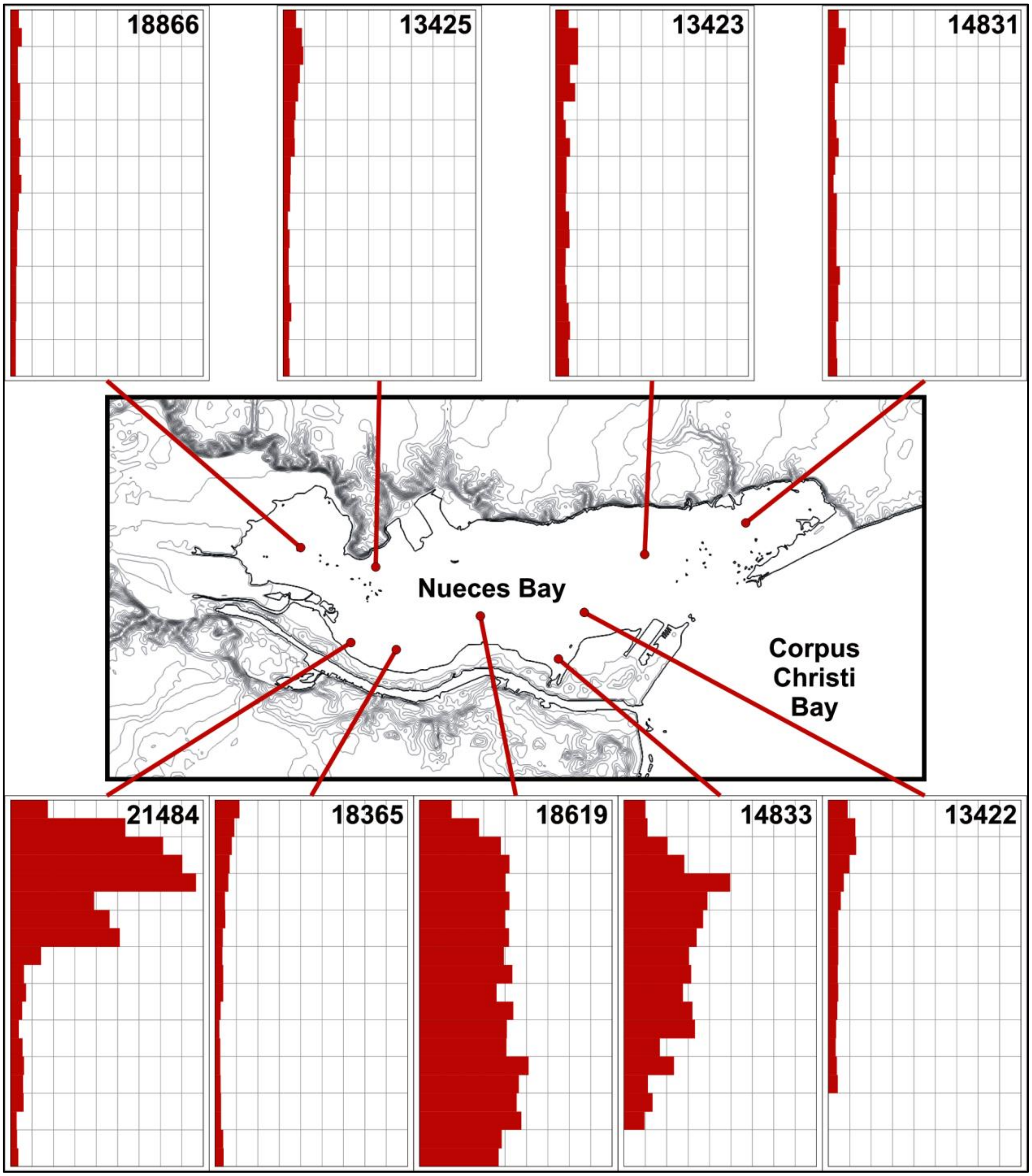


Figure ES 2. Zinc concentration profiles for Nueces Bay sediment cores from 0-100 cm depth. The horizontal scale for all nine plots is identical, and ranges from 0-450 mg/kg. The graticules mark increments of 10 cm in the vertical direction, and 50 mg/kg in the horizontal direction. The profiles have a blocky appearance because samples were analyzed in 5 cm stratigraphic intervals.

Though attempts at directly dating the stratigraphy by radioanalysis of $^{137}Cs/^{210}Pb$ were problematic, we suggest an alternative indirect dating solution based on a historical analysis of ASARCO zinc production rates, and the zinc concentrations seen in the sediment core from Station 21484.

Historical references were gathered from a variety of sources to assemble an estimated zinc production rate curve for the ASARCO plant from the start of production (October 1942) up to the closure of the facility in 1985 ([http://tshaonline.org/handbook/online/articles/dkl0](http://tshaonline.org/handbook/online/articles/dkl0)). The production rate curve is admittedly an estimate because it is built from both hard and inferred/anecdotal data. Altogether, these data points were used to assemble the production rate curve seen in (Fig. ES 3).

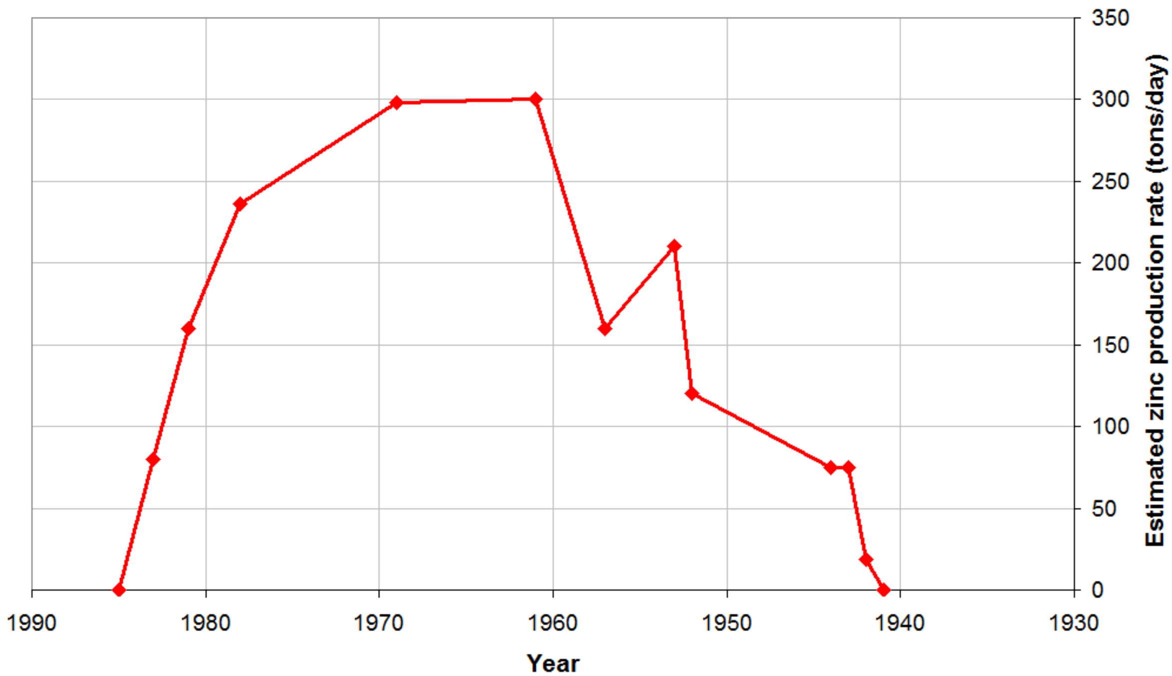


Figure ES 3. Estimated zinc production rate at ASARCO plant based on historical analysis.

The curve shows a rapid ramp up in 1942 when the plant first came online in October of that year to help with production for World War II. A second quick ramp up occurs in the early 1950's, and is probably related to production increases for the Korean War. Another ramp up occurs from 1960-1961 when ASARCO brought online a new plant that essentially doubled production capacity. From 1970 onward the production rate decreases till the plant finally closed in 1985.

If we assume that the amount of effluent from the plant is proportional to the overall zinc production rate, the estimated historical production rate curve shows a remarkable similarity to the shape of the zinc concentration levels seen in the sediment core from Station 21484. This can be seen in Figure ES 4, which shows multiple data sets plots along the length of the core. In this figure, the estimated historical production rate curve has been overlaid on to the zinc concentration data to show the notable correspondence between the two curves. We therefore offer this as an indirect dating solution for the stratigraphy at Station 21484.

Station 21484 zinc data clearly shows current surficial zinc deposition in Nueces Bay is lower than historical loads related to ASARCO/ENCYLE operations. This study identified sinks or hotspots in Nueces Bay where zinc has the potential to be rereleased back into the water column via natural or human disturbance. Current surficial levels of zinc collected from this study are below TCEQ's 410 mg/kg criteria. However, at deeper levels elevated concentrations do exist. Reduced surficial zinc concentrations may be contributed to natural sedimentation rates in Nueces Bay reducing surface zinc concentrations or biological uptake via filtering from the oyster population in Nueces Bay. Future projects involving activities which disturb sediments in Nueces Bay can be better managed since areas with elevated levels of zinc have been identified.

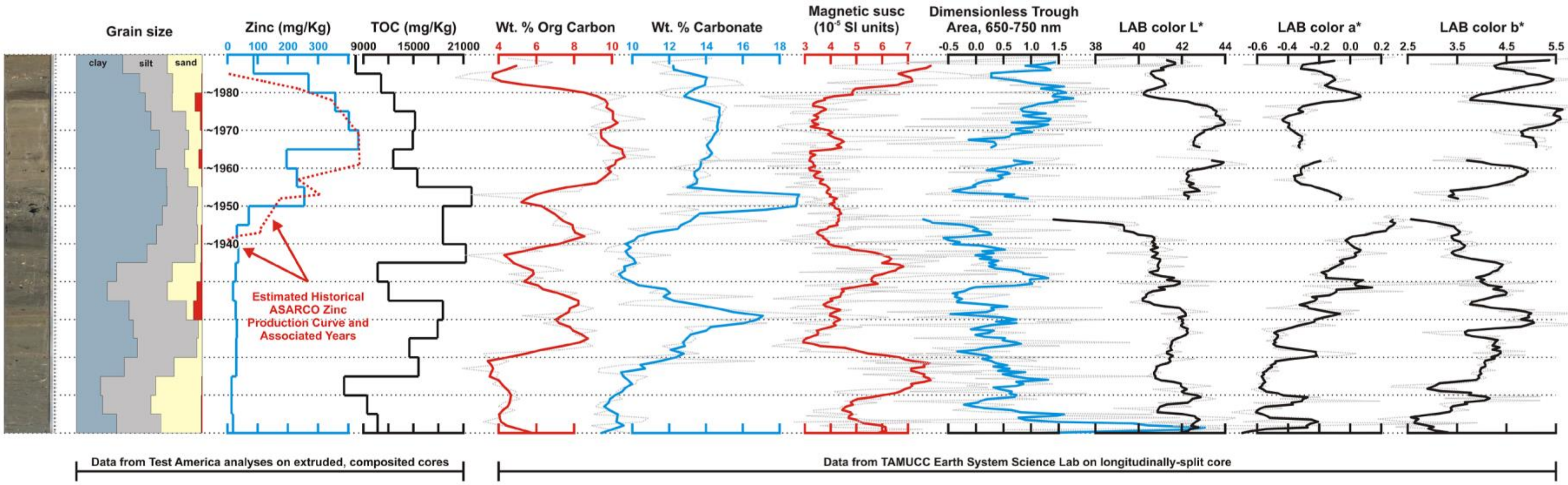


Figure ES 4. High-resolution multi-proxy results for the Station 21484 sediment core. This figure shows a color image of the longitudinally-split core from Station 21484 from 0-100 cm (image at left) along with ten data sets produced from analyses along the length of the core (gray dotted lines indicate 10 cm increments). Note that the estimated historical zinc production curve (dotted red curve) is overlaid on to the zinc concentration data, and their shapes are remarkably coincident. Based on this relationship, estimated ages for the stratigraphy are presented alongside the grain size data plot. The ten data sets are split into two groups. The first three data sets with the blocky appearance are from the composited, extruded sediment cores. The plots in the last seven positions were produced from high-resolution analyses of the longitudinally-split sediment core. As these two groups of data were produced from nearby but different sediment cores, a slight vertical adjustment is necessary to bring the stratigraphy into alignment based on analysis results. In particular, the data from the longitudinally-split sediment core must be shifted down ~5 cm to bring it into alignment with the results from the composited sediment core. This adjustment has not been made in this figure, i.e. both groups of data are plotted against the raw depths in their respective cores. Regarding the different appearance between the two groups of data, the composited core data has a blocky appearance because it was produced from 5-cm stratigraphic slices. Furthermore, there is generally less variability in this data because it averages together sediments from three different cores over a large stratigraphic interval. In turn, the data from the longitudinally-split sediment core shows much higher variability and higher frequency changes because analyses were run at a higher resolution (0.5 or 1.0 cm resolution) on a single sediment core. Full resolution data for these seven analyses is presented as the light gray dotted lines in the background. In turn, the visually prominent curve in each plot is a centered, five-point running mean of the full resolution data set. The weight percent organic matter and carbonate content curves were produced at 1.0 cm resolution using the loss-on-ignition method. The organic matter content as estimated by this method returns higher values than estimated by TOC analysis, but this is not uncommon as both methods have different limitations and capabilities, and the composited core data involves significant averaging as mentioned above. The large positive spike in the weight percent carbonate curve at ~40 cm reflects an abundance of shell hash. The spike at ~ 70 cm in the same curve corresponds with lighter-colored, but coarser bands in the stratigraphy, and their significance requires further analysis. The magnetic susceptibility curve generally serves as proxy for terrestrial input either via river inflow or direct surface runoff from storm events. Thus, variations along its length may represent periods of more/less river flow (i.e. more/less sediment delivery). For example, the lower values recorded between 10-50 cm may be indicative of a period of reduced inflow related to the development of the La Fruta Dam, Lake Corpus Christi, and Choke Canyon, and the return to higher values in the uppermost 10 cm may reflect the initiation of mandated water releases and freshwater inflows. However, this interpretation cannot be confirmed at this time, and further analysis is needed to rule out other changes that could have varied the amount of siliciclastic sediment delivered to the system (for example, a geomorphic change like a shift of the river mouth). The last four columns represent results from diffuse color reflectance spectrophotometric scanning. The Dimensionless Trough Area (DTA) parameter has been used as a proxy to track chlorophyll content in oceanic and lacustrine settings. We are hesitant to make an interpretation about this parameter with respect to this core because Nueces Bay is well-mixed, and additional confirmatory data such as pigment analysis by high-performance liquid chromatography (HPLC) is not available for this core. However, preliminary results from similar analyses on sediment cores from Baffin Bay show an excellent correspondence between DTA calculations and HPLC results. The LAB color L* parameter is a general measure of the lightness/darkness of a material, and this varies according to composition, grain size, organic content, redox conditions during deposition, and other factors. The LAB color a* and b* parameters track color continuums between green and red, and blue and yellow, respectively, and these are also generally reflective of changes in sediment composition.

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## Introduction

From 1941-1985 the American Smelting and Refining Company (ASARCO) was a high-grade zinc production facility located on the south side of Nueces Bay on approximately 108 acres. The ASARCO/ENCYCLE facility is located along the northern side of the Corpus Christi Inner Harbor (CCIH) and borders McBride Lane and Valero Refining to the east, and Up River Road and Dona Drive on the south (http://tceq.texas.gov/remediation/sites/encycle_facility/encycle).

This facility discharged contaminated effluent into Nueces Bay and the CCIH during its period of operation (TCEQ 2006, 2007, 2008, 2010). Between 1988 and 2002, ASARCO operated under the name ENCYCLE and was a commercial hazardous waste management facility. The effluent generated from the ENCYCLE facility was discharged to the CCIH through the permitted outfall (001) (Permit No. 00314 or NPDES Permit No. TX0003191). It is presumed that Nueces Bay received legacy zinc loadings through the Central Power and Light (CPL) electrical generating station that used CCIH water as once pass-through cooling water for facility operations until the operations ceased in December 2002 (Mrini et al. 2003). In 2004, Topaz Power Group purchased the CPL electric facility and began construction in 2008. The electric facility is now the Nueces Bay Energy Center and became commercially operational in 2010 (http://topazpowergroup.com/power-plants/nueces-bay-power-plant). The Nueces Bay Energy Center began discharging into Nueces Bay in 2010 (Permit No. WQ0001244-000).

In 1994, Texas Commission on Environmental Quality (TCEQ) confirmed zinc contamination in neighborhood soils within Dona Park, located south of the turning basin of the Port of Corpus Christi. After the state confirmed zinc contamination to residential soil, the public was concerned with seafood safety in Nueces Bay. The Texas Department of State Health Services (DSHS), formerly the Texas Department of Health (TDH) found zinc levels in oysters ranging from 2294-2482 mg/kg in Nueces Bay (CBBEP 2005). ASARCO was found legally responsible for the zinc contamination and agreed to a settlement of over $1.8B to clean up more than 80 sites in 20 states, including Nueces Bay.
(http://epa.gov/compliance/resources/cases/cleanup/cercla/asarco/asarco-fs.html;
http://tceq.state.tx.us/assets/public/remediation/variousremediationsites/settlementagreement.pdf)

The DSHS closed Nueces Bay to the harvesting of oysters in January 1995 under authority of Chapter 436 of the Texas Health and Safety Code (DSHS 2003; DSHS 2005). Following the 1995 oyster closure, Nueces Bay was put on the *Texas Water Quality Inventory and 303(d) List* for impaired oyster waters. The DSHS collected oysters from Nueces Bay in 2002 and again found elevated zinc levels in oysters ranging from 479-2300 mg/kg (CBBEP 2005). Since 2006, a Total Maximum Daily Load (TMDL) has been implemented in Nueces Bay (Segment 2482) for zinc in oyster tissue not meeting the State of Texas acceptable level of <700 mg/kg. The TMDL established total zinc criterion for surface water in Nueces Bay is 29 µg/L. For all other marine waters in the State of Texas the TCEQ established criteria for dissolved zinc in water is 87.2 µg/L and zinc in sediment is 410 mg/kg. Consuming oysters contaminated with zinc over a long period can cause systemic adverse health effects including dehydration, abdominal pain, nausea, vomiting, lethargy, dizziness, anemia and changes in blood profiles (CBBEP 2005).

Under the current FY 2013 TMDL, 10 stations are sampled for zinc in sediment and water (seven in Nueces Bay proper, one in Nueces River tidal, and two in the Corpus Christi Inner Harbor) and five stations located in Nueces Bay proper are sampled for zinc in oyster tissue (Nicolau and Nuñez 2004, 2005b, 2006b; Nicolau and Hill 2010, 2011, 2012, 2013). As of 2013, zinc in oyster tissue still exceeds the 700 mg/kg TCEQ criterion (Nicolau and Hill 2013).

**Objective**

This project addressed two important questions and complements the ongoing TMDL and Implementation Plan for zinc in Nueces Bay. This project (1) identified a legacy layer of zinc in the sediment of Nueces Bay and (2) determined that zinc sediment concentrations that are currently detected in the surficial layer are likely legacy but are also representative of the present zinc loading to Nueces Bay.

Assessment of historical records of zinc loading and deposition in Nueces Bay was determined using sediment profiling to confirm if a legacy layer exists and to what depth. The sampling design consisted of nine stations focusing on the two historical ASARCO outfalls in Nueces Bay and sites outside of the historical outfalls were sampled. A sediment profile assessment for zinc, TOC, and sediment grain size at 5 cm increments up to 1 m deep was analyzed from each station. In addition, sediment dating using lead ($^{210}Pb$ and $^{137}Cs$) was conducted for two stations.

Total organic carbon measures the long-term buildup of natural organic carbon entering the system via geology, decomposition of plant and animals, algal biomass, and living and dead microorganisms that can ascertain periods of eutrophication. However, organic carbon build-up in sediment can also be a result of anthropogenic contamination from spills or discharges into the system. Schumacher (2002) stated, total carbon contributions from contaminants are typically measured in the g/kg to mg/kg concentration range compared to the total organic carbon content of the soil or sediment measured in % which is typically small unless a spill recently occurred, raw materials are present, or a hot spot was sampled. Most analytical methods for TOC, however, do not differentiate between the sources of organic carbon types.

Sediment grain size characterizes the composition and the derived sources of sediment entering the system which affects TOC and trace metal enrichment. Sediments rich in clays can have higher TOC since clays stabilize and protect TOC from decomposing. Clays also can have higher trace metal concentrations due to the affinity metal has with clay (Sun et al. 2013).

Magnetic susceptibility essentially reflects the magnetic response of a sample to an applied magnetic field. Watershed processes like soil development and forest fires can also impart sediments with a strong magnetic susceptibility signal. For this reason, magnetic susceptibility is often used as a proxy for terrestrial and/or siliciclastic input such as that brought in by a river system, or that may enter the basin via overland flow and runoff. Importantly, one of the main uses for studying magnetic susceptibility profiles in aquatic sediment cores is to correlate stratigraphy between locations. Even if the stratigraphy is completely homogeneous with no visual cues to correlate from core to core, it is often possible to correlate between such cores simply based on their magnetic susceptibility profiles. This is the main use for magnetic susceptibility in this study.

## Study Site

Nueces Bay is a shallow secondary bay approximately 75 $km^2$ with an average depth of 2.3 m. It is located in Nueces and San Patricio County at the mouth of the Nueces River. The Port of Corpus Christi runs parallel along the bay's southern edge along with an industrial complex that includes oil refineries, chemical plants, a power plant, and a railway system. The city of Portland is on the northern edge of Nueces Bay with residential homes along the shore, vast areas of agriculture land, and the Papalote Creek Wind Farm consisting of 196 turbines. The bay is typically turbid from sediment resuspension caused by wind and wave action. Besides these natural mechanisms, the bay bottom has been pervasively disturbed through the years by a mix of human activities including dredging, and the extensive installation, development, and maintenance oil/gas wells, pipelines, and electric utility power lines.

A total of nine sampling sites were selected based on pre-existing TCEQ sites with consideration given to site accessibility and sampling crew safety (Fig. 1). Of the nine sites sampled, one request for a new identification number (21484) was submitted from the Center for Coastal Studies (CCS) at Texas A&M University-Corpus Christi to TCEQ and established a new site in Nueces Bay. TCEQ site locations were selected prior to field sampling and based on criteria described in the TCEQ Surface Water Quality Monitoring Procedures Volume 1: Physical and Chemical Monitoring Methods for Water, Sediment, and Tissue (TCEQ 2012).

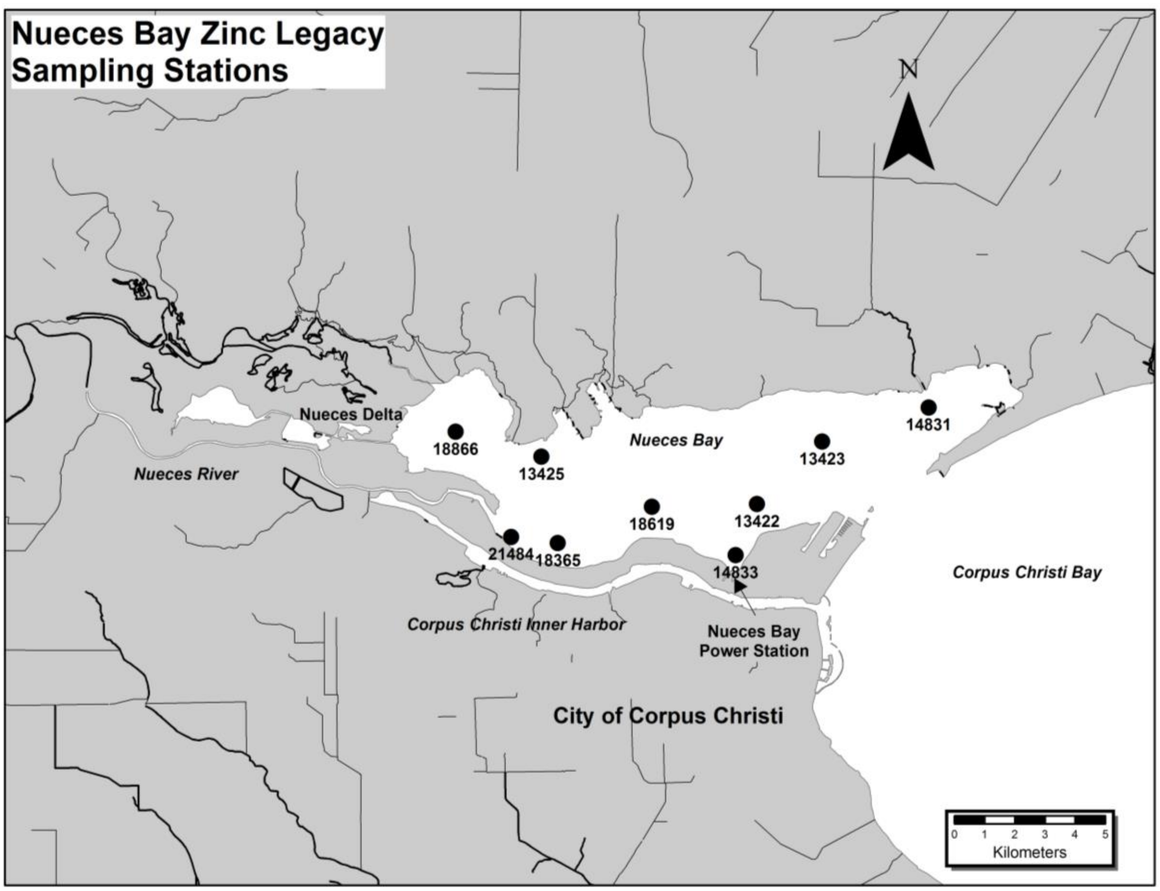



Figure 1. Map of Nueces Bay TCEQ zinc sampling sites.

## Sampling and Analysis Methods

### *Water Column Measurements*

Water column measurements were collected prior to disturbing the sediment. Measurements were taken using a YSI 6920 Multiprobe connected by cable to a display unit and included: water temperature (°C), dissolved oxygen (mg/L), conductivity (μmhos), salinity (Practical Salinity Units or PSU), and pH (standard units or su). Water column profiles were conducted when depth was > 1.5 m according to TCEQ requirements for vertical depth profiles. Secchi depth measurements were collected at each station using a standard 20-cm diameter black and white secchi disc.

### *Composited Sediment Profile*

Sediment cores were retrieved from a pontoon boat using a hand-operated hammer/percussion coring system fitted with 6.7 cm internal diameter polycarbonate tubing. Three to five cores up to ~2.0 m in length were obtained from each station; however, only the uppermost 1.0 m of stratigraphy was examined for this study.

Three of the cores from each site were immediately subsampled on return to the laboratory to provide material for the analysis of total zinc, total organic carbon (TOC), and sediment grain size (SGS). These cores were simultaneously extruded in 5 cm increments yielding 20 stratigraphic samples per site given the 1.0 m depth focus. The 5 cm increments were sliced from the cores and homogenized into final composite samples using EPA-approved, sterilized plastic scoops and containers. Each final sample was composed of grabs from at least two, but usually three, sediment cores. A new plastic scoop was used for each stratigraphic interval so as to prevent cross-contamination. Once the sediment was homogenized, approximately 114 g of composited material was transferred into clean, pre-labeled glass jars and held on wet ice at 4°C until laboratory processing. The total zinc, TOC, and SGS analyses were performed on a contract basis by TestAmerica Laboratories, Inc. (1733 N. Padre Island Drive Corpus Christi, TX 78408).

The remaining sediment cores for each site were split longitudinally down the length of the core into work and archive halves. The archive halves were curated for potential future work, and preserved in refrigerated storage at 3°-4°C. Archive halves for stations 21484 and 13422 were utilized for $^{210}Pb/^{137}Cs$ radioisotope dating analyses (see below), and are no longer available. High-resolution photographic mosaic images were produced from the work halves as a permanent visual record of the stratigraphy. These core halves were also analyzed over their length at 1 cm resolution via diffuse color reflectance scanning, and also for their magnetic susceptibility signal.

Table 1. Parameters analyzed for the Nueces Bay Legacy Project.

| FIELD PARAMETERS (Water) | Units | TCEQ Parameter Codes |
|---|---|---|
| Total Depth | Meters | 82903 |
| Depth Sample Collected (Grab) | Meters | 13850 |
| Water Temperature (Grab) | °C | 00010 |
| Dissolved Oxygen Saturation (Grab) | % | 00301 |
| Dissolved Oxygen (Grab) | mg/L | 00300 |
| Conductivity (Grab) | µS/cm | 00094 |
| Salinity (Grab) | Practical Salinity Units | 00480 |
| pH (Grab) | su | 00400 |
| Secchi Depth | Meters | 00078 |
| Tide Stage | DNR Tide Gauge | 89972 |
| Water Color | Visual assessment | 89969 |
| Water Odor | Olfactory assessment | 89971 |
| Water Surface | Visual assessment | 89968 |
| **FIELD PARAMETERS (Weather)** | **Units** | **TCEQ Parameter Codes** |
| Air Temperature | °C | 00020 |
| Barometric Pressure | mm/Hg | NA |
| Cloud Cover | % | NA |
| Dew Point | °C | NA |
| Heat Index | °C | NA |
| Present Weather | Visual assessment | 89966 |
| Relative Humidity | % | NA |
| Wind Chill | °C | NA |
| Wind Direction | Compass Direction | 89010 |
| Wind Speed | MPH | NA |
| **TRACE METALS IN SEDIMENT** | **Units** | **TCEQ Parameter Codes** |
| Zinc | mg/kg dry weight | 01093 |
| **ORGANICS** | **Units** | **TCEQ Parameter Codes** |
| Total Organic Carbon (TOC) | mg/kg dry weight | 81951 |
| Total Solids | % | 81373 |
| **SEDIMENT GRAIN SIZE** | **Units** | **TCEQ Parameter Codes** |
| SGS Clay (<0.0039 mm) | % dry weight | 82009 |
| SGS Silt (0.0039 to 0.0625 mm) | % dry weight | 82008 |
| SGS Sand (0.0625 to 2.0 mm) | % dry weight | 89991 |
| SGS Gravel (>2.0 mm) | % dry weight | 80256 |

*Sediment Dating By Radioanalysis*

The station 21484 and 13422 sediment cores were sampled and sectioned at 1-cm intervals, and freeze dried in the TAMUCC Earth System Science Laboratory. The freeze dried samples were transported to the Conrad Blucher Institute Radioanalysis Laboratory at TAMUCC for further processing.

The samples were crushed into small particles with a mortar and pestle prior to filling wear-resistant 55 mm long Nylon tubes of 9.52 mm outer diameter (OD) and 7.94 mm inner diameter (ID) with sample materials. Other possible sample-vial materials were tested, Clear Cellulose (Butyrate), Impact-Resistant Polycarbonate and Machinable and Bendable Clear PETG, as well as different vial lengths. The selected material and geometry resulted in the best signal to noise ratio. The weight of the sample was measured before filling the vial tube with material. After filling, the vial tubes were capped on each end with 7.94 mm diameter x 3 mm beveled nylon pieces and sealed hermetically with a layer of epoxy. All preparation equipment was cleaned and dried prior to contact with samples and work was conducted on a clean surface such as a large Kimwipe® which was replaced after each individual sample processing.

The spectrometer equipment and experimental geometry is presented in Figures 2 & 3. The central piece of the spectrometer is an EG&G Ortec High Purity Germanium (HPGe) well detector, model GWL-120-10-LB-AWT, with an OFHC copper Endcap and high purity aluminum well tube. The well tube has a diameter of 10 mm and a depth for 40 mm. The HPGe crystal has an active volume of 120 $cm^3$. The energy resolution (FWHM) of the detector is better than 1.2 keV at 122 keV and better than 2.10 keV at 1.333 MeV. Other parts of the system include a low-background streamline side-looking cryostat, EG&G Electronics (detector power, bias, pre-amplifier), a very low background shield including a 2 tons pre-WWII lead shroud with a graded Z shield (Copper & Cadmium). The signal from the spectrometer was analyzed by an EG&G Trump Card Multi Channel Analyzer and the EG&G Maestro®-32 Software.


Figure 2. Spectroscopy Station.

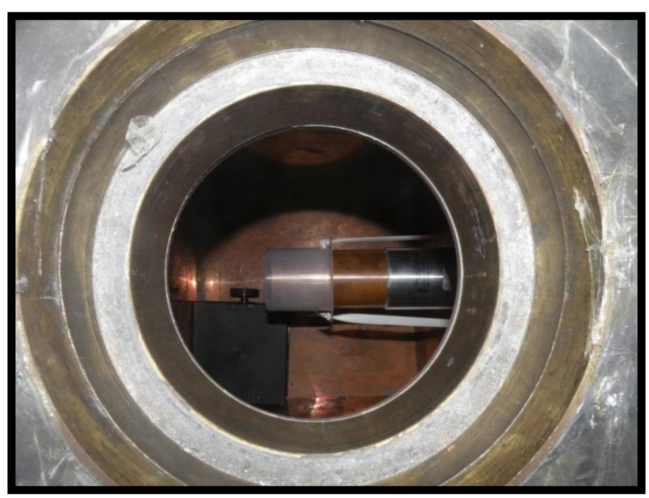


Figure 3. Experimental Geometry w/o lid.

### *Gamma Ray Analysis*

Gamma counting of the samples was performed for at least 125,000s (34 hrs) per sample for Core 21484 with an average sampling time of 195,000s (54 hrs). A total of 48 samples were analyzed for Core 21484. A smaller number of samples (10) were analyzed for Core 13422 for comparison with an average sampling time of 149,000 secs. For each spectrum the following lines in the gamma ray spectra were analyzed: $^{210}$Pb (46 keV), $^{214}$Pb (351 keV), $^{214}$Bi (609 keV), $^{137}$Cs (662 keV), $^{228}$Ac (911 keV), and $^{40}$K (1,460 keV). For gamma ray lines influenced by the background of the spectrometer, $^{214}$Pb, $^{214}$Bi, $^{228}$Ac and $^{40}$K, background counts were subtracted based on the spectrum acquisition time. Uncertainty in the count rates was computed based on the estimated standard deviation of the counts and expressed graphically with error bars representing +/- 1 standard deviation (Knoll 1989).

Counts were above the detection limit of the system for all the above lines except for most of the $^{137}$Cs measurements. For all $^{137}$Cs measurements the Minimum Detectable Activity (MDA) was computed. MDA is defined as the smallest net count that can be reported with a 95% confidence that the counts represent a true activity from a sample and not a statistical variation of the background. MDA was computed with the customary expression {1} below (Tsoulfanidis 1995) with "Counts" representing either the cumulative counts of the portion of the spectrum equivalent to the Full Width at Half Maximum of a $^{137}$Cs 661.3 Kev line or the equivalent spectral energy span on either side of the $^{137}$Cs line.

$$MDA = 2.71 + 4.66\ SQRT\ (Counts) \quad \{1\}$$

The energy span of the $^{137}$Cs was approximated at 2.0 keV or from 660.4 keV to 662.4 keV based on the more accurately measured FWHM of the $^{60}$CO 1,173 keV reference line. In the cases for which counts were measured for the $^{137}$Cs line, the background counts were totaled from 658.7 keV to 659.7 keV and 663.0 keV to 663.7 keV to match the same number of MCA channels as for cases when a spectrum was not detected.

Estimates of the radionuclide concentrations were computed based on a set of Standard Reference Materials (SRM) from the National Institute of Standards and Technology (NIST) and the International Atomic Energy Agency (IAEA). For each radionuclide a SRM was selected for its high activity and to match the specific gravity of the core samples (1.2 g/cm$^3$ to 1.7 g/cm$^3$). The respective counts in the SRM and core sample were compared while taking into account the respective materials mass, spectrum acquisition time, and for short half-life radionuclides, the decay of the standard material. Each radionuclide efficiency calibration was then verified to be within 10% of other standards with high activity for this radionuclide and similar specific gravity with the exception of $^{210}$Pb where differences in the standard materials specific gravity and the low energy of the gamma ray line lead to a larger difference (14%) as discussed in the results section.

Materials from the standards were prepared similarly to the study samples, i.e. the standard materials were sealed in the same vials and placed in the HPGe gamma ray spectrometer with identical geometry. For reference materials with relatively short half-lives such as $^{137}$Cs the activity of the materials was adjusted to take into account the time difference between the materials reference date and the date of the spectrum. For quality control, $^{60}$Co spectra were measured at regular intervals to verify the stability of the efficiency calibration of the system.

Table 2. Standard Reference Materials used for quantitative analysis of the radionuclide cores.

| Standard | Description | Reference Date/Material | Activity [mBq/g] | Uncertainty/95% Confidence Interval |
|---|---|---|---|---|
| NIST 4357 | Ocean Sediment Environmental Radioactivity | 2/6/1994 | | |
| | Relevant Certified Radionuclide Activities: | $^{137}Cs$ | 12.7 | +/- 0.2 |
| | | $^{40}K$ | 225 | 190-259 |
| | | $^{232}Th$ | 13 | +/- 0.3 |
| IAEA-315 | Radionuclides in Marine Sediment | 1/1/1993 | | |
| | Relevant Certified Radionuclide Activities: | $^{40}K$ | 297 | 288-303 |
| | | $^{232}Th$ | 25.6 | 24.5-27.5 |
| IAEA-375 | Radionuclides and Trace Elements in Soil | 12/31/1991 | | |
| | Relevant Certified Radionuclide Activities: | $^{40}K$ | 424 | 417-432 |
| | | $^{137}Cs$ | 5280 | 5200-5360 |
| IAEA-447 | Natural and Artificial Radionuclides in Most Soil | 11/15/2009 | | |
| | Relevant Certified Radionuclide Activities: | $^{137}Cs$ | 425 | +/- 10 |
| | | $^{210}Pb$ | 420 | +/- 20 |
| IAEA-313 | Ra-226, Th, U in Stream Sediments | 1/30/1988 | | |
| | Relevant Certified Radionuclide Activities: | $^{226}Ra$ | 343 | 307-379 |
| IAEA-314 | Ra-226, Th, U in Stream Sediments | 1/30/1988 | | |
| | Relevant Certified Radionuclide Activities: | $^{226}Ra$ | 732 | 678-787 |
| IAEA-434 | Ra-226, Th and U in stream sediment | 1/1/2008 | | |
| | Relevant Certified Radionuclide Activities: | $^{210}Pb$ | 680 | +/- 58 |

## Results

### *Hydrological Data*

Nine TCEQ stations in Nueces Bay were sampled in June 2013. Mean water temperature was 28.93° C with station 14833, located near the Topaz Power Group’s Nueces Bay Energy Center, having the warmest reading at 30.40° C (Table 3). Mean salinity was 38.2 ppt with station 18866 located in back Nueces Bay having the highest salinity at 40.09 ppt. Mean pH was 7.93 and mean DO % and mg/L were 90.94 and 5.65, respectively.

Table 3. Hydrological data collected from the nine TCEQ sites June 2013.

| Station | Date | Total Depth (m) | Depth (m) | Temp (°C) | Cond (μmhos) | Salinity (ppt) | pH (su) | DO (%) | DO (mg/L) | BP (mm) |
|---|---|---|---|---|---|---|---|---|---|---|
| 21484 | 6/4/2013 | 1.60 | 0.30 | 29.33 | 59590 | 39.76 | 7.98 | 105.20 | 6.46 | 764.0 |
| | | | 0.80 | 29.20 | 59555 | 39.74 | 7.97 | 103.10 | 6.35 | 763.7 |
| | | | 1.30 | 28.93 | 59652 | 39.81 | 7.91 | 87.20 | 5.34 | 763.6 |
| 18866 | 41429 | 1.30 | 0.30 | 28.40 | 59982 | 40.09 | 7.97 | 86.50 | 5.38 | 760.2 |
| 13425 | 41429 | 1.10 | 0.30 | 28.40 | 58094 | 35.67 | 7.93 | 89.20 | 5.59 | 762.9 |
| 14831 | 41431 | 1.40 | 0.30 | 28.63 | 55549 | 36.75 | 7.95 | 91.10 | 5.74 | 757.6 |
| 13423 | 41431 | 1.80 | 0.30 | 28.88 | 56424 | 37.39 | 7.91 | 88.70 | 5.55 | 759.7 |
| | | | 0.90 | 28.87 | 56389 | 37.37 | 7.92 | 86.90 | 5.44 | 759.7 |
| | | | 1.50 | 28.84 | 56423 | 37.39 | 7.95 | 84.70 | 5.31 | 759.7 |
| 13422 | 41431 | 1.750 | 0.30 | 29.80 | 56155 | 37.16 | 7.97 | 95.90 | 5.93 | 763.0 |
| | | | 0.85 | 29.05 | 57769 | 38.40 | 7.98 | 93.20 | 5.79 | 763.1 |
| | | | 1.45 | 28.97 | 58277 | 38.79 | 7.97 | 87.70 | 5.43 | 763.4 |
| 14833 | 41436 | 1.20 | 0.30 | 30.40 | 54905 | 36.20 | 8 | 98.70 | 6.08 | 765.9 |
| 18619 | 41436 | 1.70 | 0.30 | 28.58 | 58205 | 39.00 | 7.85 | 92.60 | 5.75 | 764.5 |
| | | | 0.85 | 28.59 | 58264 | 37.75 | 7.88 | 87.40 | 5.46 | 764.6 |
| | | | 1.40 | 28.57 | 58304 | 38.82 | 7.89 | 86.50 | 5.41 | 764.6 |
| 18365 | 41436 | 1.40 | 0.30 | 28.45 | 59082 | 39.40 | 7.93 | 81.40 | 5.08 | 762.7 |

### *Magnetic Susceptibility Profiles*

Magnetic susceptibility profiles for eight of the cores are presented in Figure 4. A magnetic susceptibility profile is not available for location 14833 as that core was significantly disturbed during transport, and discarded. The majority of the cores (13425, 13423, 14831, 21484, 18365, and 13422) show a long term trend towards decreasing magnetic susceptibility values from 100 cm depth upwards. This decreasing trend is replaced by a relative strong increase towards generally maximum susceptibility values over the uppermost 20-40 cm of sedimentation. These long term trends are interrupted by higher frequency variability and excursions in all of the cores.

Cores from 18866 and 18619 show magnetic susceptibility profiles that are different from the other station's cores. The 18866 core, from back Nueces Bay, shows a long term increasing trend from the base upwards followed by a decrease over the last 30 cm of sedimentation. This pattern is essentially the opposite of the six cores described above. The core from station 18619 shows a muted susceptibility signal from 100 cm depth up to 20 cm depth, and then a relatively strong increase in values over the last 20 cm of sedimentation, like the first six cores mentioned above.

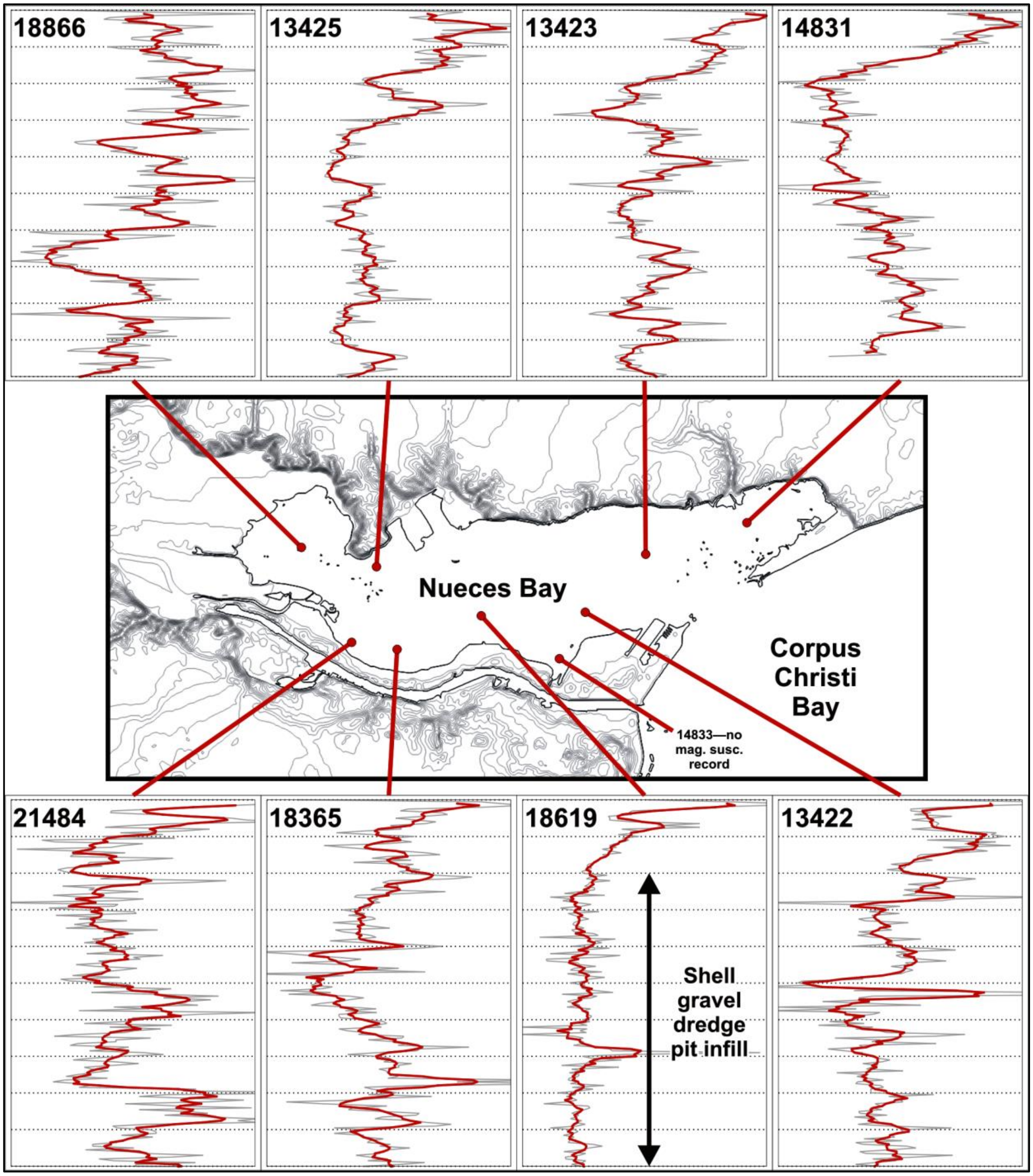



Figure 4. Magnetic susceptibility profiles for Nueces Bay sediment cores from 0-100 cm depth. The thin gray lines in each plot represent the full data set at 1 cm resolution, and the thicker red lines represent 5-point, centered running means. The horizontal scales on the plots for stations 13423, 21484, 18365, 18619, and 13422 are equivalent, and range in value from 0 (left) to 1.0E-04 (right) SI units. The horizontal scale for station 14831 is slightly different, and ranges up to 1.1E-04 SI units, and for stations 18866 and 13425 it ranges up to 1.5E-04 SI units. The muted response from 20-100 cm depth for station 18619 is interpreted to represent rapid, homogenous infill of a shell gravel dredge pit or channel. The sediment core retrieved for this analysis from station 14833 was significantly disturbed during transport, and it was discarded.

**Station 21484**

Elevated subsurface zinc levels at Station 21484 were identified and exceeded the TCEQ criteria of 410 mg/kg at a depth of 20-25 cm (433 mg/kg) (Fig. 5). Surface zinc levels were below TCEQ's criteria of 410 mg/kg and is the stratum currently sampled for the TMDL. Zinc concentrations were almost three times higher below the surface at 5-10 cm and continued to increase and then decrease to surface zinc levels at 40-45 cm. Sediment grain size was composed predominately of clay and silt. Total organic carbon was highest at 35-40 cm (22,000 mg/kg) and lowest at 85-90 cm (6680 mg/kg).

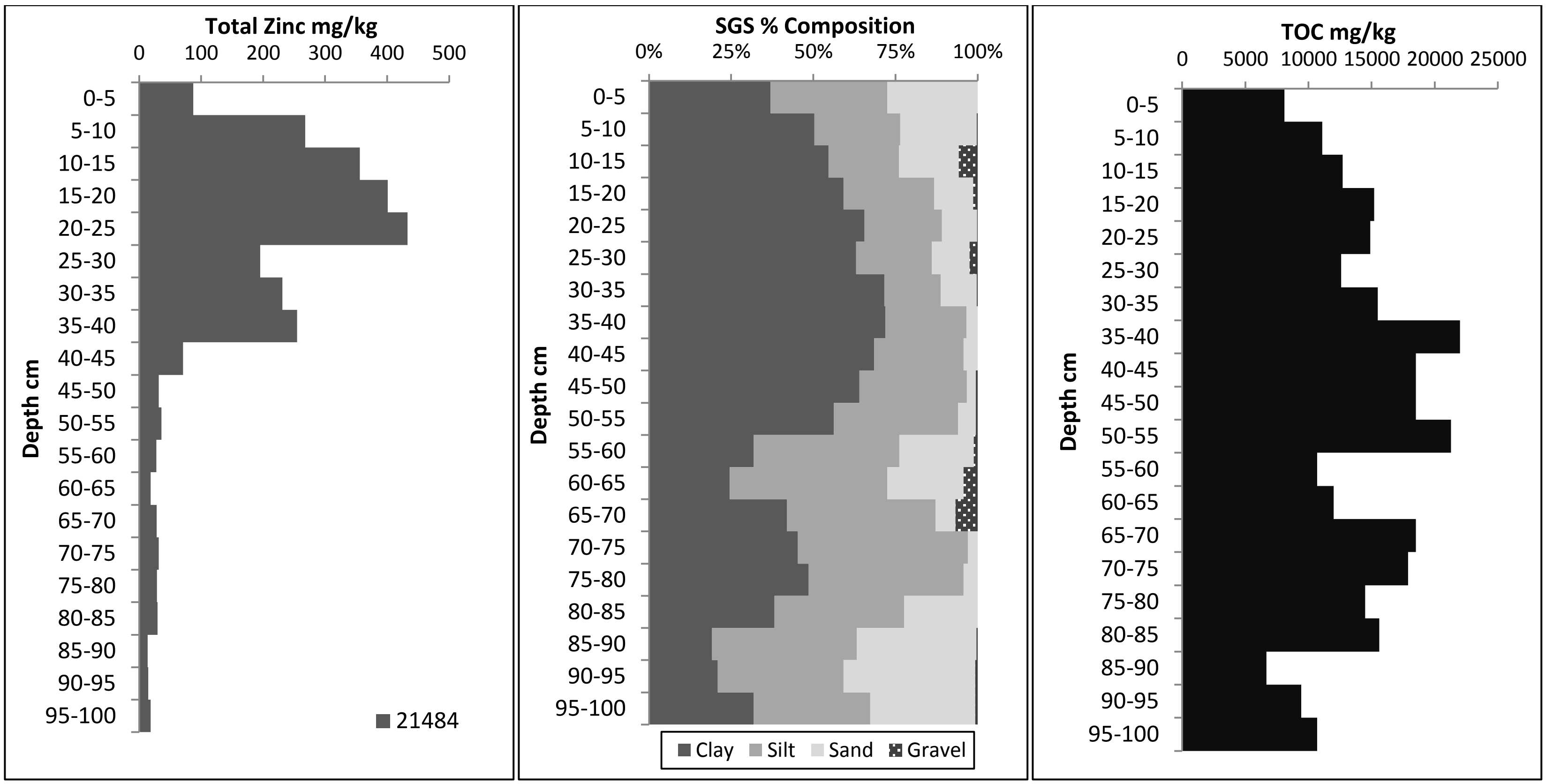



Figure 5. Station 21484 total zinc, sediment grain size, and TOC content in sediment.

**Station 14831**

Station 14831, located in the northeast portion of Nueces Bay borders Portland, TX and is in the vicinity of Gum Hollow. Station 14831 had low levels of total zinc throughout the 1 m profile with the highest concentration at 5-10 cm (41.3 mg/kg) (Fig. 6). Sediment grain size was composed mostly of sand and gravel with clay and silt mixed in. The gravel component was mainly oyster shell which was found at 15-20 cm below the surface indicating this was a historic oyster reef. Total organic carbon was highest at 70-75 cm (10,300 mg/kg) and lowest on the surficial layer 0-5 cm (4650 mg/kg).

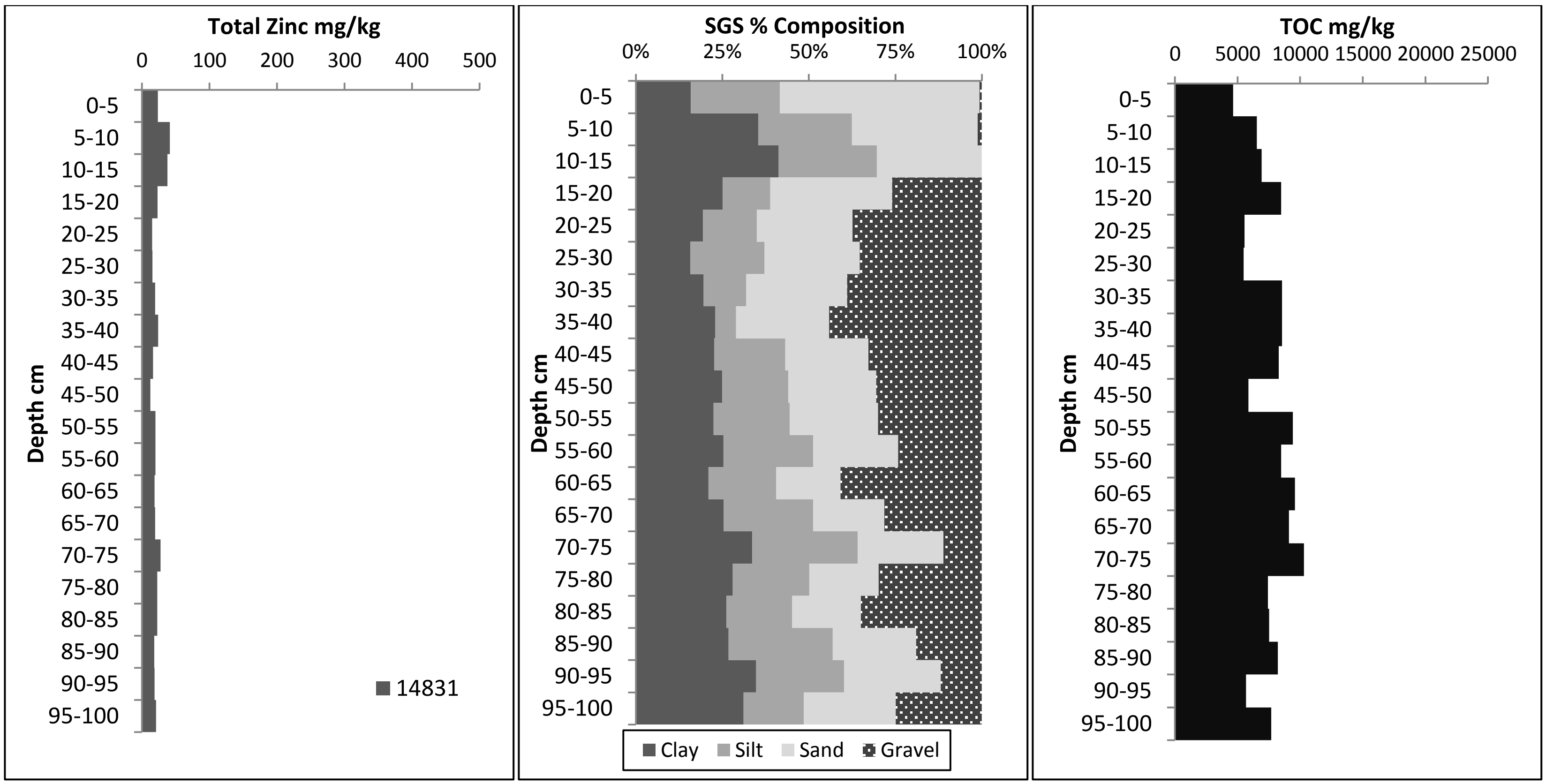



Figure 6. Station 14831 total zinc, sediment grain size, and TOC content in sediment.

**Station 13423**

Station 13423, located in the northeast portion of Nueces Bay had low levels of total subsurface zinc concentrations with the highest level at 5-10 cm (52.4 mg/kg) (Fig. 7). Sediment grain size was dominated by clay, silt and sand with sand being more dominant in the top layers down to 10-15 cm. Total organic carbon was highest at 35-40 cm (12,500 mg/kg) and lowest at the surface 0-5 cm (5460 mg/kg).

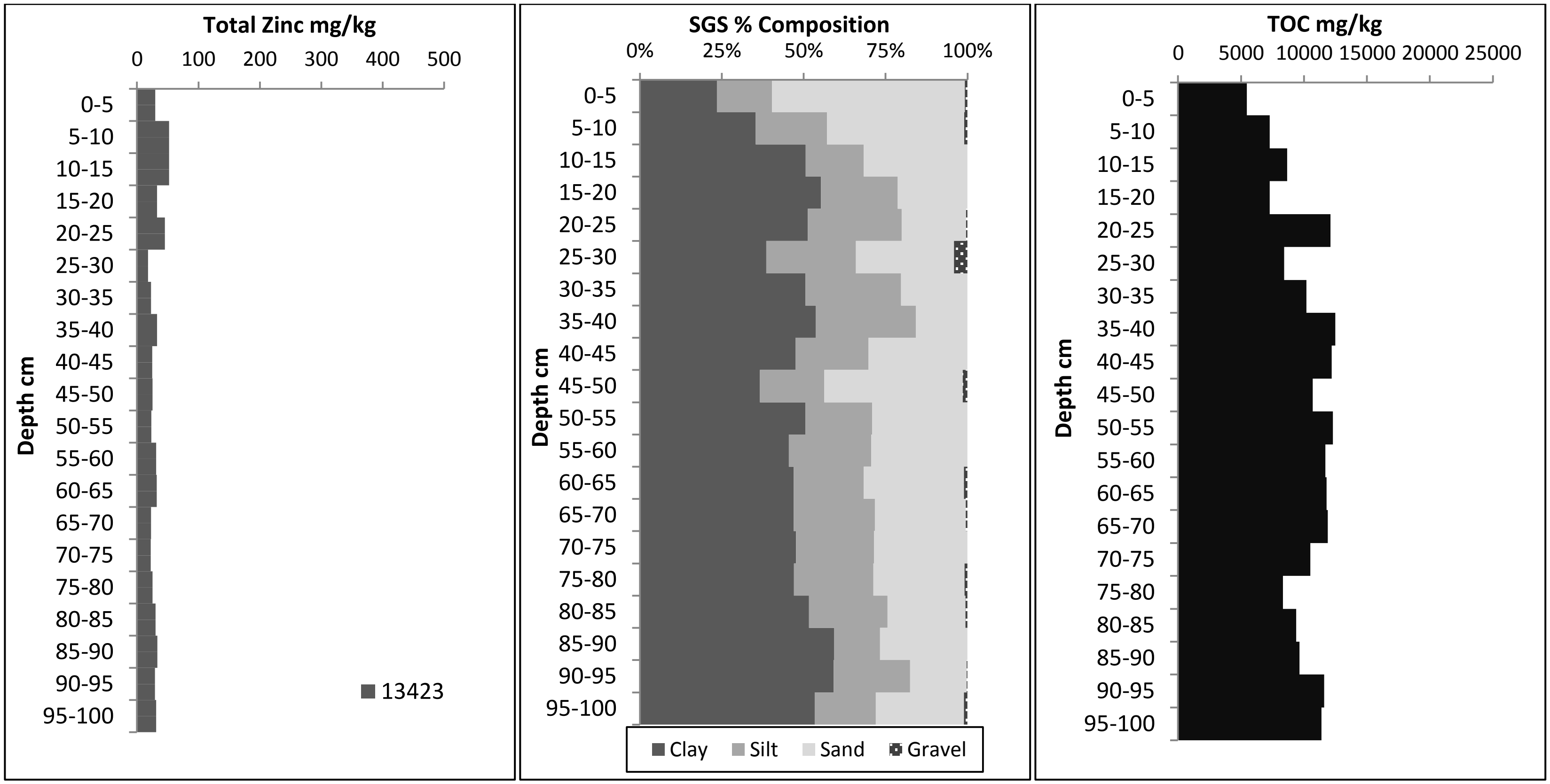



Figure 7. Station 13423 total zinc, sediment grain size, and TOC content in sediment.

**Station 13422**

Zinc concentrations at Station 13422 were low but did have a slight increase starting at 5-10 cm with the highest concentration at 10-15 cm (64.9 mg/kg) and then decreasing at 25-30 cm (Fig. 8). Sediment grain size was composed mostly of clay, silt, and sand. Total organic carbon was highest at 50-55 cm (13,200 mg/kg) and lowest at 5-10 cm (5920 mg/kg). Sediment data only goes to 75-80 cm due to sediment compaction once the core was collected.

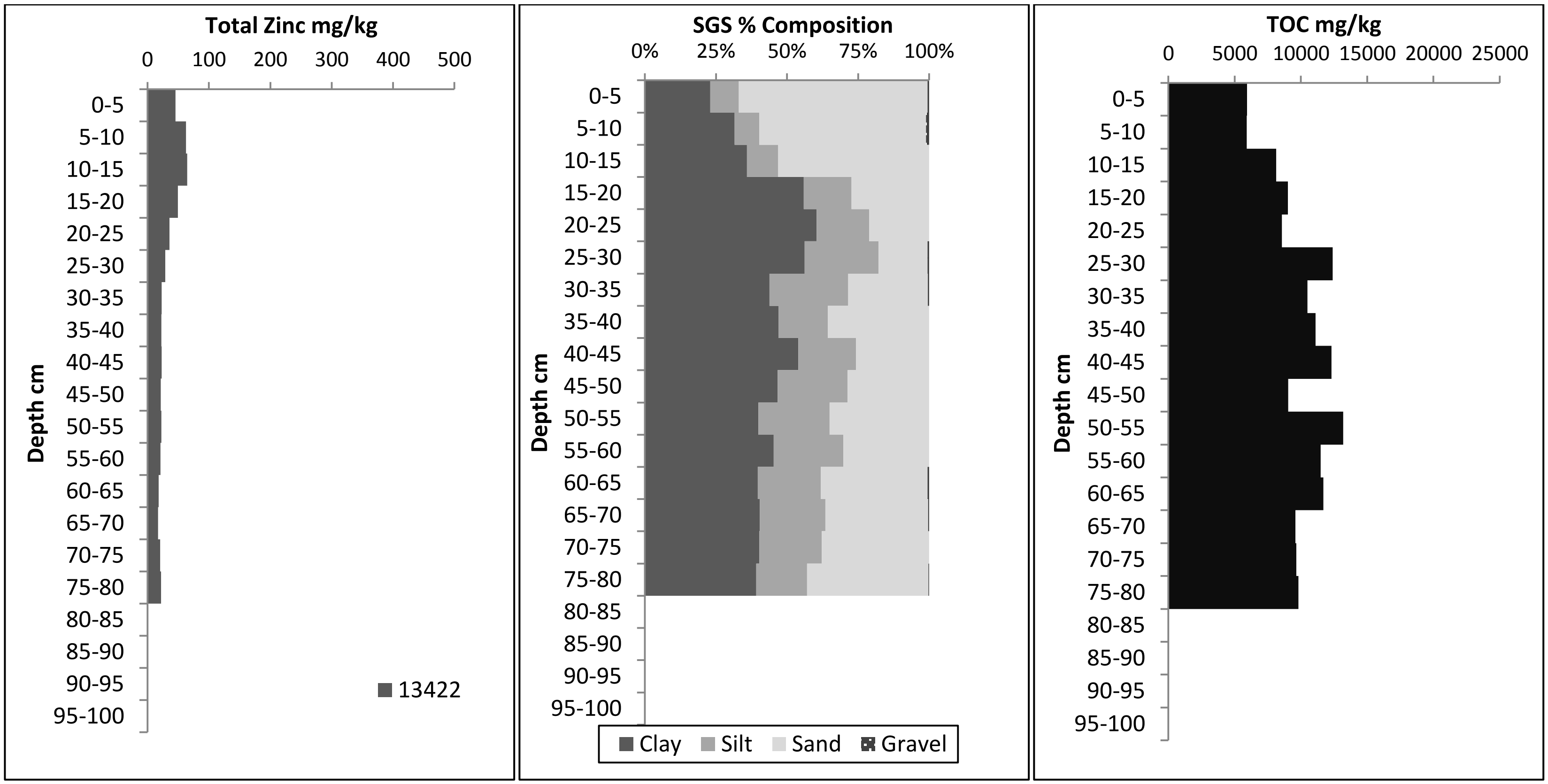



Figure 8. Station 13422 total zinc, sediment grain size, and TOC content in sediment.

## Station 18866

Station 18866, located in the back western part of Nueces Bay is surrounded by extant oyster reefs near the mouth of the historic Nueces River, Rincon Bayou. Station 18866 had low levels of total zinc throughout the 1 m profile with the highest level at 5-10 cm (25.8) (Fig. 9). Sediment grain size consisted primarily of sand mixed with clay and silt with gravel identified at 50-55 cm which consisted of oyster and *Rangia cuneata* shell. Total organic carbon was highest at 85-90 cm (7110 mg/kg) and lowest at 40-45 cm (1890 mg/kg).

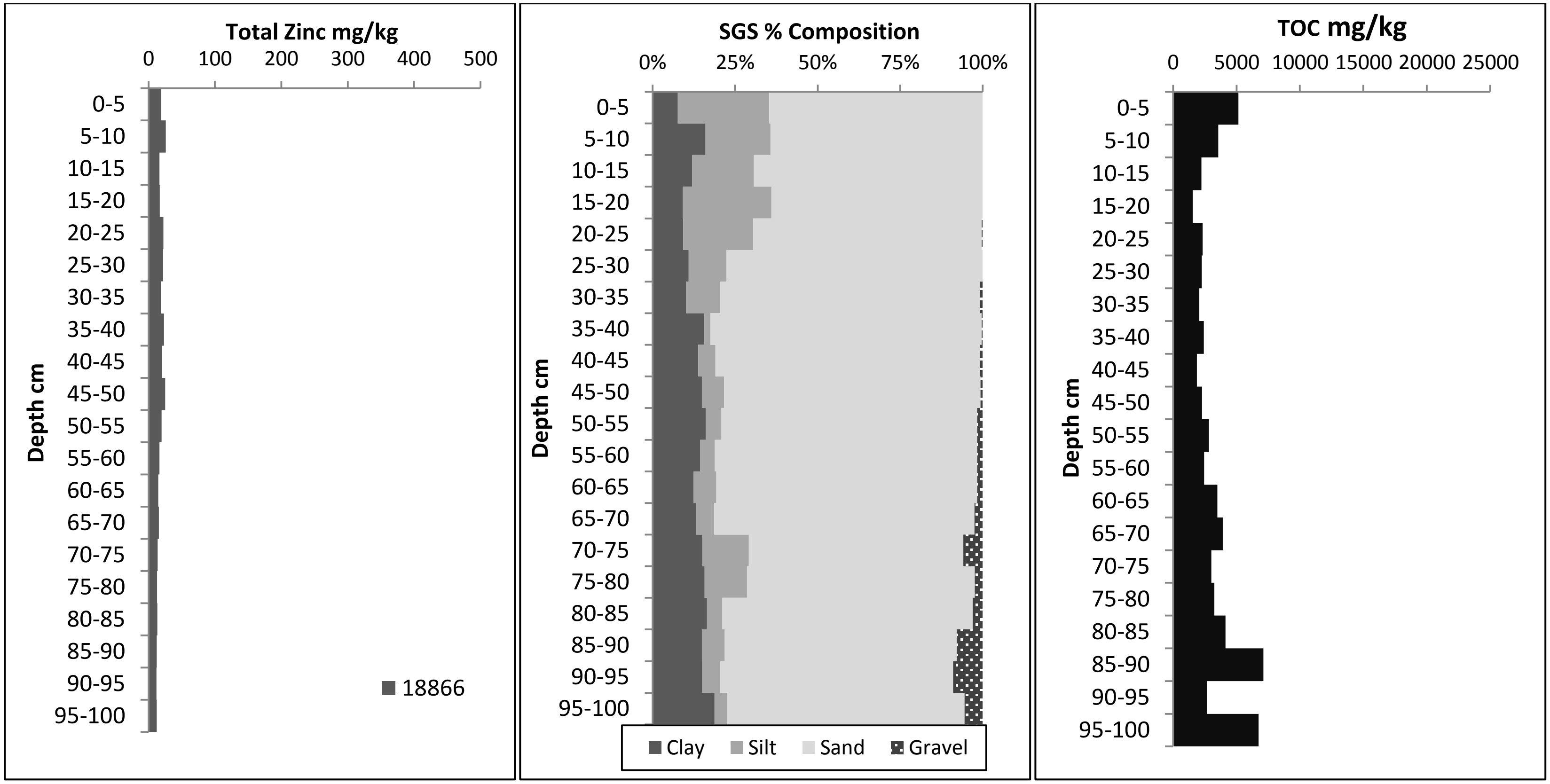



Figure 9. Station 18866 total zinc, sediment grain size, and TOC content in sediment.

**Station 13425**

Station 13425 is located in the western part of Nueces Bay near White Point and is surrounded by extant oyster reefs. Station 13425 had low levels of total zinc throughout the 1 m profile (Fig. 10). The highest zinc concentration was at 10-15 cm (46.6 mg/kg) and lowest at 55-60 cm (11.1 mg/kg). Sediment grain size was a mix of silt and sand in the upper profile layers with clay grain size increasing at 15-20 cm. Oyster shell was also found in the core at multiple depths, but was not dominant. Total organic carbon was highest at 35-40 cm (12,900 mg/kg) and lowest at 55-60 cm (7060 mg/kg).

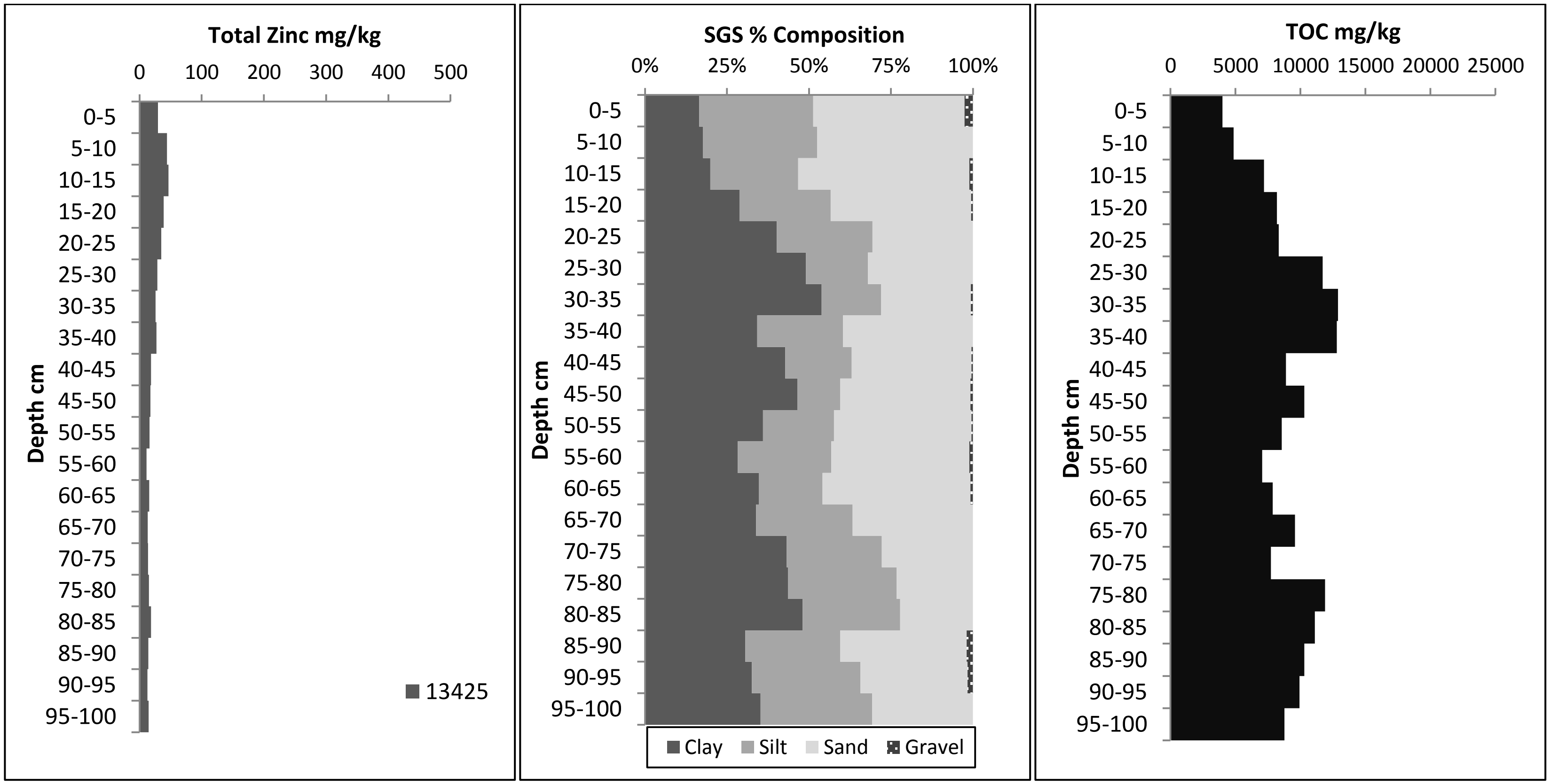



Figure 10. Station 13425 total zinc, sediment grain size, and TOC content in sediment.

## Station 14833

Station 14833, located in the southern part of Nueces Bay in front of the Topaz Energy Center outflow, had increased levels of total zinc throughout the 1 m profile starting at 10-15 cm and peaking at 20-25 cm before dropping back down to surficial zinc concentrations (Fig. 11). Highest zinc concentration was measured at 20-25 cm (248 mg/kg) and lowest at 85-90 cm (48.3 mg/kg). The elevated zinc concentrations identified in the core profile did not exceed TCEQ's criteria of 410 mg/kg. The zinc concentration followed an upward trend as clay grain size and TOC increased. Sediment grain size was a mix of silt and sand in the upper profile layers with the clay grain size fraction increasing at 15-20 cm. Total organic carbon was highest at 25-30 cm (19,300 mg/kg) and lowest at the surface 0-5 cm (4240 mg/kg). Sediment data only goes to 85-90 cm due to sediment compaction once the core was collected.

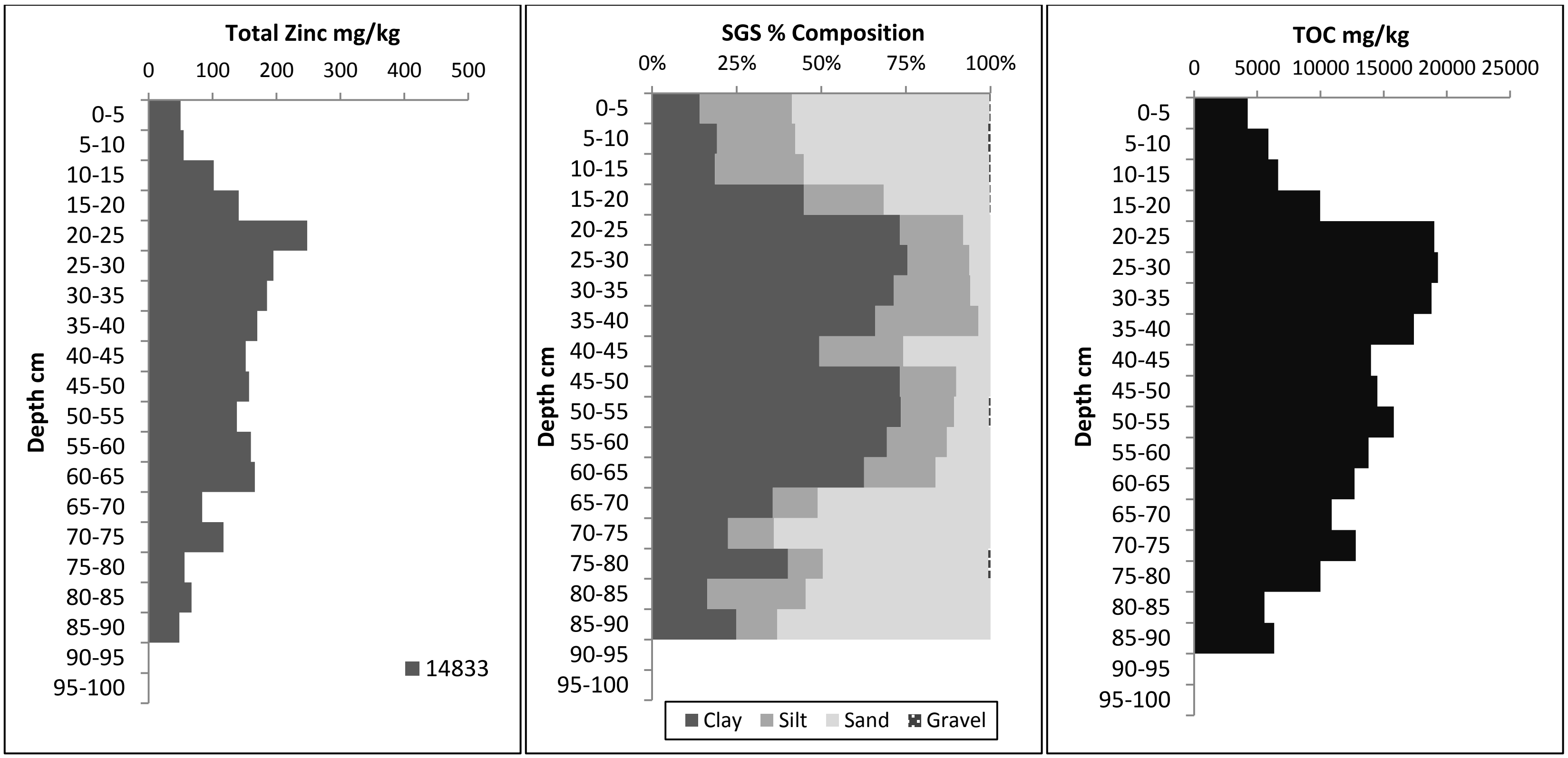



Figure 11. Station 14833 total zinc, sediment grain size, and TOC content in sediment.

### Station 18619

Station 18619, located west of the Topaz Energy Center outflow in Nueces Bay, had increased levels of total zinc throughout the 1 m profile starting at 5-10 cm (Fig. 12). The highest zinc concentration was at 70-75 cm (255 mg/kg) and lowest at the surface 0-5 cm (75.5 mg/kg). The elevated zinc concentrations were relatively constant throughout the core, but did not exceed TCEQ's criteria of 410 mg/kg. Sediment grain size was predominantly clay with silt and sand mixed in. Total organic carbon was highest at 35-40 cm (26,300 mg/kg) and lowest at the surface 0-5 cm (11,900 mg/kg).

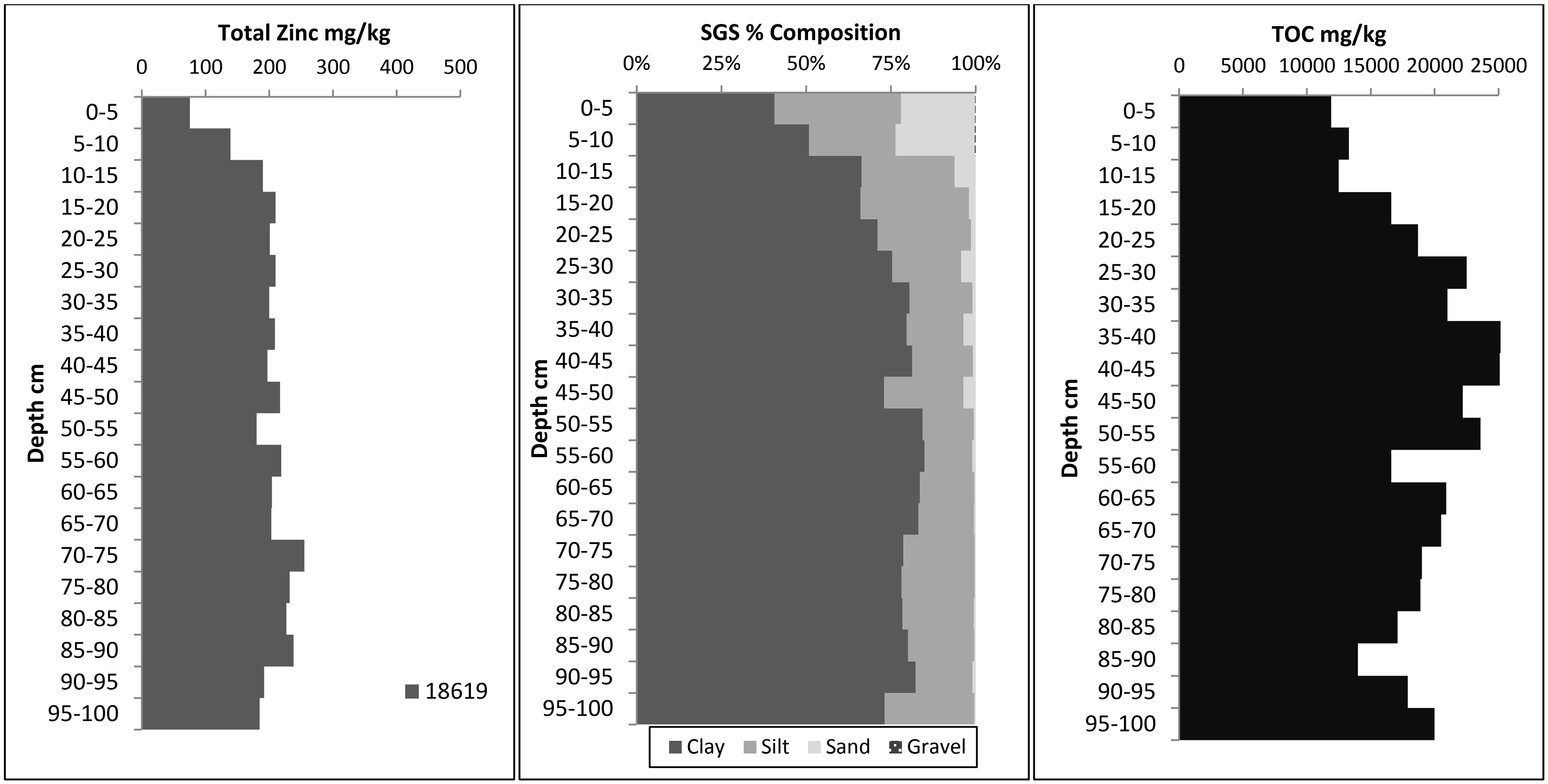



Figure 12. Station 18619 total zinc, sediment grain size, and TOC content in sediment.

**Station 18365**

Station 18365 is located in the southern part of Nueces Bay near ASARCO's historical discharge point and close to Station 21484. Low levels of total zinc were identified throughout the 1 m profile (Fig. 13). Highest zinc concentration was measured at the surface 0-5 cm (57.5 mg/kg) and lowest at 60-65 cm (9.66 mg/kg). Sediment grain size was predominant clay in the upper profile layers with silt and sand increasing at 35-40 cm. Gravel size *Rangia cuneata* shells were also found in the core at multiple depth profiles but were not dominant. Total organic carbon was highest at 15-20 cm (19,700 mg/kg) and lowest at 60-65 cm (10,300 mg/kg).

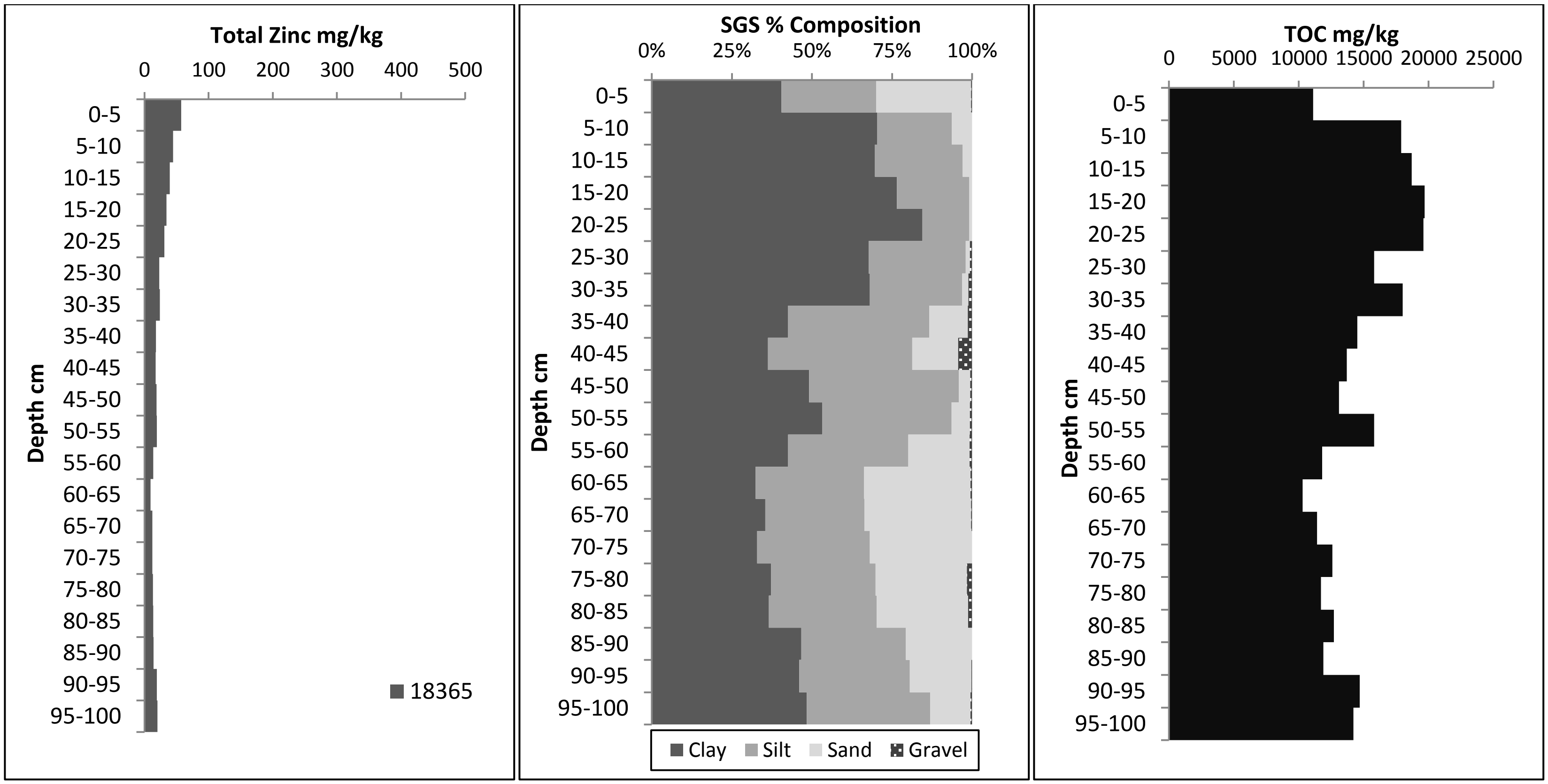



Figure 13. Station 18365 total zinc, sediment grain size, and TOC content in sediment.

## Zinc Legacy Layer

A legacy layer of zinc was identified in sediment cores in the southern part of Nueces Bay near the historical ASARCO/ENCYCLE and CPL discharge points (Fig. 14). Based on the min and max sediment profile zinc concentrations it was determined the natural occurring zinc in sediment in Nueces Bay appears to be < 124 mg/kg in the middle and northern parts of the bay. This concentration is below the Threshold Effects Level (TEL) based on Long et al. (1995) classification (Long et al. 1995; MacDonald et al. 1996) but Stations 18619 and 14833 had zinc concentrations within the Effects Range Low (ERL) and Station 21484 exceeded the Effects Range Median (ERM) (Table 4).

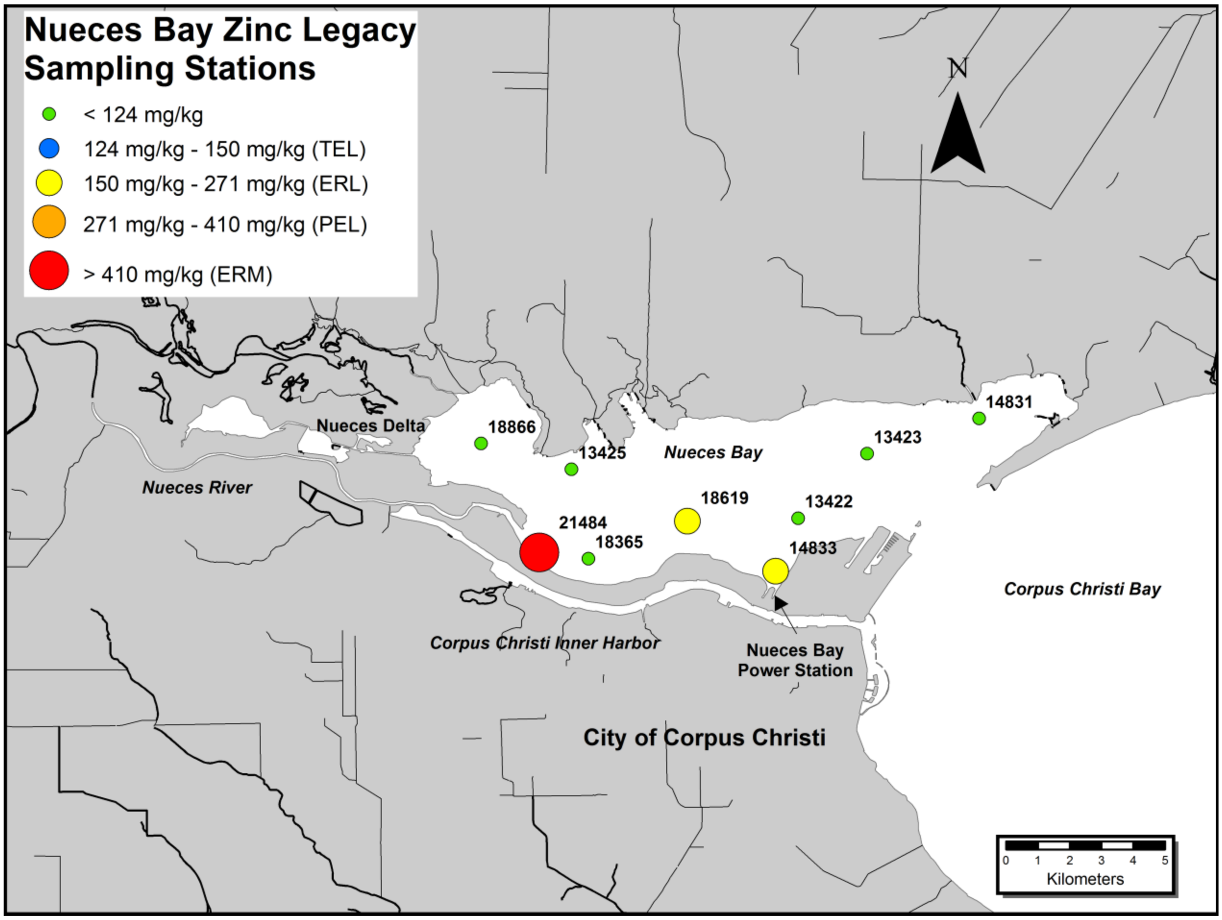



Figure 14. Maximum concentration of zinc in sediment (mg/kg) collected from Nueces Bay sediment profile assessment.

Table 4. Classification and terminology of sediment contamination and level of biological effects (Long et al. 1995; MacDonald et al. 1996).

| | | |
|---|---|---|
| Threshold Effects Level | TEL (124 mg/kg) | Rare adverse effects observed |
| Effects Range Low | ERL (150 mg/kg) | Effects begin to occur in sensitive species |
| Probable Effects Level | PEL (271 mg/kg) | Frequent adverse effects observed |
| Effects Range-Median | ERM (410 mg/kg) | Median concentration of compiled toxic data |

## Sediment Dating By Radioanalysis

### *Cesium-137*

Cesium-137 concentrations were measured based on the radionuclide 661-keV gamma ray line. The conversion of counts to activity was based on comparison with the IAEA-375 SRM. The calibration was verified based on IAEA-447 SRM. The $^{137}$Cs depth profile is presented in Figure 15 for Station 21484. For most of core 21484 and for all measured samples for core 13422, $^{137}$Cs activities were below the detection limit of the instrumentation for the selected geometry and acquisition times. Minimum Detectable Activities (MDAs) were computed for all measurements following the methodology presented in the above Methods section. In Figure 16 the $^{137}$Cs depth profile of the upper portion of core 21484 is presented and compared with the corresponding individual MDA for each measurement. The fluctuations in the MDA are due to variation in acquisition time and activities of other radionuclides in the samples.

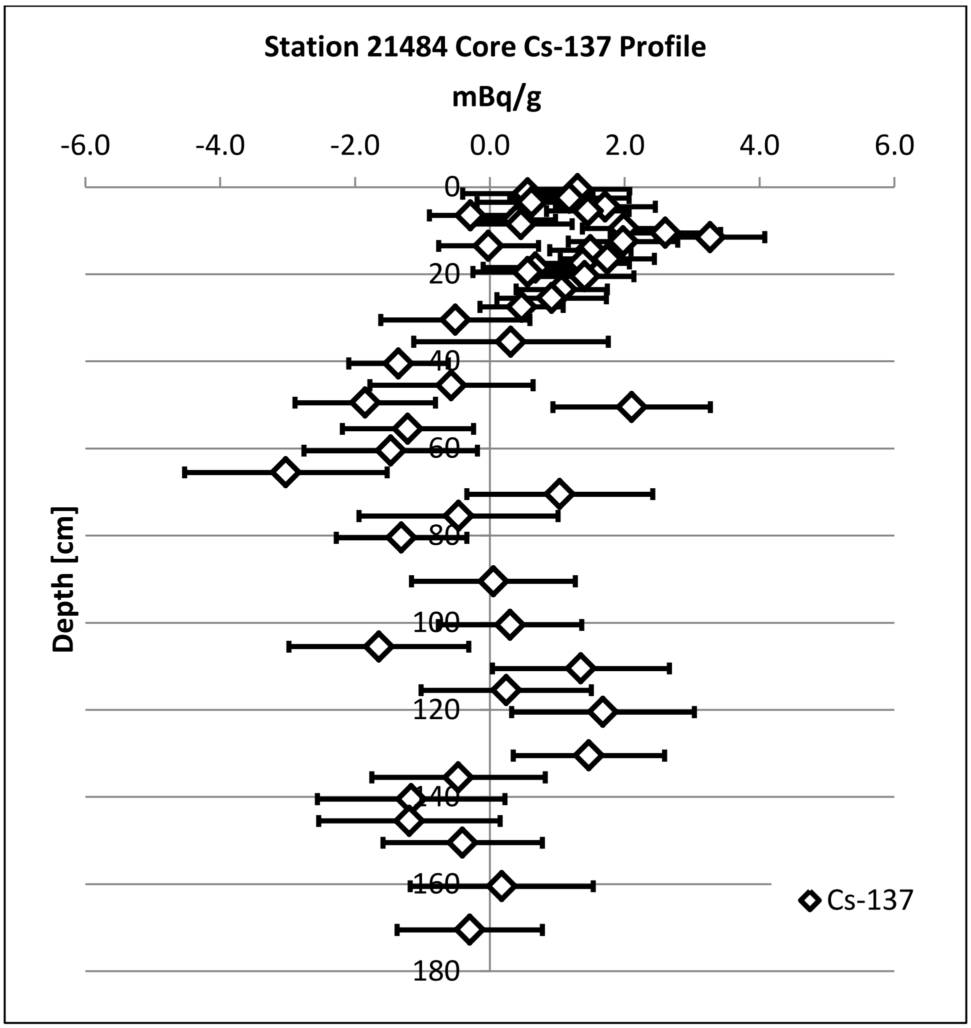



Figure 15. Cesium-137 depth profile for Station 21484 core including activities and counting uncertainties.

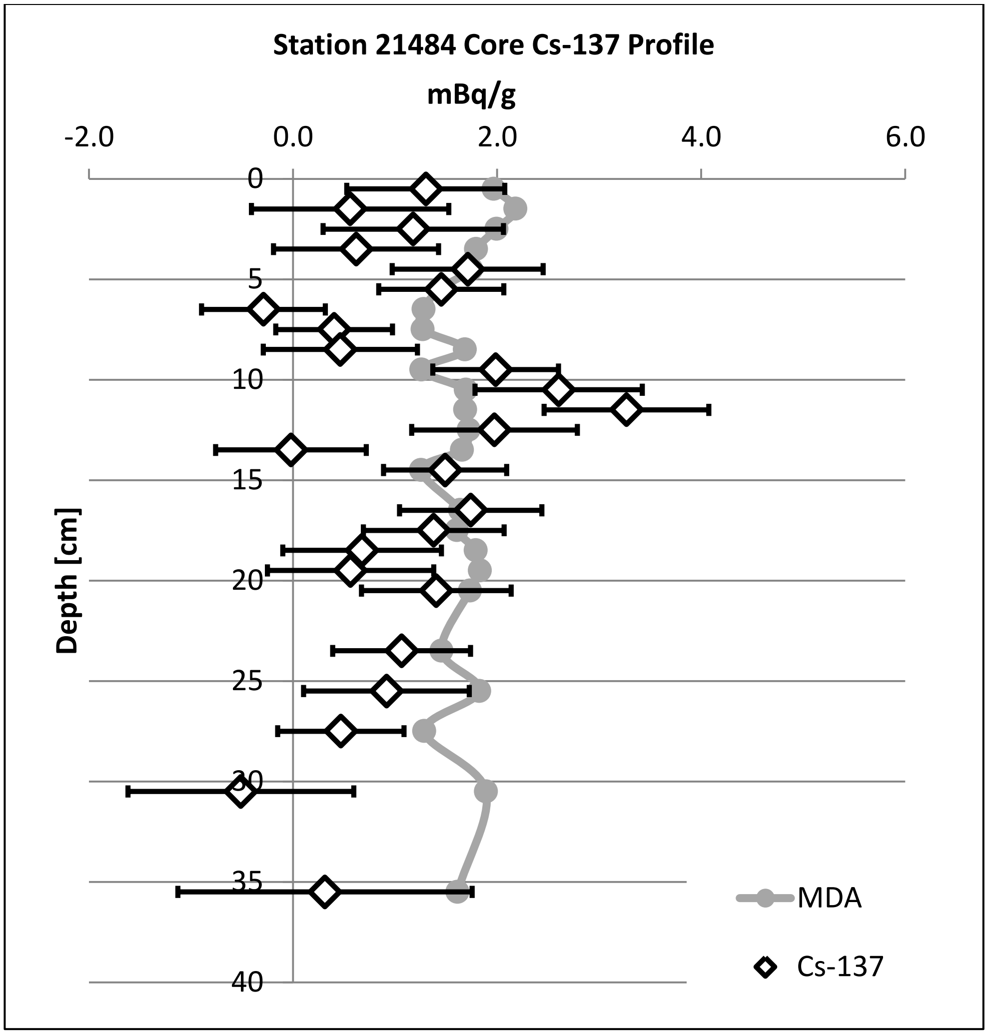



Figure 16. Cesium-137 depth profile for the top 36 cm of Station 21484 including activities, counting uncertainties and Minimum Detectable Activities.

As can be seen in Figure 16 only four measurements were clearly above the MDA, activities for the 9 cm through 13 cm samples with the highest activity of 3.3 +/- 0.8 mBq/g measured for the 11-12 cm sample. The peak of the $^{137}$Cs depth profile is typically associated with the maximum of the atomic open air testing outfall in 1964. A deposition of 11.5 cm in 49 years leads to an average depositional rate of 0.23 cm/yr or 0.28 g/cm$^2$/yr assuming an average sediment density of 1.2 g/cm$^3$. This depositional rate is retained as the result of the $^{137}$Cs analysis for the station 21484 core. Above MDA $^{137}$Cs activities were not measured for the Station 13422 core.

While associating the peak of the $^{137}$Cs profile with 1964 is the usual analysis, Nueces Bay has previously been influenced by substantial flooding along the Nueces River. Such flooding can result in a change of the distribution of sedimentary deposits including a larger contribution from top soils richer in $^{137}$Cs. The largest such event (CCWFO 2013) was experienced in 1967 due to the passage of Hurricane Beulah. The potential impact of this flooding event on the $^{137}$Cs profile does not influence the sedimentary depositional rate analysis as its date is close to 1964. The second largest event at the nearby Nueces River station of Calallen was recorded in 2002

(CCWFO 2013). If this flooding event led to the visible $^{137}$Cs peak this would result in a very high and unlikely depositional rate of about to 1cm/yr. This hypothesis is not retained. Other influential events in the Nueces Bay watershed include the initial impoundment of Lake Corpus Christi in 1929 with the construction of the La Fruta Dam (Texas Water Development Board 2014a), the completion in 1958 of the Wesley E. Seale dam on the same lake and the upstream impoundment of Choke Canyon Reservoir in 1982 (Texas Water Development Board 2014b). Nueces Bay was also impacted by the devastating 1919 Corpus Christi Hurricane. These events could not be correlated with horizons along the core depth profiles.

Finally, while the stratigraphy in this core appears to be relatively undisturbed, a comparison of this core with the core from nearby Station 18365 suggests that the top portion of this core may have been removed or clipped due to anthropogenic activity. This is based on the presence of a visually distinct, brown mud band in both cores. In the Station 21484 core, the band is centered on ~10.5 cm depth, while in the Station 18365 core it is centered on ~21.5 cm depth (Fig. 17).

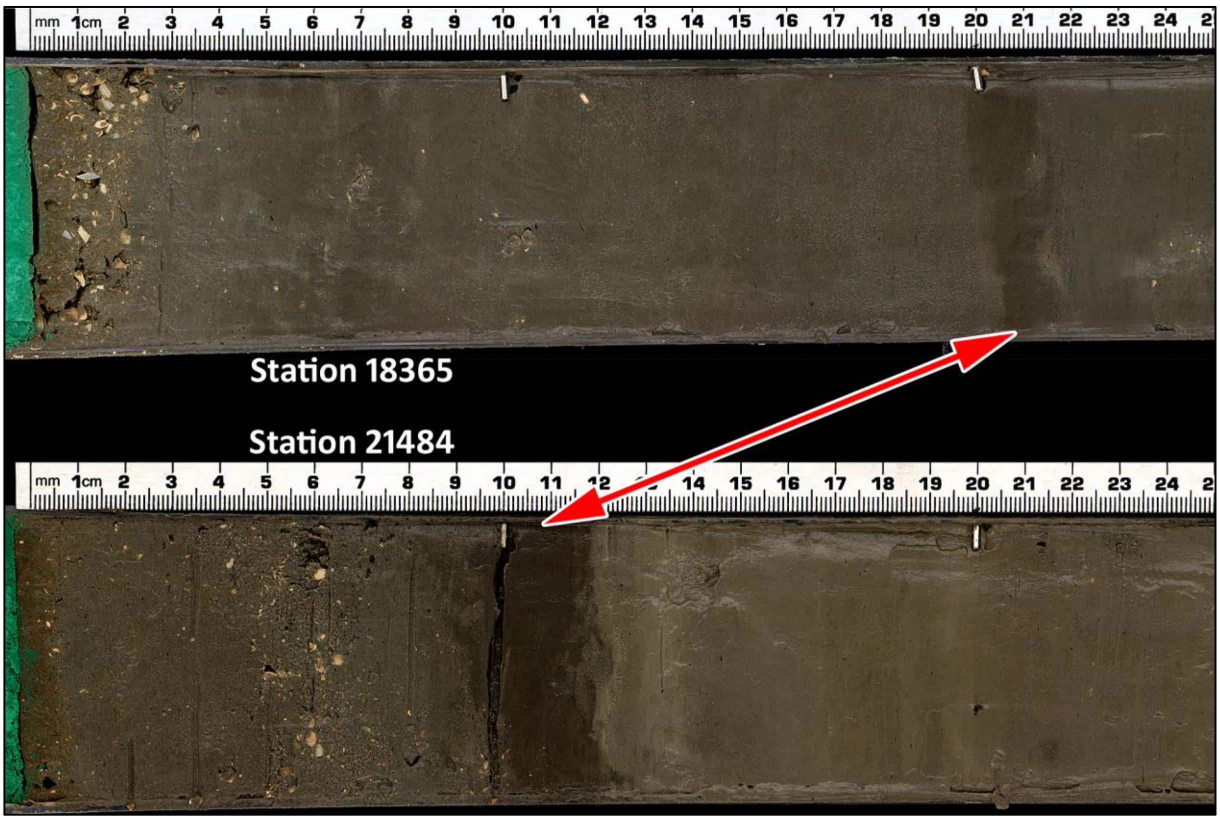


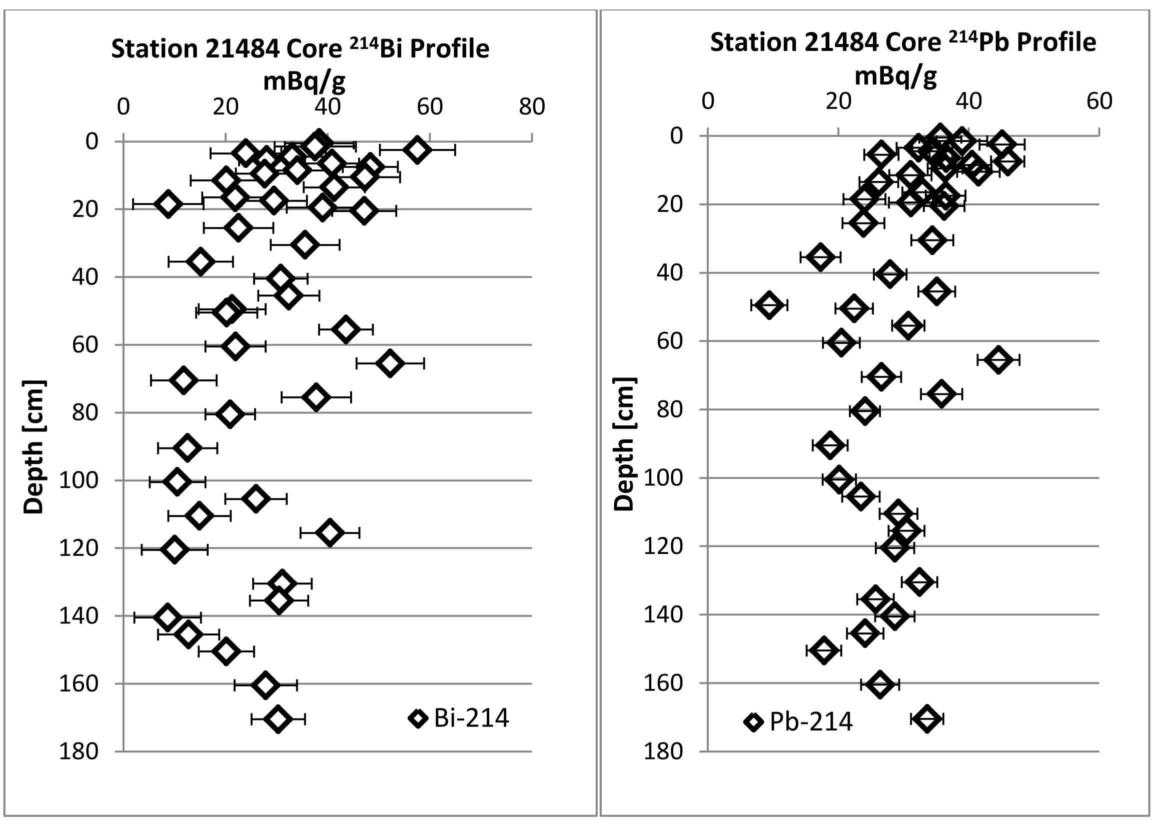

Figure 17. Visual comparison between the upper 0-25 cm of cores from Stations 21484 and 18365. The distinct brown mud band in the 21484 core is found ~10 cm higher in the stratigraphy. This observation supports the assertion that the sediments at Station 21484 may have been disturbed, and may be truncated by ~10 cm (or more).

A missing top portion of core 18365 would modify the estimated sedimentation rate. A deposition of 21.5 cm in 49 years would lead to an average depositional rate of 0.44 cm/yr or 0.53 g/cm$^2$/yr assuming an average sediment density of 1.2 g/cm$^3$. A comparison of this updated sedimentation rate with a sedimentation rate based on a historical analysis of ASARCO zinc production rates is presented in the Discussion section. Figure 17 also illustrates the large spatial variability of core stratigraphy in Nueces Bay. Extensive anthropogenic activity such as oil and gas exploration and production, dredging, extraction of oyster shells for road construction, etc. has had a considerable impact on the bay. Therefore the chronology obtained for one core may not be directly applicable to a nearby core in Nueces Bay.

### *Radium-226*

The Radium-226 activity was measured through the $^{214}$Pb and $^{214}$Bi gamma ray lines. While the half-life of Radium-226 is 1600 years, its daughters decay in rapid succession starting with Radon-222 with a half-life of 3.82 days. The following elements in the decay chain are $^{218}$P, $^{214}$Pb, $^{214}$Bi and $^{214}$Po, all with half-lives shorter than 30 minutes up to the next element in the chain, $^{210}$Pb, which has a half-life of 22 years.

In a sealed environment the elements achieve decay equilibrium after a few half-lives of the longer lived radionuclide resulting in the same activity for all elements along the chain allowing for the measurement of Radium-226 activity based on radionuclides with more easily identified gamma ray signatures, $^{214}$Pb and $^{214}$Bi. The conversions of counts to activity were based on comparison with the IAEA-314 Standard Reference Method (SRM) and the calibrations were verified based on IAEA-313 SRM for both radionuclides. The depth profiles for the activities of both radionuclides are presented in Figure 18 (a) and (b) for core 21484.




(a) (b)

Figure 18. $^{214}$Pb (a) and $^{214}$Bi (b) profiles for Station 21484 including activities and counting uncertainties.

As expected both spectra show the same profile with a range of activities from 9 to 60 mBq/g. The variability of the measurements is a little higher for the $^{214}$Bi measurement as compared to the $^{214}$Pb measurements mostly because of the largest count rates for the $^{214}$Pb 351 keV line as compared to the $^{214}$Bi 609 keV line. Concentrations are relatively constant with possibly more variability in the first 80 cm. The depth profiles do not identify substantial features helpful for the dating the cores, therefore no dates could be determined for the stratigraphy using this methodology. Results for core 13422 were similar with similar activity ranges and absence of noticeable horizons. It was originally hypothesized that onset of oil and gas exploration in Nueces Bay in the early 20$^{th}$ century could have resulted in increased $^{226}$Ra in the sediments.

### *Lead-210*

Lead-210 concentrations in the core samples were measured based on the 46-keV gamma ray line. The conversion of counts to activity was based on comparison with the IAEA-434 SRM. The calibration was verified based on IAEA-447 SRM. For this radionuclide only these two SRMs were available with certified values. The calibration check (IAEA-447) had a $^{210}$Pb activity of 14% below that of the main standard used for the calibration (IAEA-434). This larger difference is due to the low energy of the $^{210}$Pb gamma ray line (46 keV) and the higher specific gravity of the check standard (1.13 g/cm$^3$) as compared to the main standard (0.80 g/cm$^3$). A self-absorption correction was not computed as the difference is still small, especially since the depth profile rather than activity values are of interest. The full depth spectrum of $^{210}$Pb activity is presented in Figure 19.

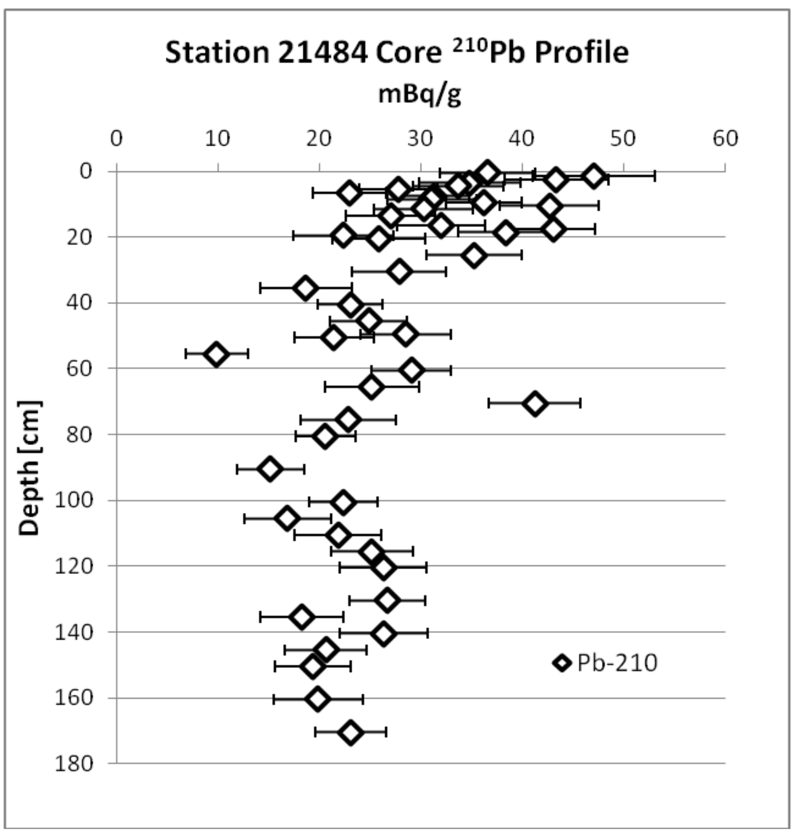



Figure 19. Lead-210 depth profile for Station 21484 including activities and counting uncertainties.

The $^{210}$Pb activity can be divided into geologically supported $^{210}$Pb, i.e. the concentration supported by the $^{238}$U decay series content of the sediments, and unsupported $^{210}$Pb contributed by atmospheric deposition. The second contribution concentration will decrease with depth as excess $^{210}$Pb is only contributed at the surface rather than generated continuously in the sedimentary materials. The decay with depth of the unsupported $^{210}$Pb is based on its 22.3 years half-life and the location's sediment accumulation rate.

Different methods can be used to estimate the unsupported $^{210}$Pb concentrations, two such methods are tested hereafter. In the first method the supported $^{210}$Pb activity was estimated as the average activity in the deeper layers of the core. Based on the change with depth of the $^{210}$Pb profile presented in Figure 19, an average supported $^{210}$Pb activity of 23 mBq/g was computed as the average activity between 35 cm and 170 cm. Subtracting this component leads to the estimated unsupported $^{210}$Pb profile presented in Figure 20. Some variability around the average supported concentration is to be expected related to the variability of the sedimentary materials deposited in Nueces Bay.

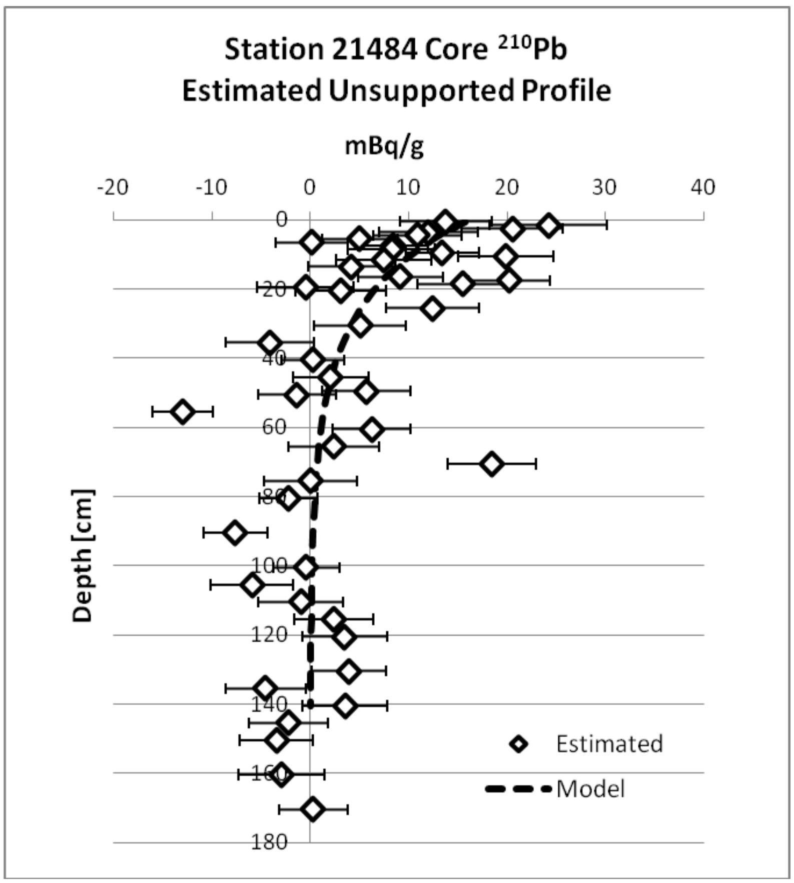



Figure 20. Modeled of excess $^{210}$Pb depth profile for the 21484 core based on assuming a supported lead concentration as the average of the lead concentrations below 35cm.

An estimated unsupported $^{210}Pb$ concentration profile was modeled using the usual exponential decay equation below:

$$^{210}Pb(z) = \ ^{210}Pb(surface)e^{-\left(\frac{\lambda}{S}\right)z}$$

with λ (0.031 $yr^{-1}$) the $^{210}Pb$ decay constant, $^{210}Pb$ (surface) the surface unsupported $^{210}Pb$ concentration and S the sediment accumulation rate. The parameters S and $^{210}Pb$ (surface) were estimated using Matlab. The estimated parameters with their 95% confidence intervals were respectively $^{210}Pb$ (surface) = 16 [10 – 22] mBq/g and S = 0.69 [0.41 - 3.16] $g/cm^2/yr$. Model values were then computed using the sedimentation rate of 0.69 $g/cm^2/yr$ or 0.58 cm/yr using an average sediment density of 1.2 $g/cm^3$. The 95% confidence interval for the sedimentation rate using the 1.2 $g/cm^3$ sediment density is [0.34 – 2.63] cm/yr. Model computations are compared with estimated unsupported $^{210}Pb$ activities in Figure 20. A main characteristic of this estimate is its very large 95% confidence intervals. The large variability in the estimates and models are due in part to the high supported $^{210}Pb$ concentrations of the sediments and keeping the top mixed layer as part of the analysis.

Another attempt at estimating the sedimentation rate based on the $^{210}Pb$ profile was computed by subtracting the $^{214}Pb$ activities from the $^{210}Pb$ activities. The resulting profile is presented in Figure 21. The results show that the surface variability of the total $^{210}Pb$ activity is mostly explained by the supported $^{210}Pb$ concentration. Also, the overall difference between measured $^{210}Pb$ and $^{214}Pb$ activities is 2.5 mBq +/- 8 mBq/g (1 standard deviation).

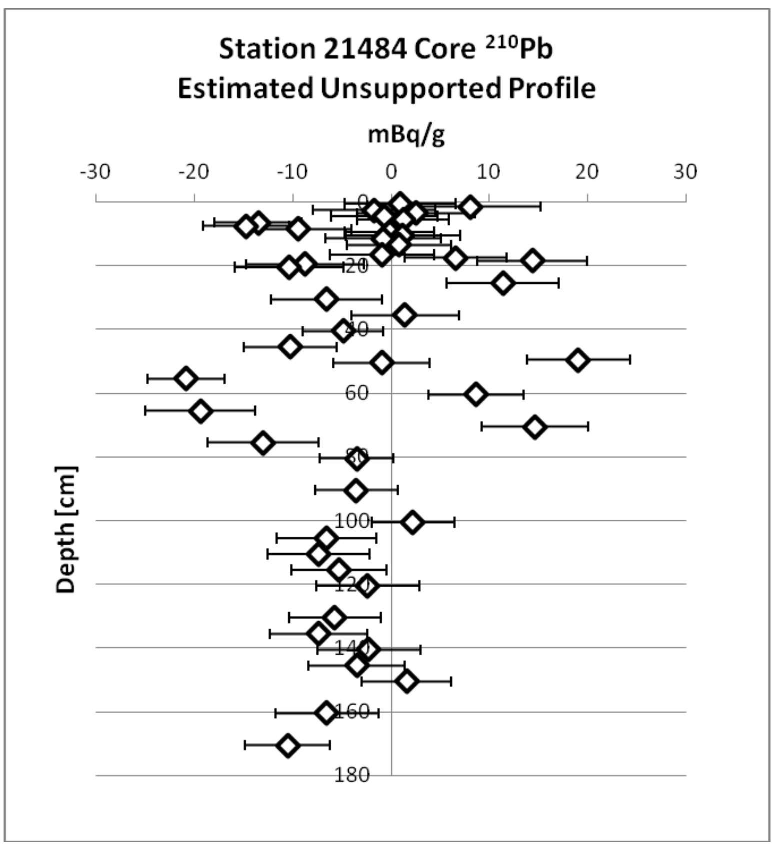



Figure 21. Model of excess Lead-210 depth profile for Station 21484 based on the difference between measured $^{210}Pb$ and $^{214}Pb$.

It is therefore concluded that $^{210}Pb$ is not an appropriate method to estimate the sedimentation rate for this core. The above comparison and the $^{214}Pb$ and $^{214}Bi$ depth profiles show that the supported $^{210}Pb$ concentrations are high in Nueces Bay due to the natural sediment composition making it difficult to identify the unsupported $^{210}Pb$ concentrations above the natural variability of the supported component. The number of samples analyzed for core 13422 (10 samples) was insufficient to attempt such analysis. $^{210}Pb$ average concentrations in the top 10 cm of this core was 33 mBq/g while the average concentrations for samples extracted between 15 cm and 41 cm was 17 mBq/g. These concentrations are similar to those measured for core 21484.

***Potassium-40***

The Potassium-40 activities were measured for Stations 21484 and 13422 through the $^{40}K$ 1,460 keV line. The depth profiles are presented in Figure 22. The conversion of counts to activity was based on comparison with the IAEA-375 SRM. The calibration was verified based on IAEA-315 SRM. The cores' activities range from 370 to 700 mBq/g with the exception of a measurement of 161 mBq/g at 55.5 cm for Core 21484. The origin of this horizon in the $^{40}K$ profile is unknown. Based on a 0.23 cm/yr sedimentation rate this depth would correspond to ~1780 and based on a 0.44 cm/yr this depth would correspond to ~1890. These estimated dates are prior to historical anthropogenic zinc deposition in Nueces Bay and do not correspond to obvious prior events that could help in further determining this core sedimentation rate.

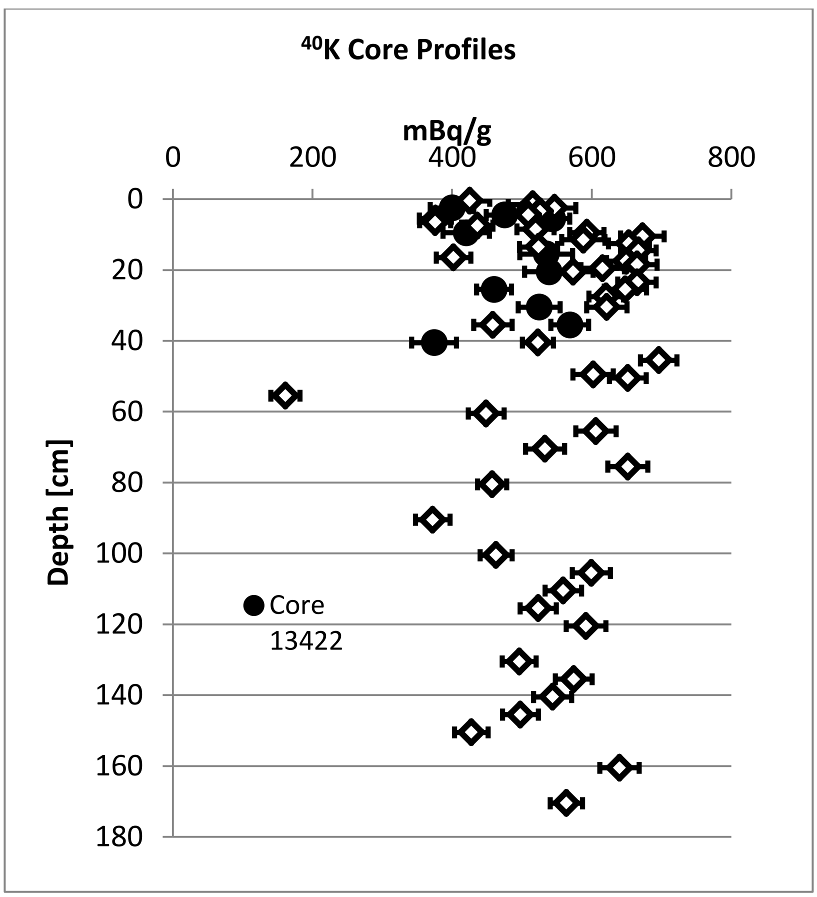



Figure 22. K-40 depth profile for Station 21484 and 13422 including activities and counting uncertainties.

***Thorium-232/Radium-228***

Thorium-232 has a long half-life (1.41 x $10^{10}$ years) compared to its immediate decay products, $^{228}$Ra and $^{228}$Ac have much shorter half-lives or 5.7 years and 6.1 minutes, respectively. By measuring the $^{228}$Ac line, the variability with depth of $^{232}$Th/$^{228}$Ra can be assessed. The conversion of counts to activity was based on comparison with the IAEA-315 SRM. The calibration was verified based on NIST-4357 SRM. The results for Stations 21484 and 13422 (up to 41 cm) are presented in Figure 23 with an activity range of 11 to 39 mBq/g. Average concentrations for core 13422 are somewhat lower than that of core 21484, 21 mBq/g versus 30. mBq/g for the first 41 cm.

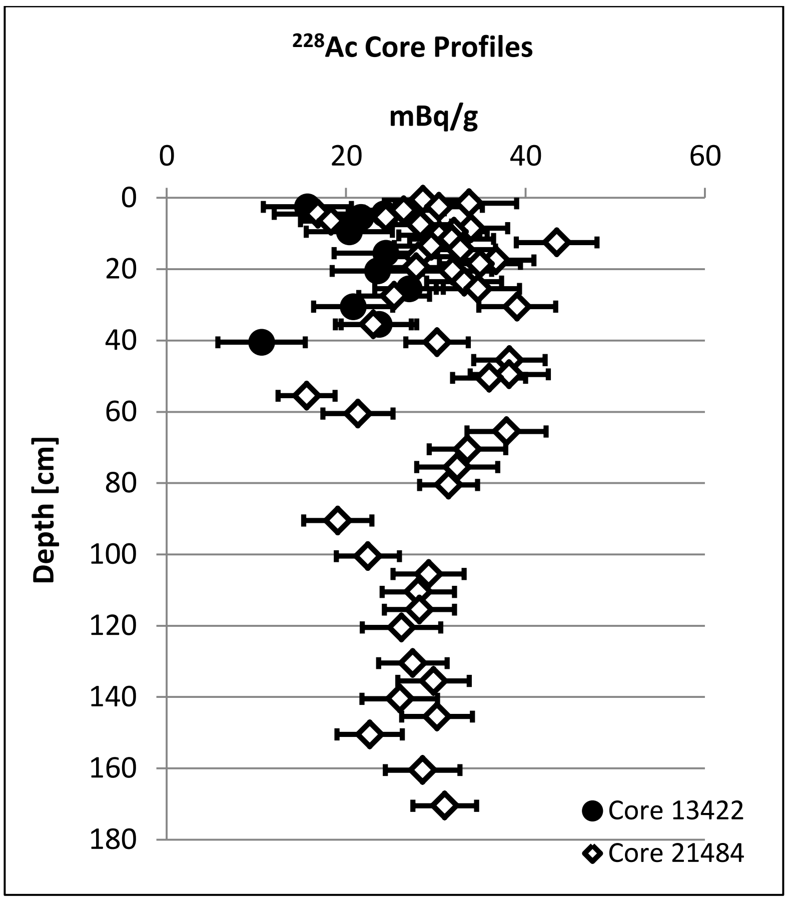



Figure 23. Thorium profile for Stations 21484 and 13422 including activities and counting uncertainties.

## Discussion

### *Sediment Profile Assessment, Zinc Distribution, and Dredge Pits and Channels as Zinc Sinks*

A sediment record up to 1 m deep for zinc, TOC, and sediment grain size now exists for nine TCEQ stations and magnetic susceptibility for eight TCEQ stations in Nueces Bay. This study confirmed that a legacy layer of zinc in sediment exists in the southern part of Nueces Bay. Data collected from this study provides current, past, and naturally occurring background levels of zinc prior to anthropogenic activity in and around Nueces Bay.

An immediate observation based on results of the analyses mentioned above is that the Nueces Bay bottom sediments are relatively inhomogeneous. Broad trends in the downcore analysis results are generally similar, and this is especially noticeable with the TOC (Fig. 24) and magnetic susceptibility data (refer to Fig. 4).

But on a finer scale, correlating stratigraphy from sediment core to sediment core is difficult. Natural processes including wind driven circulation and wave activity play a significant role in affecting the bottom, but there is also clear evidence of pervasive disturbance by human activity in the form of dredge pits, channels, and similar. Our data suggests the features play a significant role regarding the distribution of zinc in the sediments as discussed below.

The distribution of zinc in the bottom sediments is highly variable. Station 21484, located near the historical ASARCO/ENCYLE discharge point in Nueces Bay and the mouth of the Nueces River had the highest concentration of zinc and exceeded the TCEQ criteria of 410 mg/kg at a depth of 20-25 cm (Fig. 25). Yet the sediments from Station 18365, which is actually closer than Station 21484 to the historical ASARCO/ENCYCLE discharge area, reached a high value of only 57.5 mg/kg in the uppermost portion of the core (0-5 cm depth). This is a relatively a low value, and the remainder of the core profile only shows concentrations of zinc that are equivalent to the natural background values.

Slightly further to the east in the vicinity of the historical CPL discharge, and now currently the Nueces Bay Power Station discharge, Stations 18619 and 14833 both show elevated zinc concentrations over the lengths of their cores, but values do not exceed the 410 mg/kg TCEQ criteria. We postulate this unintuitive distribution is directly related to bottom disturbance by human activity because Stations 18619 and 14833 are former shell gravel dredge pits or channels that subsequently turned into sinks for high zinc concentrations as explained further below.

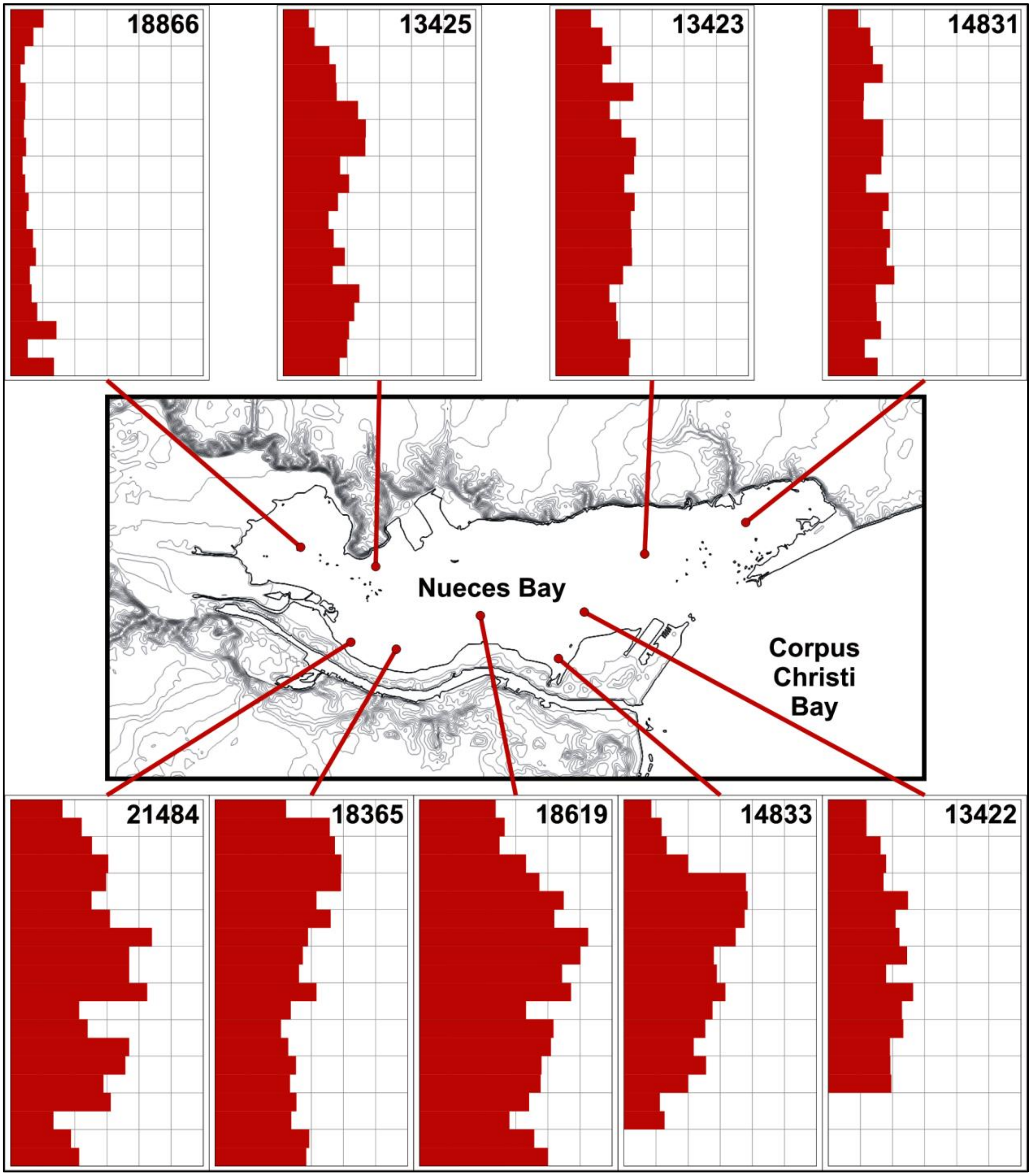



Figure 24. Total organic carbon concentration profiles for Nueces Bay sediment cores from 0-100 cm depth. The horizontal scale for all nine plots is identical, and ranges from 0-30,000 mg/kg. The graticules mark increments of 10 cm in the vertical direction, and 5,000 mg/kg in the horizontal direction. The profiles have a blocky appearance because samples were analyzed in 5 cm stratigraphic intervals.

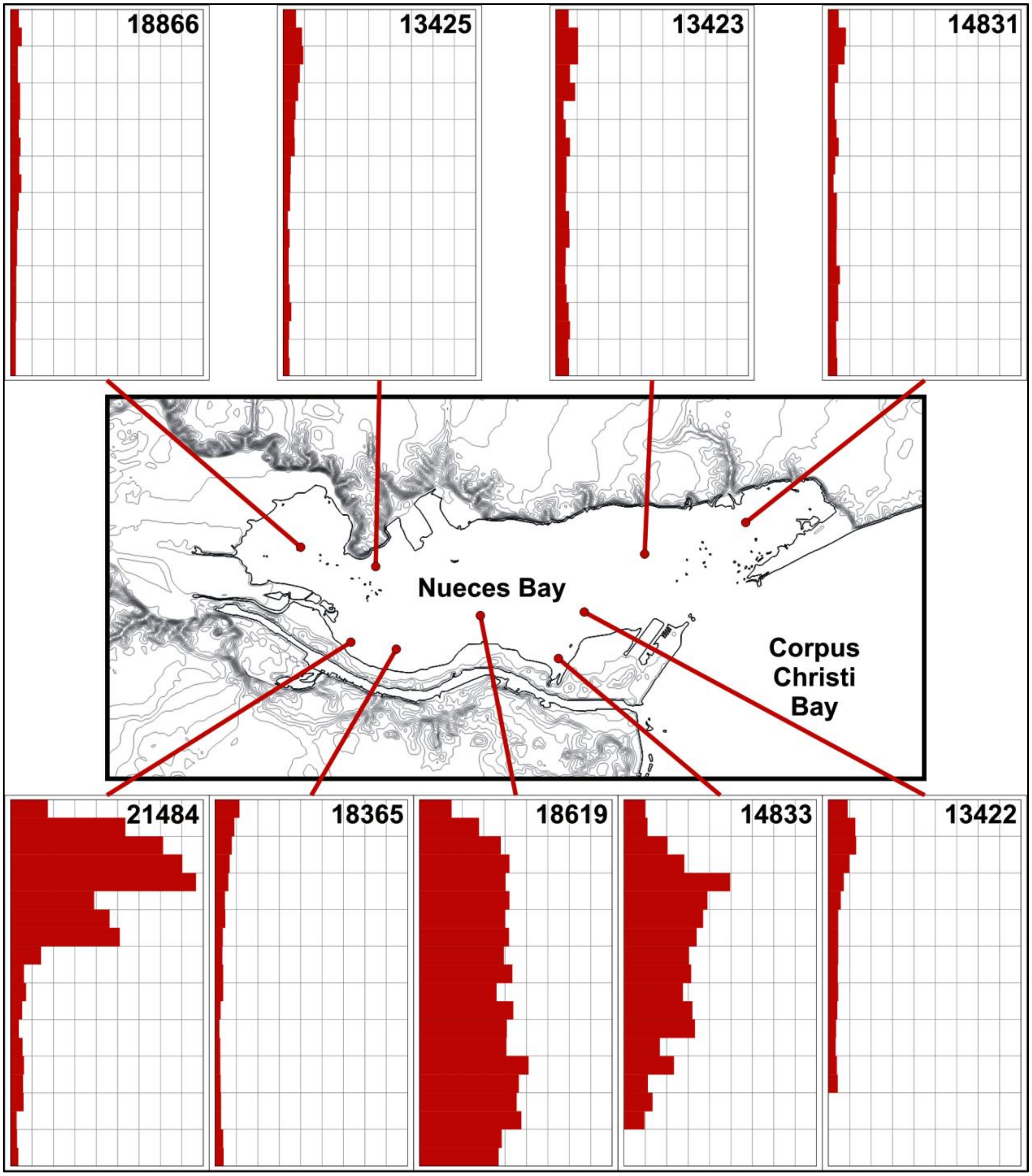



Figure 25. Zinc concentration profiles for Nueces Bay sediment cores from 0-100 cm depth. The horizontal scale for all nine plots is identical, and ranges from 0-450 mg/kg. The graticules mark increments of 10 cm in the vertical direction, and 50 mg/kg in the horizontal direction. The profiles have a blocky appearance because samples were analyzed in 5 cm stratigraphic intervals.

First, several lines of evidence support the interpretation that the cores from Stations 18619 and 14833 are penetrated infilled shell gravel dredge pits or channels. The sediments in those localities are extremely soft and poorly consolidated, and this was noted during the field collection of cores (whereas at the other stations, repeated percussion blows were needed for the coring system to penetrate the sediment). At Stations 18619 and 14833 the coring system easily penetrated the sediments under its own weight, and with gentle pressure applied to the coring system head. Though the core from Station 14833 was lost during transport, in the field it was clearly observed through the polycarbonate barrel that the stratigraphy consisted of a series of sand/shell hash and mud layers with abrupt lower and upper bounding surfaces.

Supporting evidence also comes from the lab analyses results. First, the elevated zinc concentrations in both cores extend over their whole length instead of just the upper ~40 cm like for Station 21484. And particularly for Station 18619, the zinc values are very homogenous. Second, the magnetic susceptibility profile for Station 18619 shows a muted response compared to the other cores collected from the bay. In fact, while only the uppermost 100 cm of that core is presented in this report, that core shows an abrupt lithologic discontinuity at 130 cm depth (Fig. 26).

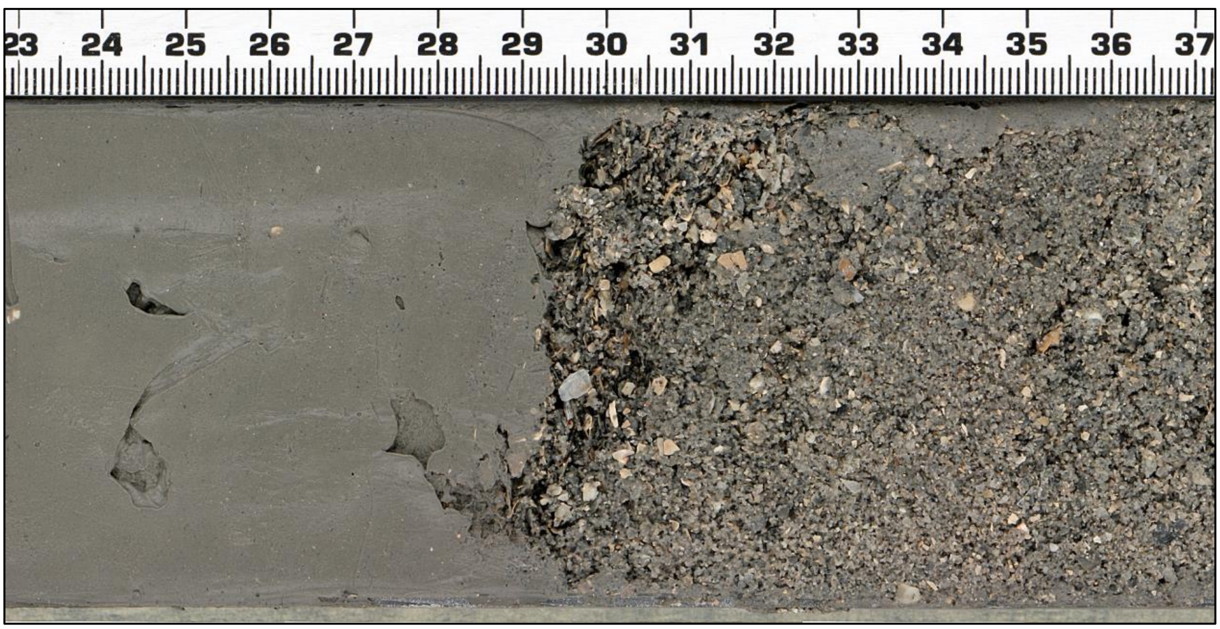



Figure 26. Abrupt transition from shell hash to mud at ~130 cm depth in the sediment core from Station 18619. This abrupt transition, together with a muted magnetic susceptibility profile, relatively constant zinc concentration values down the length of the cores, and the observations made while coring, suggest that this location is a former shell dredge pit or channel that was subsequently filled in rather rapidly.

These lab results suggest that after these areas were dredged, they were rapidly infilled, which is unsurprising given the strong wind- and wave-driven circulation that moves around the bay bottom sediments. In sum, at these two stations, the sediment cores do not display characteristics of long-term accumulation like at the remaining seven stations that were examined. Instead, Stations 18619 and 14833 show characteristics that suggest excavation followed by rapid infilling, and thus, these localities are interpreted as infilled shell gravel dredge pits or channels.

The above interpretation has very significant implications for the distribution of zinc in the bay bottom sediments. It means that any pre-existing depression or new dredge pit or channel that was excavated after the ASARCO plant began operation in 1942 may serve as a sink for sediments with high zinc concentrations. This essentially would have occurred through the process of sediment focusing (Blais and Kalff 1995) - sediment that was resuspended or moved along the bottom by wind and wave-driven circulation would have tended to settle in bathymetrically lower spots (i.e. the excavated dredge pits or channels).

At the same time, this also leads to a significantly different interpretation than what is presented in Fig. 14 about the maximum concentration of zinc around the bay. Whereas Station 21484 clearly reaches a peak zinc value (433 mg/kg) that was higher than all the other cores, the elevated zinc values in that core are confined to the upper ~40 cm of stratigraphy. In turn, for the cores from Stations 18619 and 14833, elevated but lower zinc concentration values are present, but they extend over the whole length of the core. Thus, if we integrate the total zinc content down the length of the core, a different picture emerges. Station 21484 contains a total of 2575.9 mg/kg over its length, but Station 14833 reaches quite close at 2281.1 mg/kg. But the 1-m integrated total for Station 18619 reaches an extremely elevated 3983.5 mg/kg, which is ~55% than Station 21484 (Table 5).

Table 5. Total zinc concentrations (mg/kg) when summed over the whole length of the core for station(s) 21484, 18619, and 14833.

| Station 21484 | Station 18619 | Station 14833 |
|---|---|---|
| 2575.9 | 3983.5 | 2291.1 |

A significant reminder about the above is that the sediments at Station 18619 and 14833 are very soft and poorly consolidated. So not only do they contain higher total amounts of zinc, they can be more easily disturbed resulting in the re-release of contaminants back into the water column. The remaining seven stations sampled in Nueces Bay had low zinc in sediment values compared to Stations 21484, 18619, and 14833. However, each one of these stations sampled showed higher zinc concentrations below the surficial layer starting at 5-10 cm except Station 18365 which the surficial layer 0-5 cm was the highest. This upward trend in zinc concentration starting at 5-10 cm and then decreasing down the profile assessment was observed in each station’s sediment profile. These low values in the very uppermost sediments may reflect depletion of the zinc due to constant wind and wave driven resuspension. The physical and chemical characteristics of the surficial layer are the results of interactions that control chemical input and particle dynamics of the sediment (USEPA 2004).

Several factors influence the extent of contamination; one in particular is fine-grained, organic rich sediments like clay and silt (USEPA 2004). These fine-grained sediments are characteristic of Nueces Bay and can be easily resuspended and transported to other areas within the bay. Zinc partitioning and bioavailability is also determined by the quality of the organic material associated with sediment contaminates. The three basic types of carbon in sediment are elemental, inorganic, and organic (Schumacher 2002). Organic material is the primary food source for the benthic community living atop the sediment that includes worms, crabs, mollusks, and shrimp. Increased TOC levels derived from anthropogenic contamination and from biological biomass can be detrimental to the benthic community as oxygen is depleted during decomposition and trace metals become biologically available. Sediment grain size also plays a role in determining the cation exchange of the organic fraction and/ or trace metal accumulation.

In general, elevated TOC concentrations are associated with sediments high in silt and clay content which most of the stations sampled in Nueces Bay exhibit. Generally, TOC values < 20,000 mg/kg indicate low enrichment, 20,000 - 50,000 mg/kg indicates moderate enrichment, and > 50,000 mg/kg indicates high enrichment. Clay and silt were the most dominant sediment particle size at all stations sampled except Station 14831 which consisted of more sand and gravel, Station 13422 had more sand in the upper sediment profile down to 15 cm, and sand was most dominant at Station 18866.

In this study, relatively low TOC concentrations are in the upper profile layers in Nueces Bay from 0-20 cm (<10,000 mg/kg) except at Stations 18365, 18619, and 21484. These stations are all located in the southern part of Nueces Bay near the historical ASARCO/ENCYCLE discharge point and the mouth of the Nueces River (see Fig. 24). Stations 18619 and 21484 both had TOC concentrations > 20,000 mg/kg but < 50,000 mg/kg deeper in the profile assessment. Station 18619 had the highest TOC between 25-70 cm and Station 21484 had the highest between 35-55 cm. Increased TOC at these stations, especially at the lower depths, may identify increased inflow periods from the Nueces River which brought organic matter to the bay.

***Comparison with Prior Studies:***

A substantial study of Nueces Bay and the Nueces Delta sediments was conducted by the Laboratory for Oceanographic and Environmental Research at Texas A&M University at Galveston (Santschi and Yeager 2004). While the sedimentation rates can vary substantially in an estuary, this past study measured radionuclide surface and depth profiles at several locations in Corpus Christi Bay, Nueces Bay and the Nueces Bay Delta providing a good comparison for the present study.

Differences between the studies include different equipment for the gamma ray spectroscopy with a larger HPGe well detector with inner diameter of 1.3 cm vs 1.0 cm and length of 9.4 cm vs <5.0cm used in the Santschi et al. study. Also $^{210}$Pb activities were measured using alpha spectrometry. This study, similarly to the present project, could not measure unsupported $^{210}$Pb in their Nueces Bay core closest to the Nueces River mouth (Nueces Bay Core 1). $^{137}$Cs surface activities were measured between 0.7 and 2.8 mBq/g in the Nueces Bay cores.

Measurements from the present study are compatible with these past findings. Santschi and Yeager (2004) were more successful when analyzing sediments from locations in Nueces Bay further away from the mouth of the Nueces River with $^{137}$Cs activities up to 3.3 mBq/g (13 cm) for Nueces Bay Core 2 and up to 2.0 mBq/g for Nueces Bay Core 3 (11 cm). Unsupported $^{210}$Pb activities up to 22 mBq/g and 13 mBq/g were measured for these two cores. The Nueces Delta cores yielded unsupported $^{210}$Pb concentrations ranging from 1.0 to 76 mBq/g, and unsupported $^{210}$Pb concentrations ranging from 0.5 to 32 mBq/g were measured in Corpus Christi Bay cores.

Based on these results Santschi and Yeager (2004) estimated ranges of sedimentation rates in Nueces Bay and Corpus Christi Bay versus distance from the mouth of the Nueces River (see Figure 23). Mean sedimentation rates based on $^{137}$Cs and $^{210}$Pb estimates decrease from 0.42 +/- 0.28 g/cm$^2$/yr to 0.26 +/- 0.0.08 g/cm$^2$/yr A sedimentation rate of 0.28 g/cm$^2$/yr previously estimated in this report for core 21484 is within the estimated sedimentation rate computed by Santschi and Yeager (2004) for a location relatively close to the mouth of Nueces River. The sedimentation rate of 0.53 g/cm$^2$/yr computed after assuming that the first 10 cm of core 21484 had been removed through recent anthropogenic event(s) is within that range as well.

An estimate of 0.28 g/cm$^2$/yr or 0.23cm/yr is a somewhat problematic match with the zinc depth profile measurements and the start of operations at the ASARCO plant. The comparison is not direct as the materials for the radionuclide analysis come from a different core than those for the Zn measurements. Initial Zn measurements start in the 40-45 cm depth slice of a nearby core. Assuming a 0.23 cm/yr estimated sedimentation rate is valid for both cores, this would place the start of the Zn signal in the core about 170 years ago considerably before the start of operation at the ASARCO plant in the fall of 1942. Assuming that the top 10 cm of core 21484 was removed and a sedimentation rate of 0.44 cm/yr still leads to a date of 1922 for the 40 cm layer. While this second sedimentation rate estimate is a better match to the core of Station NB-18365, one should keep in mind the large spatial variability and impact of anthropogenic events when analyzing. The comparison between these two cores continues below.

When comparing the stratigraphy of the Station 21484 core with the nearby cores its 0-10 cm stratigraphy is more sandy and includes sandy/shelly lag deposits as opposed to more clayey deposits at the surface of the nearby core. This may indicate that some material could have been removed from the surface due to prior unidentified anthropogenic activity such as fishing or coastal engineering. This possibility is reinforced by the presence in both cores of a very distinct brownish band. While the band is located at a depth of about 10-12 cm depth in the Station 21484 core, the same distinct band can be seen about 10 cm deeper in the stratigraphy of the core of station NB-18365 core, the nearest adjacent core. If we assume that ~18 cm of the top of core 21484 is missing the adjusted depth of the $^{137}$Cs peak corresponding to 1964 now changes from ~ 12 cm to ~30 cm. This leads to an average sedimentation rate of ~0.6 cm/yr. This places 1942 at a ~ 40cm depth and the start of zinc production at the ASARCO plant (Fig. 24 and Fig. 25).

A sedimentation rate of 0.6 cm/yr or 0.72 g/cm$^2$/yr is still within the wide range of the sedimentation accumulation rates found by Santschi and Yeager (2004) for locations close to the mouth of Nueces Bay (Fig. 27). A combination of removal of the top sediment layer of the Station 21484 core with possibly a different sedimentation rate at the two nearby core location likely explains the discrepancy between the unmodified $^{137}$Cs sedimentation rate and the start of production at the ASARCO plant.

Santschi and Yeager (2004) also explain the relatively low radionuclide concentrations measured ($^{137}$Cs and unsupported $^{210}$Pb) as a likely consequence of a combination of "1) the wide range of sediment grain sizes represented (coarser sediments do not provide a substrate conducive to adsorption of these isotopes) and; 2) the semi-arid climate here, where sparse precipitation results in considerably less deposition of the fallout isotopes to the land surface."

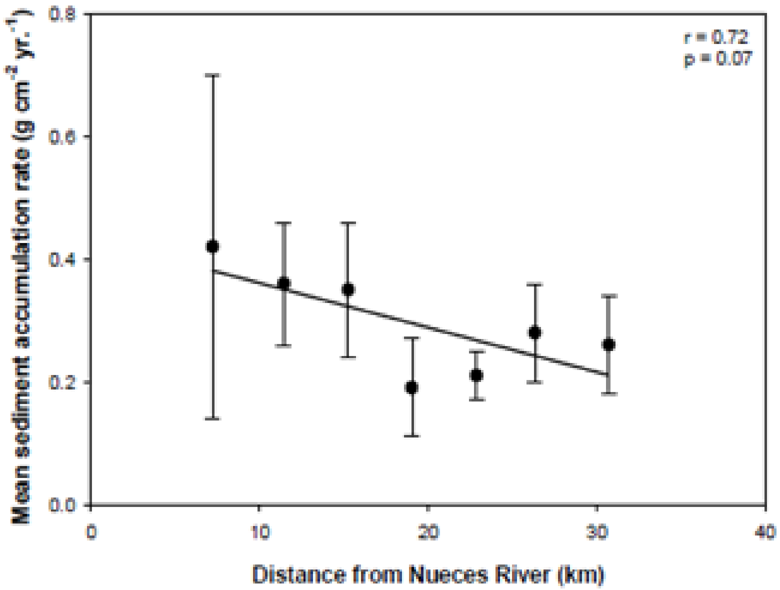



Figure 41: Mean sediment accumulation rate for each bay core versus distance from the Nueces River mouth.

Figure 27. Santschi and Yeager (2004) mean sediment accumulation rate for Nueces Bay.

**Alternate Sediment Chronology Based on Historical Analysis of ASARCO Zinc Production Rates**

Though attempts at directly dating the stratigraphy by radioanalysis of $^{137}$Cs/$^{210}$Pb were problematic, we suggest an alternative indirect dating solution based on a historical analysis of ASARCO zinc production rates, and the zinc concentrations seen in the sediment core from Station 21484.

Historical references were gathered from a variety of sources to assemble an estimated zinc production rate curve for the ASARCO plant from the start of production (October 1942) up to the closure of the facility in 1985. The production rate curve is admittedly an estimate because it was built from both hard and inferred/anecdotal data. One primary source of data was a full-page advertisement about the ASARCO plant that was published in the Corpus Christi Caller-Times in early 1969 (Corpus Christi Caller-Times, 1969). The advertisement was taken out by ASARCO itself, and provides a short corporate history of the plant. It includes some employment numbers through time, and also production rates of zinc in tons per day as the plant brought new facilities online, and increased capacity. Several data points came from the U.S. Bureau of Mines Minerals Yearbook data, which is admittedly generalized. And several data points were estimated based on comments in the online TSHA Handbook of Texas (see http://www.tshaonline.org/handbook/online/articles/dkl01). Altogether, these data points were used to assemble the production rate curve seen in (Fig. 28).

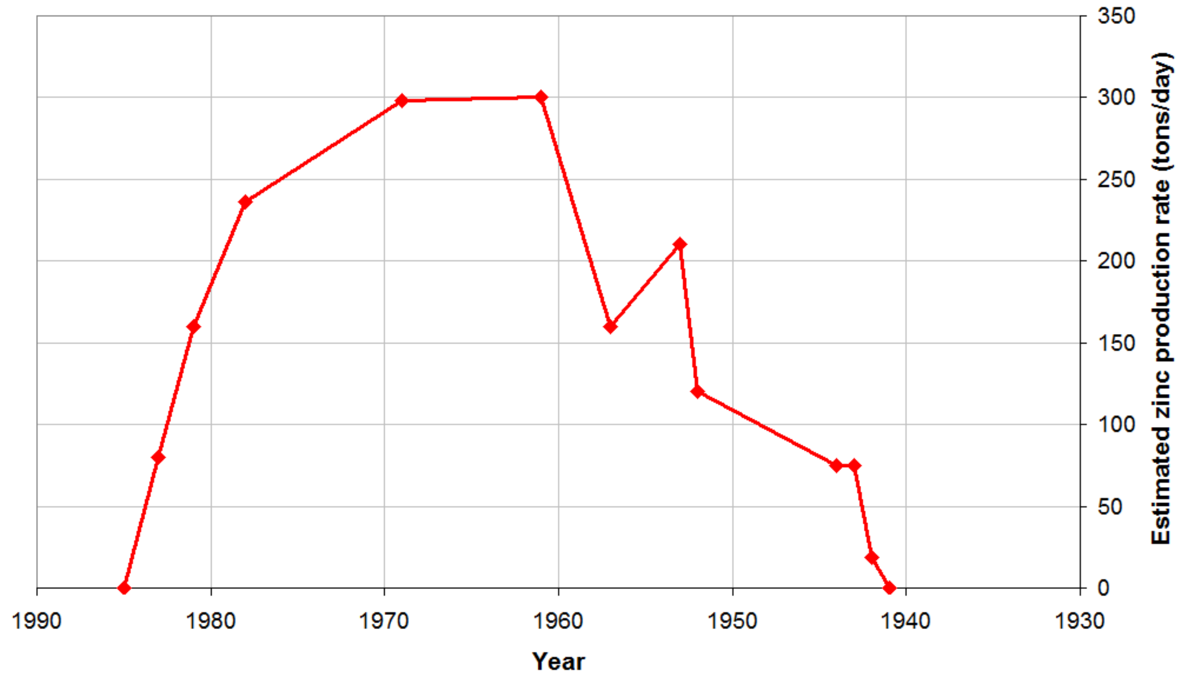



Figure 28. Estimated zinc production rate at ASARCO plant based on historical analysis.

Briefly, the curve shows a rapid ramp up from in 1942 when the plant first came online in October of that year to help with production for World War II. A second quick ramp up occurs in the early 1950's, and is probably related to production increases for the Korean War. Another ramp occurs from 1960-1961 because ASARCO brought a new plant online that essentially doubled its production capacity. And then from 1970 onward the production rate decreases till the plant is finally closed in 1985.

If we assume that the amount of effluent from the plant is proportional to the overall zinc production rate, the estimated historical production rate curve shows a remarkable similarity to the shape of the zinc concentration levels seen in the sediment core from Station 21484. This can be seen in Figure 29, which shows multiple data plots along the length of the core. In this figure, the estimated historical production rate curve has been overlaid on to the zinc concentration data to show the notable correspondence between the two curves. We therefore offer this as an indirect dating solution for the stratigraphy at Station 21484.

We note that this interpretation does conflict with the radioanalysis data. Specifically, $^{137}Cs$ was detected in the stratigraphy at low amounts from 9-13 cm depth, and since it is the only cesium

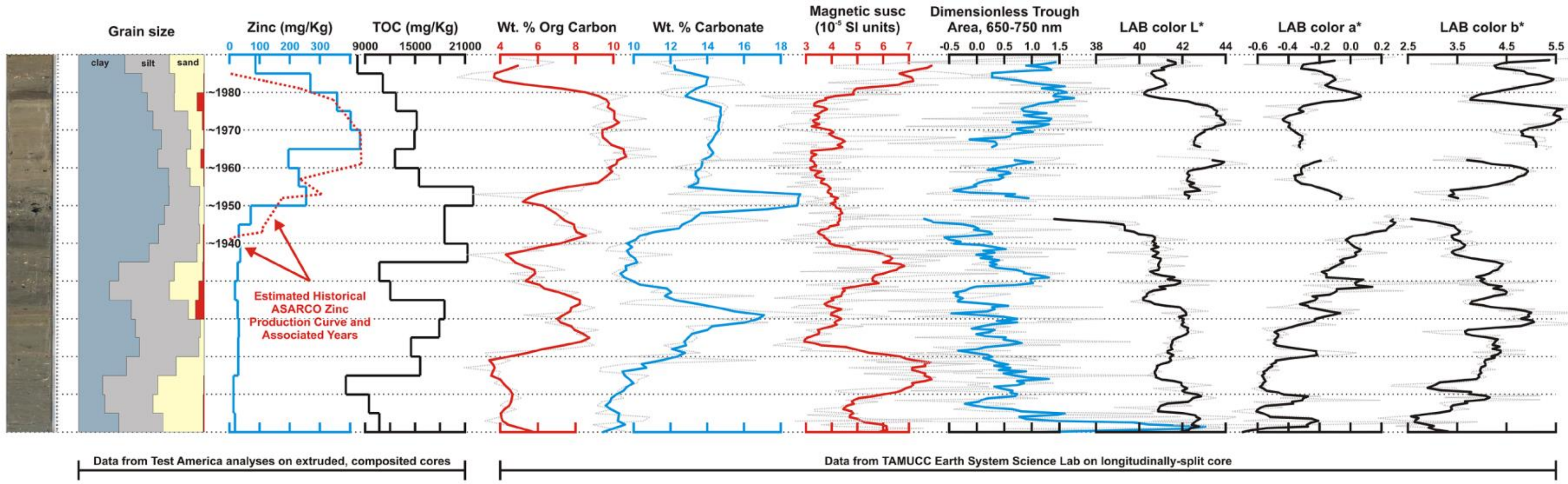



Figure 29. High-resolution multi-proxy results for the Station 21484 sediment core. This figure shows a color image of the longitudinally-split core from Station 21484 from 0-100 cm (image at left) along with ten data sets produced from analyses along the length of the core (gray dotted lines indicate 10 cm increments). Note that the estimated historical zinc production curve (dotted red curve) is overlaid on to the zinc concentration data, and their shapes are remarkably coincident. Based on this relationship, estimated ages for the stratigraphy are presented alongside the grain size data plot. The ten data sets are split into two groups. The first three data sets with the blocky appearance are from the composited, extruded sediment cores. The plots in the last seven positions were produced from high-resolution analyses of the longitudinally-split sediment core. As these two groups of data were produced from nearby but different sediment cores, a slight vertical adjustment is necessary to bring the stratigraphy into alignment based on analysis results. In particular, the data from the longitudinally-split sediment core must be shifted down ~5 cm to bring it into alignment with the results from the composited sediment core. This adjustment has not been made in this figure, i.e. both groups of data are plotted against the raw depths in their respective cores. Regarding the different appearance between the two groups of data, the composited core data has a blocky appearance because it was produced from 5-cm stratigraphic slices. Furthermore, there is generally less variability in this data because it averages together sediments from three different cores over a large stratigraphic interval. In turn, the data from the longitudinally-split sediment core shows much higher variability and higher frequency changes because analyses were run at a higher resolution (0.5 or 1.0 cm resolution) on a single sediment core. Full resolution data for these seven analyses is presented as the light gray dotted lines in the background. In turn, the visually prominent curve in each plot is a centered, five-point running mean of the full resolution data set. The weight percent organic matter and carbonate content curves were produced at 1.0 cm resolution using the loss-on-ignition method. The organic matter content as estimated by this method returns higher values than estimated by TOC analysis, but this is not uncommon as both methods have different limitations and capabilities, and the composited core data involves significant averaging as mentioned above. The large positive spike in the weight percent carbonate curve at ~40 cm reflects an abundance of shell hash. The spike at ~ 70 cm in the same curve corresponds with lighter-colored, but coarser bands in the stratigraphy, and their significance requires further analysis. The magnetic susceptibility curve generally serves as proxy for terrestrial input either via river inflow or direct surface runoff from storm events. Thus, variations along its length may represent periods of more/less river flow (i.e. more/less sediment delivery). For example, the lower values recorded between 10-50 cm may be indicative of a period of reduced inflow related to the development of the La Fruta Dam, Lake Corpus Christi, and Choke Canyon, and the return to higher values in the uppermost 10 cm may reflect the initiation of mandated water releases and freshwater inflows. However, this interpretation cannot be confirmed at this time, and further analysis is needed to rule out other changes that could have varied the amount of siliciclastic sediment delivered to the system (for example, a geomorphic change like a shift of the river mouth). The last four columns represent results from diffuse color reflectance spectrophotometric scanning. The Dimensionless Trough Area (DTA) parameter has been used as a proxy to track chlorophyll content in oceanic and lacustrine settings. We are hesitant to make an interpretation about this parameter with respect to this core because Nueces Bay is well-mixed, and additional confirmatory data such as pigment analysis by high-performance liquid chromatography (HPLC) is not available for this core. However, preliminary results from similar analyses on sediment cores from Baffin Bay show an excellent correspondence between DTA calculations and HPLC results. The LAB color L* parameter is a general measure of the lightness/darkness of a material, and this varies according to composition, grain size, organic content, redox conditions during deposition, and other factors. The LAB color a* and b* parameters track color continuums between green and red, and blue and yellow, respectively, and these are also generally reflective of changes in sediment composition.

that was detected along the length of the core, standard analysis interprets that as the 1964 nuclear testing peak. But according to the historical production curve overlay, that depth in the stratigraphy should correspond to approximately 1980. However, we do note that there is an apparent erosional surface in the stratigraphy of the core between 9-10 cm. Based on previous discussion and Fig. 17, it is clear that at least ~10 cm of stratigraphy is missing from the core top. So the overlay curve may actually have to be stretched vertically to account for this.

Regarding dating for the elevated zinc profiles seen in the sediment cores from Stations 18619 and 14833, given the postulated infill mechanism, we can only offer post-quem dates. Since the shell gravel dredge pits and channels from those localities contain elevated zinc concentration, the depressions must have been in existence in 1942, or excavated after that point, as that is when zinc production began at the ASARCO plant.

## Suggestion for Future Work

One of the compelling observations made in this study was that the dredge pits, channels, and other preexisting depressions that existed when ASARCO started production in late 1942, may very well serve as sinks for sediment with high concentrations of zinc. In this study, only two stations out of nine were inferred to be located in areas of former dredge pits and channels (i.e. Stations 18619 and 14833), but the sediment cores from both of those stations showed elevated zinc levels along their entire length. The simple conceptual model that sediment redistribution due to wind- and wave-driven circulation helps to quickly fill in these depressions, this suggests that other post-1942 depressions in Nueces Bay may have similar concentrations of zinc.

Thus, these disturbed areas may serve as localized sinks for sediment with high zinc concentrations. Though the level of zinc in the cores from these localities does not reach the TCEQ criteria of 410 mg/kg in any of the composited stratigraphic levels, they do reach moderately high levels of ~200 mg/kg. Furthermore, as the sediments at these localities are very soft and poorly consolidated, they are more easily subject to resuspension than other parts of the bay bottom. Since bioconcentration can easily magnify the level of trace metals in sediments by ten-fold or greater (Mrini et al. 2003), these moderately high levels can easily surpass the TCEQ criteria of 410 mg/kg. A suggestion for future work is to further examine the role that these bottom depressions may play. If elevated zinc levels are found concentrated in these depressions or hot spots, this has implications for management, and potentially even remediation.

## Conclusion

Station 21484 zinc data clearly shows current surficial zinc deposition in Nueces Bay is lower than historical loads related to ASARCO/ENCYLE operations. This study identified sinks or hotspots in Nueces Bay where zinc has the potential to be rereleased back into the water column via natural or human disturbance. Current surficial levels of zinc collected from this study are below TCEQ’s 410 mg/kg criteria however, at deeper levels elevated concentrations exist. Reduced surficial zinc concentrations may be contributed to natural sedimentation rates in Nueces Bay reducing surface zinc concentrations or biological uptake via filtering from the oyster population in Nueces Bay. Future projects involving activities which disturb sediments in Nueces Bay can be better managed since areas with elevated levels of zinc have been identified.

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