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HOLOCENE FORMATION HISTORY OF MUD DEPOCENTERS ON THE CONTINENTAL SHELF IN THE GULF OF CADIZ, SOUTHWESTERN SPAIN

By

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Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Coastal Marine and Wetland Studies in the School of the Coastal Environment Coastal Carolina University July 2018

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Abstract

Holocene mud accumulation on the continental shelf in northern Gulf of Cadiz, from the Guadalquivir River to the Tinto-Odiel Estuary, is described as two types of mud depocenters (MDCs): a sheet-like prodelta and mud belt. Despite a substantial number of investigations of this continental shelf (Somoza et al., 1997; Hernández-Molina et al., 2000; Lobo et al., 2001; synthesis: Lobo et al., 2015), information on Holocene sediment facies and a robust stratigraphic age model remained unestablished (Lobo et al., 2002; and Lobo and Ridente, 2014). Objectives of this study are to describe the dynamics of MDC formation in a chrono- and litho-stratigraphic approach as well as to calculate a sediment budget. Research cruise POS482 on the German RV Poseidon collected 2,040 km of seismo-acoustic profiles and forty sediment cores in March 2015 with collaborative partners of the CADISED project. X-ray fluorescence core scanning, used in combination with magnetic susceptibility, porosity, high resolution core imaging, lithology description, and radiography depict five successive sedimentary facies since 9.0 cal ka BP. Boomer data sets from 1992 and 1986 combined with new CADISED seismo-acoustic profiles provide detailed insight to the geometric formation of this depocenter. Of particular surprise is that the sheet-like prodelta MDC is locally subsiding as a result of semi-recent active extension faults related to local salt diapir uplift. \(^{14}\)C and \(^{210}\)Pb dating provide an age control to the history of mud accumulation. Grain density and sedimentation rates determine accumulation trends in the range of 0.03 to 0.46 grams per cubic millimeter a year (g mm\(^{-2}\) yr\(^{-1}\)) from early Holocene times until 2.7 cal ka BP. The following 1500 yrs show rates increasing by up to ninety times (0.32 to 2.66 g mm\(^{-2}\) yr\(^{-1}\)), correlating with a widespread humid climate period from 2.6 to 1.6 cal ka BP and enhanced mining and agricultural activity by the
Roman Empire. Since 1.0 cal ka BP, accumulation rates increase even further due to industrialization and intense land use (1.09 to 28.63 g mm$^{-2}$ yr$^{-1}$). Smaller climatic events also contributed to changes in sediment accumulation. For example, the Medieval Climate Anomaly (MCA) coincided with a decrease from 1.05 to 0.7 cal ka BP. The total volume of the MDCs is 5.80 km$^3$ with a total and dry sediment mass of 12,971 Mt. Total Organic Content (TOC) mass of 85 Mt and a 0.038 km$^3$ volume with a CaCO$_3$ mass of 3,637 Mt and a 1.63 km$^3$ volume makes this depocenter an important quasi-modern sink in the marine sector of the regional carbon cycle.
# Table of Contents

Acknowledgements .......................................................................................................... iii

Abstract ............................................................................................................................... v

1.0 Introduction .................................................................................................................... 1

2.0 Background – Northern Gulf of Cadiz Continental Shelf ........................................ 3

2.1 Mud Depocenter Classification .................................................................................... 3

2.2 Holocene Sea Level History and Response of the Sedimentary System .................. 5

2.3 The Holocene as a Climatic Epoch .............................................................................. 6

2.4 Regional Oceanographic Currents .............................................................................. 9

2.5 Fluvial Sources – Characterization and Geologic Foundation .................................. 11

2.6 Shelf Characteristics and Stratigraphy ....................................................................... 14

3.0 Objectives and Research Questions ....................................................................... 16

3.1 Chrono- and Lithostratigraphy of Mud Depocenters ................................................ 16

3.2 Budget Calculation of Mud Depocenters .................................................................. 17

4.0 Materials and Methods ............................................................................................. 18

4.1 Seismo-Acoustic Data ............................................................................................... 19

4.2 Multi-Sensor Core Logger (MSCL) Data ................................................................... 20

4.3 Sediment Properties and Budget Calculation ............................................................ 20

4.4 X-ray Fluorescence Element Scanning ..................................................................... 22

4.4.1 Element Intensity Ratios ..................................................................................... 22

4.4.2 X-ray Fluorescence Powder Element Measurement ........................................... 24

4.5 $^{14}$C Dating .............................................................................................................. 24

4.6 $^{210}$Pb and $^{137}$Cs Dating ........................................................................................ 25

4.7 High-Resolution Core Imaging .................................................................................. 26

5.0 Critical Evaluation of Stratigraphic Age Model and Material Budgets .................... 27

5.1 Calculation of Sedimentation Rates .......................................................................... 27

5.2 Calculation of Material Budgets ................................................................................ 29

6.0 Results .......................................................................................................................... 30

6.1 Age framework .......................................................................................................... 30

6.2 Determination and Timing of Sedimentary Facies .................................................... 30

6.3 Stratigraphic Architecture ......................................................................................... 34

6.4 Material Budget Calculation ...................................................................................... 38

6.5 Carbon Budget Calculation ....................................................................................... 38
List of Tables

Table 1. Justification to use specific data for each Thesis Objective.

Table 2. Justification for stations selected in the study area based on preliminary interpretation of acoustic data. (1)Representative stations used for correlating element intensity ratios to create a robust age framework for MDCs.

Table 3. Data sets collected at coring stations within study area.

Table 4. Summary of MDCs facies characterization by sediment properties.

Table 5. Sediment cores with coordinates, water depth taken, sediment sample depth in core, measured conventional radiocarbon ages (+1σ error), calibrated radiocarbon ages (+1σ error, calibrated with CALIB software version 7.10 with data set "marine13.14c") (Stuiver and Reimer, 1993; Reimer et al. 2013).

Table 6. Age models for Cores 19534-3, 19520-3, 19512-3, and 19535-3, using $^{210}$Pb and $^{137}$Cs dating methods. All ages are given in Common Era (CE). Constant Rate of Supply (CRS) and Constant Initial Concentration (CIC) models were used for $^{210}$Pb ages.

Table 7. Sedimentation rates (cm ka$^{-1}$) calculated between two age points using $^{210}$Pb profiles and $^{14}$C dating. Listed by coring site. Example of how to read the table: The lowermost part of Core 19521 has a sedimentation rate of 12 cm ka$^{-1}$ from 8.98 to 6.67 cal ka BP.

Table 8. Accumulation rates (g cm$^{-2}$ ka$^{-1}$) based on $^{210}$Pb profiles and $^{14}$C dating. Listed by stations. Example how to read this table: The base of 19521 has an accumulation rate of 16 g cm$^{-2}$ ka$^{-1}$ from 8.98 to 6.67 cal ka BP.

Table 9. Summary of MDCs sediment properties by time slice as defined from seismo-acoustic profile analysis.

Table 10. Representative total carbon content (TC), total organic content (TOC), and calcium carbonate content (CaCO$_3$) for MDCs.

Table 11: Comparison of three shelf systems with a confined MDCs, for which a high-resolution budget analysis was performed. (1) This study; (2) Lantzsch et al., 2009; (3) Brommer et al., 2009. Although the base of the MDCs from the Gulf of Cadiz are dated at 10.0 ± 1.0 cal ka BP, the regime change occurred at 6.5 cal ka BP (comparable to the other systems). (*) Calculated number.
List of Figures

Figure 1. The Guadalquivir River in southeastern Spain pushing a sediment filled plume into the northern Gulf of Cadiz on 13 November 2012 (Schmaltz, 2012). The red circle represents the study area for this study.

Figure 2. (A.) Location map of Iberian Peninsula in relation to study area. (B.) Zoomed in to track lines of POS482 echosounder data (black lines). (C.) Study area between the Tinto-Odiel Estuary and Guadalquivir River. Due to map size, Station names were reduced to their representative last two digits: Station 19513 is location 13, etc. Station location numbers that are focused on have a pink background. Figure locations of seismo-acoustic profiles are depicted.

Figure 3. Suspended sediment discharges from a freshwater plume forming a bottom layer that is driven by gravity and bottom currents. This bottom layer either deposits forming MDCs or bypasses the system off the shelf edge (Hanebuth et al., 2015).

Figure 4. Surface distribution of sediment. (A) Faro-Tavira wedge; (B) inner wedges; (C) shelf aggradational deposits (C1: undifferentiated shelf aggradational deposits, C2: shelf muddy belts, or shelf aggradational deposits with elongated patterns; C3: main MDCs of shelf muddy belts); (D) Guadalquivir wedge (Lobo et al., 2004).


Figure 6 (A). A high-resolution seismo-acoustic profile off the Guadalquivir River. (B). Interpretations of the high-resolution profile depict a TST and the repetition of progradational and aggradational deposition units during the Holocene HST (Lobo et al., 2005; modified from Fernández-Salas et al., 2003). Location of this profile is depicted on Figure 2.

Figure 7. Relative mean sea level curve since 9.0 cal ka BP from the Quarteira coast, in the Gulf of Cadiz, Portugal. Each box is error represented for one sample from lagoon and estuarine sediments. Image modified by Zazo et al. (2008) from Teixeira et al. (2005).


Figure 9. Surface circulation patterns of the southwest Iberian Peninsula. N2 and N1 are described by García-Lafuente et al., 2006 as cores of eastward flowing water. N2 is a portion of large-scale circulation current that drives the geostrophic flow around the southeastern Iberian Peninsula from the Portuguese Current, also referred to simply as the NASW (Lobo et al., 2004). N2 flows east through the Strait of Gibraltar into the Mediterranean or veers south becoming part of the Canary current. N2 is warmer and saltier than N1, suggesting N1 contains water from another body.
The dashed line at the southeast indicates closure of core N1 with the Coastal Counter Current (CCC). The CCC feeds core N1 in the west, however, under favorable conditions can bypass Cape Santa Maria westward feeding the Cape San Vicente cyclonic eddy (SVE) (García-Lafuente et al., 2006).

Figure 10. Basic Geologic Map of Spain depicting the location of the Guadalquivir basin and insert (a.) depicting in detail the Iberian Pyrite Belt (IPB) composed of three lithological groups: the Phyllite-Quartzite Group, Volcano-Sedimentary Complex (VS), and the Culm Group (Spanish Geological Survey IGME 1998; (a.) Onézime et al., 2003).

Figure 11. Pb/Al ratio concentrations with overlapping human impact time periods that have caused chronological markers as early as the Bronze Age in the Alboran Sea and Zoñar Lake in Spain (Martín-Puertas et al., 2010).

Figure 12. Ln Ti/Fe ratio, comparing two proxy elements used in identifying terrigenous material from cores that include all facies (19535-3, 19538-3, and 19513-3). The \(^{14}\)C ages presented are those collected from the depth portrayed. See Figure 2 for coring station locations.

Figure 13. Interpretive stratigraphic core correlation represented by orange lines of ln (Ca/Fe) from the Tinto-Odiel Estuary to the Guadalquivir River (distal to shore) Cores 19538-3, 19513-3, and 19518-3. The red lines indicate calibrated \(^{14}\)C ages collected from the core. For location of core transect see Figure 2.

Figure 14. Ln Ti/Al ratio, comparing two proxy elements used in identifying terrigenous material from cores that include all facies (19535-3, 19538-3, and 19513-3). The \(^{14}\)C ages presented are those collected from the depth portrayed. See Figure 2 for coring station locations.

Figure 15. Interpretive stratigraphic core correlation represented by orange lines of ln (Ca/Fe) in cores 19534-3, 19535-3, and 19538-3 located perpendicular to shore from the Tinto – Odiel Estuary. The red lines indicate calibrated \(^{14}\)C ages collected from the core.

Figure 16. Combined stratigraphic correlation of element intensity ratios and magnetic susceptibility from stations perpendicular to shore from Tinto-Odiel region to Guadalquivir. Numbers above red lines on cores are radiocarbon samples dated in cal ka BP. The same interpretive correlation in Figure 15 of ln Ca/Fe is also represented here by orange lines in correlation 19534-19535-19538. The multi-color grey and white boxes indicate different facies interpretations represented within the cores (Figure 21). Core lengths are indicated by the extent of the facies boxes.

Figure 17. Combined stratigraphic correlation of element intensity ratios and magnetic susceptibility from stations parallel to shore from proximal to distal. Numbers above red lines on cores are radiocarbon samples dated in cal ka BP. The same interpretive correlation in Figure 13 of ln Ca/Fe is also represented here by orange...
lines in correlation 19538-19513-19518. The multi-color grey and white boxes indicate different facies interpretations represented within the cores (Figure 21). Core lengths are indicated by the extent of the facies boxes.

Figure 18. Depth – Age representation of sedimentation rates given in thousands of years (cm/ka) for transect near the Guadalquivir River (Site locations: Figure 2). Ages from $^{210}$Pb located at tops of cores are given in Common Era (CE). Ages with an asterisk (*) indicate data was extrapolated from seismio-acoustic profiles. For a complete list of sedimentation rates refer to Table 7. Note that depth profiles are not the same size due to differences in rates of sedimentation.

Figure 19. Depth – Age representation of sedimentation rates given in thousands of years (cm/ka) for transect shore-perpendicular through the central portion of the study area (Site locations: Figure 2). Ages from $^{210}$Pb located at tops of cores are given in Common Era (CE). For a complete list of sedimentation rates refer to Table 7.

Figure 20. Depth – Age visual representation of sedimentation rates given in thousands of years (cm/ka) for transect shore-perpendicular near the Tinto-Odiel Estuary (Site locations: Figure 2). Ages from $^{210}$Pb located at tops of cores are given in Common Era (CE). Ages with an asterisk (*) indicate data was extrapolated from seismio-acoustic profiles. For a complete list of sedimentation rates refer to Table 7. Note that depth profiles are not the same size due to differences in rates of sedimentation.

Figure 21. Idealized profile and lithology descriptions of the successive sedimentary facies units (A – F) synthesized from the sediment cores collected. Yellow ages are the range at which the facies boundaries are present in cores, depending on core location and accumulation rate. Ages listed next to the core image of 19538-3 were amassed through the age model created for site 19538 and fall within facies boundary age ranges. Ln Ti/Zr ratio depicts a fining upward of sediment. Ln Ca/Fe ratio shows a general increasing trend of terrigenous material up core. Sequence stratigraphic interpretation includes transgressive systems tract (TST), maximum flooding surface (mfs), and highstand systems tract (HST).

Figure 22. Ln Ti/Zr ratio used as a grain size proxy. Depth axis are not depicted by the same scale to clearly show similar grain size trends from cores that include all facies (19535-3, 19538-3, and 19513-3). The $^{14}$C ages presented are those collected from the depth portrayed. See Figure 2 for coring station locations.

Figure 23. Photos from selected cores illustrating sedimentary facies of mud accumulation of MDCs on the continental shelf in the Gulf of Cadiz, Southwestern Spain.

Figure 24. Compilation of the 98 accumulation rates from MDCs. The green background envelope includes accumulation rates from the prodelta MDC and the purple of the mud belt MDC. Three high accumulation rates from modern deposition are not shown to depict in greater detail older accumulation rates. Two rates from 4.72 to 1.95 cal ka BP and one rate from 1.95 to 0.88 cal ka BP were not used in the prodelta MDC envelope due to the higher error associated with the seismio-acoustic extrapolated ages. Low accumulation rates were persistent until 2.7 to 0.4 cal ka BP when
the rates increased to about 1.4 g mm\(^{-2}\) ka\(^{-1}\). From 0.4 cal ka BP to present, accumulation rates increased exponentially to as high as 29 g mm\(^{-2}\) ka\(^{-1}\).

Figure 25. (A.) Seismo-acoustic profile and (B.) with interpretations, depicting Holocene mud accumulation near the Tinto-Odiel estuary. The zoomed-in section shows in high-resolution the internal stratification of the mud belt MDC. Major horizons are traced and correspond to the age model collected from \(^{14}\)C dates. Location of this profile is depicted on Figure 2.

Figure 26. (A.) Seismo-acoustic profile and (B.) with interpretations, depicting Holocene mud accumulation of the northwestern portion of the prodelta MDC, shore-perpendicular. The zoomed-in section shows in high-resolution the internal stratification around mud entrapments. Major horizons are traced and correspond to the age model collected from \(^{14}\)C dates. Location of this profile is depicted on Figure 2.

Figure 27. Notable features relating to the MDCs overlain on ship track lines and station locations. The faults labeled are found only within the Holocene sediment. Faults associated with Structures are speculative. The prodelta MDC is centrally located near two acoustically masked locations. The southwestern acoustically masked area is below the Holocene sediment. There are deeper extension faults located in correlation with diapirs.

Figure 28. (A.) Seismo-acoustic profile and (B.) with interpretations, depicting Holocene mud accumulation of the southeastern portion of the prodelta MDC, shore-perpendicular. The zoomed-in section shows in high-resolution the internal stratification are traced and correspond to the age model collected from \(^{14}\)C dates. Horizons stop at acoustic masking locations. Location of this profile is depicted on Figure 2.

Figure 29. Mud Belt MDC (coring sites 19534, 19535, 19538) and Prodelta MDC (coring sites 19512, 19513, 19518, 19519, 19520, 19521) central depositional locations outlined by contour thickness of 6 m. Coring sites are distinguished by blue dots.

Figure 30. Isopach map of the MDCs from stratigraphic base to modern seafloor. Blue dots are coring locations for reference.

Figure 31. (Profile A) One lobe of the eastern diapiric uplift, close to the Guadalquivir River, 40 m from mean sea level. (Profile B) The cap rock of the diapir has penetrated the base of the prodelta MDC, 3 m from seafloor. Location of seismio-acoustic profiles in Figure 2.

Figure 32. Western diapir with related extension faults, located near shelf edge below the base of the prodelta MDC. Location of seismio-acoustic profile in Figure 2.

Figure 33. Isopach map from the base of the MDCs to sediment horizon dated at 2.0 ± 0.1 cal ka BP (Slice 1). Blue dots are coring locations for reference.

Figure 34. Isopach map from sediment reflector dated at 2.0 ± 0.1 cal ka BP to sediment reflector dated at 1.0 ± 0.1 cal ka BP (Slice 2). Blue dots are coring locations for reference.

Figure 35. Isopach map from sediment reflector dated at 2.0 ± 0.1 cal ka BP to modern
seafloor (Slice 2.5). Blue dots are coring locations for reference.

Figure 36. Isopach map from sediment reflector dated at 1.0 ± 0.1 cal ka BP to modern seafloor (Slice 3). Blue dots are coring locations for reference.

Figure 37. Entrapping structures subsiding as a result of overbearing sediment weight causing major horizons and prodelta MDC base to dip towards the central accumulation center of the depocenter. Location of seismio-acoustic profile in Figure 2.

Figure 38. Comparison of sedimentation rate trend from the MDCs (orange line), based on sediment cores in this study, with an idealized sedimentation rate trend from estuaries (blue line), modified from Lario et al. (2002). (For accumulation rates for this study, see Figure 23).

Figure 39. Evidence of block-like subsidence occurring between the two main diapir locations affecting the prodelta MDC. Location of seismio-acoustic profile in Figure 2.

Figure 40. Acoustic masking due to the presence of gaseous sediments near the western diapir along the shelf edge. Location of seismio-acoustic profile in Figure 2.
1.0 Introduction

Fluvial sources supply the majority of continent derived, fine grained sediment to a continental shelf. If adequate ocean currents exist, further transport of sediment will occur until currents dissipate, allowing for deposition. These depositional locations, commonly described as mud depocenters (MDCs) or mudbelts, form during periods of slow sea level change or standstill (Hanebuth et al., 2015a).

The study area is confined to the northeastern Gulf of Cadiz in water depths ranging from 15 to 200 m. The Gulf of Cadiz shelf has a diverse depositional system with multiple fluvial sources of sediment influx (Lobo et al., 2004). The Guadalquivir River is the main source, delivering a large sediment plume, altered by ocean currents (Figure 1). Previous studies on the shelf, near on the Guadalquivir River, depict transgressive units overlain by two sequences of progradational and aggradational units in the Holocene highstand systems tract (Lobo et al., 2005).

The interplay between sediment supplied by several rivers, a complex ocean current system, climatic events, fluctuating sea level, and anthropogenic modifications on land can control the depositional architecture of highstand MDCs on the continental shelf in the northeastern portion of the Gulf of Cadiz, Spain. Previous investigations of MDCs in the Gulf of Cadiz have relied almost exclusively on subbottom echosounder data (Lobo et al., 2001, 2002, 2004, 2005; synthesis: Lobo et al., 2015). The seismic stratigraphic architecture has been generally described in several studies (Somoza et al., 1997; Hernández-Molina et al., 2000; Lobo et al., 2001; synthesis: Lobo et al., 2015; Lobo and Ridente, 2014).
Despite a substantial number of investigations in the Gulf of Cadiz, information on sediment facies types and accumulation rates from the Holocene are limited by location (Guadalupe: Mendes et al., 2010, 2012; Martins et al., 2012) or by age coverage and resolution (Nelson et al., 1999; Abrantes et al., 2017). The first objective of this master’s thesis is to fill that void by investigating the chrono- and litho- stratigraphy based on a set of sediment cores in combination with seismo-acoustic data sets, while speculating on mechanisms controlling sediment deposition. The other objective is to devise volume and mass budget calculations for the Gulf of Cadiz MDCs.

This thesis will utilize an extensive seismo-acoustic data set and eighteen marine sediment gravity cores to determine the formation history of confined shelf MDCs related to the Guadalquivir River and various other surrounding sources. Subbottom echosounder profiles and sediment cores were collected on March 14-25, 2015 during RV Poseidon cruise POS482 CADISED (Cadiz Shelf Sediment Depocenters), providing excellent data coverage for this study (Figure 2). Gravity cores and sediment samples are compared to the seismo-acoustic data set and analyzed for magnetic susceptibility, porosity, density, element intensity distribution, element concentrations, radiocarbon (\(^{14}\text{C})\) dates, and Lead-210 (\(^{210}\text{Pb}\)) and Cesium-137 (\(^{137}\text{Cs}\)). These analyses provide a basis for development of age models leading to detailed insight of centennial through millennial changes of shelf mud accumulation patterns, driven by climatic changes and anthropogenic industrial-scale advancements.
2.0 Background – Northern Gulf of Cadiz Continental Shelf

2.1 Mud Depocenter Classification

MDC formation begins as freshwater and sediment discharges from a fluvial source onto the continental shelf creating a freshwater plume (Figure 3). Sediment falls out of suspension from the plume to form a distinct turbid (nepheloid) bottom layer, driven mainly by bottom currents and gravity (Figure 3; Hanebuth et al., 2015a). Through shelf currents, gravity forcing of the nepheloid layer, wave and tidal action, sediment either deposits, forming MDCs or bypasses them across the shelf break (Hill et al., 2007; Hanebuth et al., 2015a).

Although there are many ways to classify a MDC, there are some common traits used to define them. A MDC must have at least a 25% mud concentration (George and Hill, 2008), whereas mud is defined as material that is < 63 micrometers (μm) (McCave, 1972) which is a mixture of silt and clay. Most MDCs contain a mixture of sand, silt, and clay with an occasionally strong silt fraction (Hanebuth and Lantzch, 2008).

MDCs form differently on continental shelves due to shelf gradient, sediment discharge from fluvial sources, local hydrodynamic forcing, current strength and direction, and sea level rise or stand still. Walsh et al., 2009 defined a hierarchical tree to predict marine accumulation systems at most river mouths using morphologic and oceanographic characteristics. Their system relies on having knowledge of the sediment quantity discharged per yr, shelf width, and wave and tidal conditions in the area. Depocenter locations can rapidly shift in response to short-term sea-level fluctuations (Hanebuth et al., 2011).
Hanebuth et al. (2015a) defined eight different kinds of MDCs: prodelta, subaqueous deltas, mud patches, mud blankets, mud belts, shallow-water contourite drifts, mud entrapments, and mud wedges. Walsh et al., 2009 defined additional locations of deposition, such as a canyon or past the shelf break. For this study, the focus is on prodelta, mud blankets, mud belts, and mud entrapments due to an abundant terrestrial sediment supply and previous morphological characterization of MDCs on this shelf (Lobo et al., 2004, 2005; Hanebuth et al., 2015a).

Sheet-like prodelta MDCs are attached to a fluvial point source pinching-out seaward (Hanebuth et al., 2015a). A MDC formed by the Guadalquivir River in the Gulf of Cadiz has been identified as a prodelta type due to mainly aggradational trends found within seismo-acoustic data (Figure 4; Fernández-Salas et al., 2003; Lobo et al., 2004, 2005). Analysis of these seismo-acoustic profiles depicts alternating sequences of progradational deposits overlain by aggradational subunits (Lobo et al., 2005).

Rarely found mud blankets have extensions that are near to sediment source with equal shelf-wide and sheet-like sediment distribution in various directions (Hanebuth et al., 2015a). Acoustic profiles of mud blankets, either attached to the point source or closely associated, depict a more or less constant thickness over the continental shelf (Hanebuth et al., 2015a). The MDC formed by the Guadalquivir River has also been described as having mud blanket like shelf-wide extensions (Lobo et al., 2004).

Mud belts are elongated sediment bodies with aggradational deposition thinning seaward and typically form parallel to bathymetry with detachment from the point source (Hanebuth et al., 2015a). The shelf off Galicia in northwest Spain and parts of the Gulf of
Cadiz (Figure 4) are examples of classic mud belts (Fernández-Salas et al., 2003; Lobo et al., 2004, 2005; Hanebuth et al., 2015a).

Locally defined mud entrapments occur where sediment becomes trapped around an obstacle or in a depression on the seafloor. Mud entrapments contain a planar surface and show a homogeneous to slightly horizontal internal stratification (Hanebuth et al., 2015a). Acoustic profiles of mud entrapments also depict detachment from point source with sheet to trough-like fill (Lantzsch et al., 2009; Hanebuth et al., 2015a).

2.2 Holocene Sea Level History and Response of the Sedimentary System

High-resolution seismic stratigraphy at various shelf locations depicts inconsistent sea-level changes, during the Holocene (Lobo et al., 2001, 2002, 2004, 2005), owing to localized isostatic effects (Hernández-Molina et al., 1994). Lobo et al. (2001) proposed a chronostratigraphic framework for Gulf of Cadiz shelf deposits based upon correlation of seismo-acoustic data with eustatic sea-level curves from Fairbanks (1989), Stanley (1995), Hernández-Molina et al. (1994), and Bard et al. (1996) (Figure 5). The trend of all these sea-level curves indicates the Iberian Peninsula experienced sea-level rise during the early Holocene and slow sea-level rise or standstill during the late Holocene (Figure 5; Lobo et al., 2001).

Sea level rose relatively fast after 11.7 cal ka BP (start of the Holocene) with intermittent moments of sea level stability due to melting of high latitude icecaps (Bird et al., 2007) to a point around 8.0 cal ka BP (MWP-2 – Alley et al., 1997; Bird et al., 2007). The filling of incised valleys and continued shoreline retrogradation, during rapid sea level rise, is described as being part of a transgressive systems tract (TST) (Van Wagoner et al., 1988). A TST is preserved on the Gulf of Cadiz shelf by localized sediment beds deposited at fast
rates or areas of little accumulation (Figure 6; Van Wagoner et al., 1988; Lobo et al., 2001, 2004). A period of deceleration in sea level rise occurred from about 8.0 cal ka BP until 6.5 cal ka BP, when sea level began to stabilize forming a maximum flooding surface (mfs) (Figure 7; Dabrio et al., 2000; Lario et al., 2002; Zazo et al., 2008 from Teixeira et al., 2005). A mfs occurs when sea level reaches its highest point in flooding the continental shelf (Van Wagoner et al., 1988) and is associated in the Gulf of Cadiz shelf with a condensed sedimentological record (Dabrio et al., 2000; Lario et al., 2002).

After 6.5 cal ka BP, sea level stabilized to the present position (Figure 7; Dabrio et al., 2000; Lario et al., 2002; Zazo et al., 2008 from Teixeira et al., 2005), allowing a highstand unit (HST) form with a depositional geometry characterized by aggradational and progradational clinoforms (Van Wagoner et al., 1988; Lobo et al., 2005). HST occurs during the latest portion of sea level rise, standstill, and the early portion of following sea level fall (Van Wagoner et al., 1988).

2.3 The Holocene as a Climatic Epoch

Climate variability in the Holocene is characterized by intervals of polar cooling, solar variability, and changes in atmospheric circulation (Mayewski et al., 2004). Prevailing winds in southern Iberia from 10 to 6.45 cal ka BP changed direction from SW to W prompting paleocurrents to flow NE to E (Goy et al., 1996). Eolian dune preservation from 6.45 to 3 cal ka BP indicates prevailing winds drastically changed direction causing paleocurrents to flow in a W direction. For a brief time (3 to 2.75 cal ka BP), prevailing winds shifted significantly causing paleocurrent flow direction to flip from W to E. Since 2.75 cal ka BP, a strong fluvial influence on sedimentation, indicates strong rain in short periods under drought-like conditions (Goy et al., 1996).
Rapid climate changes from 6.0 to 1.0 cal ka BP in the Northern Hemisphere featured intervals of ice-rafter debris (IRDs) and westerlies strength changes over the North Atlantic causing cold poles and dry tropics (Mayewski et al., 2004). Many studies characterize the Holocene as having 1.5 ka ± 500 yr oscillation cooling events (found by studying IRDs) commonly referred to as Bond cycles, with the most recent occurring around 2.8 and 1.4 cal ka BP (Bond et al., 1997; Darby et al., 2012; Wanner et al., 2015). Deep sea cores from the North Atlantic have revealed abrupt climatic shifts in the relatively stable Holocene climate. These IRD events were determined by studying in high-resolution, prominent concentrations of lithic grains and elevated abundance of certain planktonic foraminifera species. Studies suggest these IRD events may be triggered by decreases of solar irradiance at high latitudes leading to cooling of ocean surface and reduction of precipitation in low-latitudes (Bond et al., 2001). In contrast, more recent publications have concluded that Bond Events are not directly caused from solar forcing at high latitudes, yet there seems to be a strong link between climatic records and low latitude solar forcing (Darby et al., 2012). Since sediment cores presented in this study extend back to approximately 9.0 cal ka BP, with low rates of accumulation until 2.7 cal ka BP (see Results chapter), only Bond Events 2 and 1, the humid climate period from 2.6 to 1.6 cal ka BP, the Medieval Climate Anomaly (MCA), the Little Ice Age (LIA), and the climatic conditions during the Industrial Era are reviewed in the following.

A pollen study depicting oscillations in drought-sensitive and drought-resistant vegetation was interpreted as indicating enhanced aridification during Bond Event 2 around 3.0 cal ka BP (Jiménez-Moreno et al., 2015). Multiproxy paleohydrological records from Irish peats indicate an abrupt shift towards cooler climatic conditions around 2.7 cal ka BP,
correlating to Bond Event 2 (Goy et al., 1996; Swindles et al., 2007). In contrast, a regional humid climatic episode lasted from 2.6 to 1.6 cal ka BP, during the Roman Period, supported by regional lake level reconstructions (Martín-Puertas et al., 2008) and increased fluvial sedimentation rates caused by amplified precipitation (Goy et al., 1996).

Bond Event 1 (1.4 cal ka BP), the Dark Ages from 1.45 to 1.05 cal ka BP (commonly referred to as the Middle Ages in human history and described as the period after the fall of the Roman Empire), and the MCA from 1.05 to 0.7 cal ka BP all coincide to an aridification episode around 1.0 cal ka BP as documented by xerophytic plant species from sediment cores taken in the Doñana National Park, Spain (Jiménez-Moreno et al., 2015). In contrast, the Iberian Peninsula experienced frequent precipitation events throughout the warmer MCA and into the arid LIA, with the most extreme precipitation occurring around 0.95 cal ka BP (Abrantes et al., 2017).

In the Northern Hemisphere, during the LIA (0.6 to 0.15 cal ka BP), a drop in CO₂ and a rise in CH₄ suggest wet tropics and cold poles (Mayewski et al., 2004). Yet, dry conditions persisted from the MCA into the LIA until about 0.44 cal ka BP with an enhanced fresh water input, as interpreted from an increase in fluvial-derived terrigenous elements measured on sediment cores from the Algerian-Balearic Basin in the Western Mediterranean (Nieto-Moreno et al., 2011). Into the start of the Industrial Era (1850 CE), increasing sea surface temperatures and pollen records indicate a rise in atmospheric temperature and humidity (Abrantes et al., 2017).

Current volumetric seasonal and annual fluctuations in rainfall due to the Mediterranean climate (Sarmiento et al., 2009) affect the amount of sediment being transported by
fluvial sources to the Cadiz continental shelf (Davis et al., 2000). The Mediterranean climate is commonly known for pronounced seasonality with intense rain events and long periods of drought (Sarmiento et al., 2009). The Iberian Peninsula experiences the most rainfall in winter months, December - March, and least in the summer months, June - September (Davis et al., 2000). For example Davis et al. (2000), averaged Tinto River discharge volumes from 1966-1992 at Niebla, Spain showing the average discharge in winter was 150 cubic hectometers (hm³) per month and 30 hm³/month in summer (Figure 8, Davis et al., 2000). In addition to seasonal fluctuations in rainfall, these annual fluctuations also affect fluvial sediment transport to the continental shelf. Annual variations in water discharge from 1966-1992 along the Tinto River depict a minimum discharge of 10 hm³/yr and a maximum of 350 hm³/yr (Figure 8; Davis et al., 2000).

2.4 Regional Oceanographic Currents

The North Atlantic Gyre drives the North Atlantic Surface Water (NASW) as a coastal current along the coast of Southern Portugal. The NASW enters the Gulf of Cadiz around Cape São Vicente and follows the northern Gulf of Cadiz margin in a south-southwest orientation, some of which eventually flows through the Strait of Gibraltar into the Alboran Sea (Figure 9; García-Lafuente et al., 2006; Criado-Aldeanueva et al., 2006a; Criado-Aldeanueva et al., 2006b; Muñoz et al., 2015).

N2 and N1 are large-scale circulation currents (García-Lafuente et al., 2006) that, combined, have also been referred to as the NASW (Lobo et al., 2004). N2 is a portion of the Portuguese Current (also referred to as the NASW: Alves et al., 2002; Criado-Aldeanueva et al., 2006a; Criado-Aldeanueva et al., 2006b), that flows east through the Strait of Gibraltar into the Mediterranean Sea and also veers south becoming part of the Canary
current which flow southwest along the coast of Morocco (Figure 9; García-Lafuente et al., 2006). Current N2 surface water is warmer and saltier than N1, suggesting current N1 contains upwelling water from the North Atlantic Current Water, whereas water in current N2 is saltier and warmer due to longer exposure to air-sea exchange processes (García-Lafuente et al., 2006).

Sourcing from N1, closure of the water circulation cell on the continental shelf is caused by the northwestward circulating Coastal Counter Current (CCC), although García-Lafuente et al. (2006) indicates there is no data to support this hypothesis. The CCC then either feeds into the N1 current or pushes around Cape Santa Maria to feed the Cape San Vicente cyclonic eddy (García-Lafuente et al., 2006). Other studies indicate that the shallow CCC water is too fresh to originate from the highly studied waters in the Strait of Gibraltar, indicating an origin from the NASW (Mauritzen et al., 2001). A recent publication indicates that the CCC occurs in correlation with an unbalance of poleward alongshore pressure gradients (APGs) (Garel et al., 2016). Although the CCC origin is not clear yet, it is suggested that the presence of a hydrographic pressure gradient drives the counter flow along shore in a cyclonic direction in spring-summer and anticyclonic in autumn-winter (Relvas and Barton, 2002; García-Lafuente et al., 2006). APGs begin to form as a result of an accumulation of warmer, fresher, and therefore less dense water from land to the sea mainly via the Guadalquivir River plume (García-Lafuente et al., 2006). This warmer, fresher water, creating the APGs, is then unbalanced during weakening or reversal of normally strong upwelling winds (García-Lafuente et al., 2006; Garel et al., 2016). Although poleward winds affect the duration and velocity of the CCC, especially during winter storms, there does not seem to be a seasonal trend of CCC development. If winter storms
were overlooked, the number of times a CCC occurs would be largest in summer. These inconsistencies indicates the CCC occurs about 40% of the time in a week span (Garel et al., 2016).

Many publications discuss the mixing of the NASW current and the Mediterranean Outflow Water (MOW) in the Gulf of Cadiz. It is important to note that this research in the Gulf of Cadiz however occurred at water depths greater than 200 meters (Baringer and Price, 1999; Cherubin et al., 2000; Hanquiez et al., 2007; Mulder et al., 2013).

2.5 Fluvial Sources – Characterization and Geologic Foundation

This study focuses on four of seven rivers, Guadalquivir River, Tinto-Odiel Estuary, Piedras River, and Guadiana River, which source fine-grained material to the shelf, forming MDCs (Figure 1). Contradictory to a normal estuarine behavior, which leads to sediment trapping inside the estuary, the highly polluted Tinto-Odiel Estuary transports sediment to the Gulf of Cadiz, evident by heavy metal distribution on the shelf (Ruiz et al., 2014; Hanebuth et al., 2018).

The Guadalquivir River flows through the Guadalquivir Basin which is part of the Neogene Basins in the Betic Cordillera (Figure 10; Sanz de Galdeano and Vera, 1992). From 23 to 5.3 million yrs ago, the basin was submerged and subject to marine deposition (Sanz de Galdeano and Vera, 1992), under variable subsidence rates and high sediment supply (Hernández-Molina et al., 2000). The Guadalquivir River watershed expands 57,000 km² and contains a mean annual discharge rate of 160 m³/s according to Van Geen et al. (1997). Other sources indicate the discharge rate can exceed 5,000 m³/s in winter months, especially January to February (Rodríguez-Ramírez et al., 2016). The freshwater
discharge of the Guadalquivir River has a high mean sediment suspended load of 771 mg/L, seasonally with a minimum of 247 mg/L and maximum of 3,172 mg/L (Ruiz et al., 2013).

Tinto and Odiel Rivers meet within the Guadalquivir Basin to flow together into the Gulf of Cadiz, but they both originate from the South Portuguese Zone of the Iberian Massif (Onézime et al., 2002). Within this zone, the Tinto and Odiel Rivers flow through the Iberian Pyrite Belt (IPB) composed of three lithological groups: (1) the Phyllite-Quartzite Group (2) Volcano-Sedimentary Complex (Volcanogenic Massive Sulfide ore deposit belt), and (3) the Culm Group from the Upper Devonian to Upper Carboniferous (Figure 10; Barrie and Hannington, 1999; Onézime et al., 2002; Onézime et al., 2003; Sarmiento et al., 2009). The Phyllite-Quartzite Group consists of a thick sequence of shales and sandstones (Sarmiento et al., 2009). The Volcano-Sedimentary Complex consists of an equal distribution of siliciclastic interstratified shales with felsic and mafic volcanic rocks (Sarmiento et al., 2009; Barrie and Hannington, 1999). The Culm Group is composed of shales, sandstones and conglomerates (Sarmiento et al., 2009). Mining activities in the IPB date back to the third millennium BC with metallurgical production of copper (Nocete et al., 2005; Hanebuth et al., 2018) causing the fluvial waters to be highly acidic from the oxidation of large quantities of sulfide-rich minerals (Sarmiento et al., 2009; Cáceres et al., 2013).

The Tinto and Odiel Rivers have seasonally and annually variable water discharge patterns (Figure 8; Sarmiento et al., 2009; Davis et al., 2000). The Iberian Peninsula experiences the most rainfall in winter months, December to March with 150 hm³, and least in the summer months, June to September with 30 hm³ from 1966-1992 (Figure 8, Davis et al., 2000). The 3,400 km² Tinto-Odiel River watershed contains a mean annual discharge
rate of 20 m$^3$/s (Van Geen et al., 1997) and an estimated annual flow of 500 hm$^3$/yr (Sarmiento et al., 2009).

Similar to the Tinto and Odiel Rivers, the much smaller Piedras River also originates from the South Portuguese Zone of the Iberian Massif (Onézime et al., 2002) and flows through the Guadalquivir Basin just before entering the Gulf of Cadiz. The Piedras River watershed expands 250 km$^2$ and is thus more than thirteen times smaller than the Tinto-Odiel system (Borrego et al., 1993). Water and suspended load discharge rates for the Tinto-Odiel and Piedras Rivers are unavailable.

The Guadiana River also originates from the South Portuguese Zone of the Iberian Massif and flows through the IPB (Figure 10; Sarmiento et al., 2009; Onézime et al., 2002; Onézime et al., 2003), encompassing a 67,000 km$^2$ basin with a mean annual discharge of 80 m$^3$/s (Van Geen et al., 1997). The volume estimates for suspended sediment load (0.576 hm$^3$/yr) and bedload (0.44 hm$^3$/yr) were averaged between 1946 and 1990 (Morales, 1997).

Anthropogenic land use has caused chronological markers to occur as early as the Bronze Age in the Alboran Basin and Zoñar Lake in Spain, near to this study area (Figure 11; Martín-Puertas et al., 2010). Lead (Pb) enrichment depicts peaks during enhanced mining and smelting activity initially caused from Iberian mining beginning during Phoenician Era (3.0 to 2.6 cal ka BP), at large scale during the Roman Empire (2.05 to 1.75 cal ka BP), to a very subtle amount during Medieval Times (0.95 to 0.75 cal ka BP) and at unprecedented high levels during the Industrial Era (0.2 cal ka BP to present) (Figure 11; Martín-Puertas et al., 2010). Hanebuth et al. (2018) recently correlated heavy metal contamination signatures on the continental shelf in this study area with mining major activities during the Roman Period and the Industrial Era.
2.6 Shelf Characteristics and Stratigraphy

Under the continental shelf, the Triassic Allochthonous Unit has been undergoing extension in the NW-SE orientation due to compression in the NE-SW orientation, perpendicular to the shelf (Fernández-Puga et al., 2007; Medialdea et al., 2009). The under-compacted shale and evaporitic material have since migrated through NW-SE extension faults promoting diapiric processes since early Miocene (Fernández-Puga et al., 2007; Medialdea et al., 2009). The migration of evaporitic units has caused subsidence of overlying units by shelf extension (Nelson et al., 1999; Fernández-Puga et al., 2007; Medialdea et al., 2009).

The morpho-dynamic features of the shelf between the Tinto-Odiel Estuary and Guadalquivir River area are characterized by subsidence and a shelf gradient gentler than 0.2° (Lobo et al., 2002). In contrast, off the Guadalquivir River mouth, the shelf is characterized by uplifting due to diapiric-like structures (Lobo et al., 2002).

The muddy prodelta off of the Guadalquivir River has been characterized with five distinct units (Fernández-Salas et al., 2003). The oldest unit, identified as transgressive deposits, shows characteristics of aggradational deposition and discontinuous internal reflectors (Fernández-Salas et al., 2003). The four overlying units are characterized by prodeltaic deposits portraying two alternating sequences of progradational growth overlain by aggradational subunits (Figure 6; Lobo et al., 2005). The aggradational deposits contain sub-parallel internal reflectors while the progradational deposits contain downlapping internal reflectors (Figure 6; Lobo et al., 2004; Fernández-Salas et al., 2003).

Sedimentation rates for this region of the Gulf of Cadiz are limited to specific locations and by general age coverage. Nelson et al. (1999) calculated sedimentation rates for the entire shelf from the Guadiana River to the Bay of Cadiz (Figure 1) using eustatic
sea level curves and sediment isopach thickness. Highest rates were found closest to the Guadalquivir River at 234 cm ka\(^{-1}\) for the past 6000 yrs. One location close to shelf edge, between the Tinto-Odiel Estuary and Guadalquivir River showed a sedimentation rate of 22.6 cm ka\(^{-1}\) for the past 9000 yrs and 110 to 160 cm ka\(^{-1}\) for the recent 100 yrs (Nelson et al., 1999). Sedimentation rates based on sediment cores with good age resolution were collected close to the Guadiana River (Mendes et al., 2010, 2012) with oldest sedimentation rates averaging 10 cm ka\(^{-1}\) from 10.2 to 4.3 cal ka BP (mud body and transgressive bulge: Mendes et al., 2012). Younger sedimentation rates near the Guadiana River were 52 cm ka\(^{-1}\) from 5.2 to 3.8 cal ka BP, slightly increasing to 59 cm ka\(^{-1}\) from 3.8 to 1.3 cal ka BP, then more than doubling to 128 cm ka\(^{-1}\) from 1.3 to 0.68 cal ka BP (mud body and prodeltaic wedge: Mendes et al., 2010, 2012).
3.0 Objectives and Research Questions

To focus this thesis, two major objectives with related questions were identified. Due to substantial variety of data sets, Table 1 depicts why each methodological approach and associated data set is to be used for generating answers on the following two objectives. The third objective, which was originally part of the thesis proposal, relating to mechanisms controlling sediment accumulation within MDCs was removed due to a too limited data set and time constraints on thesis completion.

3.1 Chrono- and Lithostratigraphy of Mud Depocenters

This objective aims at determining the geometric formation of Holocene MDCs using seismo-acoustic echosounder and boomer data sets. Previous studies of seismo-acoustic datasets in this region showed that there is probably a larger sediment unit above the mfs increasing in landward direction near the Guadalquivir River, but gas masking obscures data (Fernández-Salas et al., 2003; Lobo et al., 2005). Are those stratigraphic units partly aggradational or are there definite progradational trends? Older investigations in the region determined separate aggradational and progradational units (Lobo et al., 2005; Hernández-Molina et al., 1994). Is a prodelta facies found in all of the near-shore profiles? This will be determined by studying the internal geometries of the units through seismo-acoustic profiles. Seismo-acoustic profiles along with magnetic susceptibility scans and XRF scanner intensities, will be used to correlate stratigraphic units. Lithology descriptions, radiography images, and high-resolution core images will be used for detailed facies determination. An attempt at sediment source differentiation will be conducted using
magnetic susceptibility scans, and XRF scanner element intensities combined with XRF powder element concentrations. Carbonate content, total organic content (TOC), bulk density and porosity data will help to distinguish unit boundaries within MDCs. To acquire an age control on the stratigraphy of the MDCs, $^{14}$C dates and $^{210}$Pb profiles will be used.

3.2 **Budget Calculation of Mud Depocenters**

Once correlation of stratigraphic units between cores has been completed using XRF scanner and magnetic susceptibility data, the volume of the Holocene accumulated sediment and distinguishable sub-units of the study area will be determined. By determining an age structure of the depocenter using $^{14}$C dates and $^{210}$Pb profiles and combining it with grain density data, accumulation rates will be calculated. Once volumetric and mass characteristics of the MDCs are determined, combining them with rates that fluvial sources provide sediment to the shelf can determine a full retention budget (Oberle et al., 2014). The volume and mass of the MDCs, with the carbonate content and TOC, a carbon budget can separately be calculated to further understand the retention of carbon in the MDCs. Does the part of the Holocene mudbelt, located closest to the mouth of the Guadalquivir River (assumed as the main sediment supplier), have the highest accumulation rate in the region, and did the accumulation rates vary through time? Changes in accumulation rates can potentially depict climatic and anthropogenic industrial-related changes.
4.0 Materials and Methods

In March 2015, subbottom echosounder data and sediment cores were collected in the Gulf of Cádiz during research cruise POS482 CADISED on the German RV POSEIDON near southern Portugal and southwestern Spain. One of the main goals of this cruise, involving all collaborative partners, has been to develop a robust facies framework of the sedimentary deposits in Holocene MDCs. This framework will then support various research oceanography-, climate-, and stratigraphy-related targets.

Subbottom data (2,040 km) were acquired using a 4 kHz parametric source that provided ~20 m subsurface penetration with an INNOMAR subbottom echosounder. The hull-mounted ELAC Nautik SeaBeam 3050 multibeam echosounder operated at 50 kHz collecting bathymetric, backscatter and occasionally water column imaging data (Hanebuth et al., 2014: Cruise report POS482).

Gravity cores with up to 6 m penetration were collected in regions where deposits of fine-grained sediment and mud were of significant thickness. Coincident 1.5-m long Ruhmor cores were also collected to preserve the uppermost sediment layer. Of the 40 cruise stations completed using varying coring methods, 18 stations are located within the study area.

Twelve data sets were collected and measured from echosounder data and 18 sediment cores (Table 3). High-resolution photographic images of halved sediment cores were taken using a smartCIS 1600 Line Scanner. Lithology of 18 sediment cores was described by color, grain size, and composition. Magnetic susceptibility and porosity were measured
on 15 cores. Using samples collected from gravity and Ruhmor cores from 11 stations, porosity and density were calculated by using dry bulk density. Seven gravity cores were x-ray florescence (XRF) scanned for element intensities, six of which had samples processes for x-ray powder element concentration measurement. Total Organic Content (TOC) and carbonate content (CaCO₃) were measured on five representative gravity cores. Accelerator Mass Spectrometer (AMS) ¹⁴C dating were performed for nine representative gravity cores (19512-3, 19513-3, 19518-3, 19519-3, 19520-3, 19521-3, 19534-3, 19535-3, and 19538-3: Figure 2). Samples for ²¹⁰Pb and ¹³⁷Cs excess profiles were measured from four and two, respectively, of the nine gravity cores. Radiography images were taken from Core 19520-3. A complete list of data sets collected is provided in Table 3.

4.1 Seismo-Acoustic Data

IHS Kingdom Software 2015 was used to view pre-processed seismo-acoustic profiles to correlate major internal reflectors. In addition to the POS482 seismo-acoustic data, boomer data collected with a Geopulse from 1992 and 1986 (courtesy of Dr. Lobo), were used to extend the penetration depth. Grids used for the volumetric calculations and isopach maps were created by tracing major reflectors in the echosounder profiles and using the corresponding the age model from coring sites. The “Flex Gridding” algorithm was used with 0.3 curvature, a 1 minimum smoothness, grid cell size of 100 in the X and Y direction, and a convex hull extrapolation limit of 0 m. Volumes produced utilize a sound velocity of 1500 m s⁻¹. The volume of material between two grid levels was determined by calculating the net volume using duel structure grids. Output parameters were set to the grid with the smallest surface area with an inverse distance to power weight of 2. These profiles were utilized to understand boundaries between MDC facies.
4.2 Multi-Sensor Core Logger (MSCL) Data

Sediment core sections were scanned through a multi-sensor core logger (MSCL), prior to opening. Although additional analysis was conducted, this study utilized only magnetic susceptibility and porosity values. Magnetic susceptibility intensity values were used for in-detail correlation of cores with one another to determine source differentiation, and depict changes in MDC depositional centers.

4.3 Sediment Properties and Budget Calculation

The following calculations were conducted to develop a sediment budget estimate using the sediment volume and mass through various time intervals, thereby depicting temporal changes of the MDCs.

Sediment samples were collected using 10 mL syringes at depth intervals of five to fifteen cm in each core. Before drying material, the exact sediment volume (\(V_T\)) of sediment inside the syringe was noted and the wet sediment weighed. Porosity values (Eq. 1) produced by the MSCL were compared to values calculated after drying (Oberle et al., 2014). Porosity is a unitless parameter obtained by utilizing an initial volume of water (\(V_w\)) divided by the total volume.

1. \[
\text{Porosity} (\%) = \frac{[S_w - (S_D - \text{Salt})]}{V_T} \times 100
\]

Porosity was obtained by removing the mass of wet sediment (\(S_w\)) from the mass of dry sediment (\(S_D\)) and mass of salt from the seawater in the pore space (Eq. 2), all of which is then divided by the total volume of the wet sediment (\(V_T\)). In this case, the initial volume produced uses the remaining mass of water after removing the mass of dry sediment and salt dividing it by the density of freshwater. The density of freshwater is approximately 1-
g mL⁻¹, therefore the remaining mass of the water in grams is equal to the initial volume of water in milliliters.

2. \( \text{Salt} = (S_W - S_D) \times 0.035 \)

Assuming the salinity of seawater is approximately 35ppt, it would take 0.035-g of salt to make 1-mL 35ppt saline, therefore moisture lost, found by taking \( S_W - S_D \), times 0.035, provides the mass of salt (Eq. 2) present per sample.

Using data already collected, dry bulk density (\( \rho_{\text{bulk}} \) (Eq. 3) was produced to convert sedimentation rates to accumulation rates (Oberle et al., 2014).

\[
3. \quad \rho_{\text{bulk}} = \frac{S_D - \text{Salt}}{V_T}
\]

Grain density (\( \rho_{\text{grain}} \) (Eq. 4) was calculated to determine the mass of the Holocene accumulated sediment for defined time intervals (Oberle et al., 2014).

\[
4. \quad \rho_{\text{grain}} = \frac{(S_D - \text{Salt})}{V_T - (V_w + V_{\text{Salt}})} \times 100
\]

The Volume of water (\( V_w \)) is equal to the numerator from Eq. 1: \( [S_w - (S_D - \text{Salt})] \). The Volume of salt (\( V_{\text{Salt}} \)) was determined by taking the mass of salt produced in Eq. 2 and dividing it by the density of salt, 2.165 g cm⁻¹ in seawater (Libes, 2009).

Using volumes of units (\( V_{\text{Unit}} \)) measured with the IHS Kingdom Software 2015 and average porosity concentrations for each unit, a water volume was determined. The dry sediment volume (\( V_D \)) was calculated by subtracting the volume of water from the \( V_{\text{Unit}} \). Once grain density and dry sediment volume of the Holocene accumulated sediment were determined, the sediment mass (Eq. 5) was calculated for each unit.

\[
5. \quad \text{Sediment Mass} = \frac{\text{Grain } \rho}{V_D}
\]
Porosity and dry bulk density measurements supported the identification and characterization of sedimentary facies and their stratigraphic boundaries. For instance, an increasing porosity indicates wider pore space; taking compaction into consideration, porosity should decrease with increasing depth in core. Variations in grain density and dry bulk density indicate sediment compositional changes within or between facies.

4.4 *X-ray Fluorescence Element Scanning*

Using the MSCL data and seismo-acoustic profiles, 10 representative cores were chosen for the non-destructive, high-resolution X-ray fluorescence (XRF) scanner. The archive halves of these 10 cores were analyzed at MARUM through a XRF AVAATECH (Serial No. 2) using a Canberra X-PIPS Silicon Drift Detector (SDD; Model SXD 15C-150-500) with an Oxford Instruments XTF5011 X-Ray Tube 93057. Sections containing sharp shell fragments or sandy sediment cannot be scanned. The intensities (in counts) of light elements were measured in 1 cm intervals at 10kV with a 0.2 milliampere (mA) current for 15 sec; heavy elements at 30kV with a 1.0 mA current for 15 sec. After quality checks of the processed data, not all element intensities are considered reliable due to low concentrations, limitation of the sensor sensitivity, or contamination by elements emitted by the XRF scanner components.

4.4.1 *Element Intensity Ratios*

Since element intensities do not depict true element concentrations, the ratio between two elements is used as a proxy to detect an environmental change. The ratios were then normalized to keep scales consistent by taking the natural logarithm. Element intensity ratios are often used for paleoceanographic and paleo-environmental reconstructions. Ln
Ca/Fe ratios and ln Ti/Zr were also used for transferring age tie points between the individual sediment cores, since elements show comparable and high intensities.

The weathering-resistant Zirconium (Zr) is commonly associated with coarser-grained minerals. Titanium (Ti) is associated with minerals that are more easily weathered than minerals with Zr, thus Ti is found in the finer sediment fraction. As this ratio increases, the grain size becomes finer. To calibrate this proxy, grain size measurements should have been conducted at CCU with a Laser diffraction particle size analyzer. Due to timing constraints and lasting technical issues with maintenance of both available machines, grain size measurements were not included in this study and will be performed in near future.

The ln Ca/Fe ratio depicts variations in the relative amount of marine sourced (= biogenic carbonate) to terrigenous (= siliciclastic) material (assuming iron (Fe) is entirely of terrestrial origin; Hanebut et al., 2015b). Previous studies indicated Fe and Ti are closely related to each other in the terrigenous fraction, yet Fe can be prone to secondary remobilization after deposition through diagenesis but Ti is considered chemically stable in its hosting minerals (Richter et al., 2006; Tjallingii et al., 2010). Fe is mainly present in clay minerals, pyrite, and various iron minerals derived from continental soils and magmatic rocks. Fe is also present in organic material. Since the measured TOC values range from 0.4 – 0.9% (Table 4), only a negligible fraction of Fe may be marine sourced, but it is not enough to disprove this proxy for marine sourcing vs. terrigenous. Ln Fe/Ti was plotted to verify if background levels of both elements (preanthropogenic contamination) did not show significant fluctuations, i.e., to prove that Fe was not affected by secondary ion migration, allowing Fe to be used as an indicator for primary terrigenous supply (Figure 12).
4.4.2 X-ray Fluorescence Powder Element Measurement

To convert the intensity curves of single elements of interest into true element concentration records, eight to fifteen samples per core were measured for element concentrations using a SPECTROXEPOS (methods Opti2 and 2016-CaCO$_3$). The selected samples were collectively measured for TC and TOC using a LECO CS-200 carbon and sulfur infrared detection analyzer.

4.5 $^{14}$C Dating

Eighteen depths in cores, selected by reviewing core descriptions and seismoo-acoustic profiles, were dated using AMS-$^{14}$C precision dating. If no larger and in-situ preserved bivalves or Turritella-like gastropods existed at these precise depths, foraminifera were carefully picked. Benthic foraminifera were targeted for $^{14}$C samples, but to acquire at least 20 mg per sample, all freshly preserved carbonate material had to be selected in some instances. All deteriorating, stained, broken or potentially remobilized material was avoided to not contaminate samples with old material. Of the eighteen samples, twelve were composed of foraminifera and six of in-situ bivalves or gastropods. Foraminifera samples were sieved at 63 µm to remove the mud fraction. Each sample took approximately 40 hours to complete. The samples were shipped to Poznan Radiocarbon Lab in Poland. Two benthic foraminifera samples were collected by Dr. Susana Lebreiro (IGME) and measured at the National Accelerator Center at the University of Sevilla, Spain. Once received, the conventional ages were put into version 7.10 of the CALIB Radiocarbon Calibration Program to calibrate samples to the carbon changes in the atmosphere through time using data set ‘marine13.14c’ (Stuiver and Reimer, 1993; Reimer et al. 2013). Marine $^{14}$C dated samples cannot be compared to terrestrial samples without accounting for the age of
the seawater, i.e., the reservoir age. To keep ages consistent, the global average reservoir age of 406 yrs, was removed from $^{14}$C dates. Although samples were collected from a shallower ocean system, no local reservoir was used to modify the ages, due to the possible existence of an older carbon signature by deeper upwelled water. The calibrated (cal) $^{14}$C ages are given in ‘before present’ (BP); the ‘present’ being 1 January 1950 (Currie, 2004). These dates helped to establish a shelf-wide age framework for the MDCs and to calculate time- and location-specific sedimentation and accumulation rates.

4.6 $^{210}$Pb and $^{137}$Cs Dating

Young ages from the first set of $^{14}$C samples prompted the use of $^{210}$Pb and $^{137}$Cs dating techniques on Cores 19520-3 every 10 cm for the first 150 cm (closest to the Guadalquivir River mouth), 19512-3 every 10 cm for 100 cm (center of study area), 19534-3 with 24 samples for 70 cm (closest to the Tinto-Odiel Rivers mouth), and 19535-3 every 10 cm for 100 cm (near to the Tinto-Odiel Rivers mouth). Ages for 19520-3 and 19534-3 were measured by the Laqimar Laboratory in Sao Paulo, Brazil (Dr. Paulo Alves Ferreira). Measurements for 19512-3 and 19535-3 were measured in the USGS facility in Santa Cruz (Dr. Ferdinand Oberle). Since the study area is heavily influenced by sediment supply from the continent and oceanographic currents, the also measured $^{137}$Cs profiles were reviewed critically and decidedly not used for the age model. $^{210}$Pb profiles were generated using two calculation models: Constant Rate of Supply (CRS) and Constant Initial Concentration (CIC). Since XRF element intensity curves and XRF powder concentrations showed the sediment concentration did not remain constant, the results provided by the CRS model were used, which in general seems to describe processes in shallow waters more appropriately (Appleby and Oldfield 1978; personal communication Dr. P. Alves, Dr. F. Oberle).
CRS assumes the flux of unsupported $^{210}\text{Pb}$ deposited at a constant rate. The ages produced by $^{210}\text{Pb}$ dating were also used to understand when heavy metal contamination in the Gulf of Cadiz, Spain changed through industrial periods (Hanebuth et al., 2018). $^{210}\text{Pb}$ sourced ages are given in ‘common era’ (CE). Table 1 depicts a summary of which method was used for to address each objective of this thesis.

4.7 High-Resolution Core Imaging

All cores were photographed to produce high-resolution images in millimeter scale. Radiographies were taken from Core 19520-3, located near the mouth of the Guadalquivir River, to visualize the millimeter-scale resolution depicting the succession of flood layers. Radiography images provide internal detail of sediment texture and structure. The high-resolution core images and radiography images assist in distinguishing facies boundaries.
5.0 Critical Evaluation of Stratigraphic Age Model and Material Budgets

5.1 Calculation of Sedimentation Rates

Element intensities were converted into ratios to correlate cores stratigraphically and depict changes in sediment deposition by core location. The natural log of these ratios (\(\ln(Ca/Fe)\), \(\ln(Ti/Zr)\), \(\ln(Zn/Al)\), and \(\ln(Pb/Al)\)) in each data set were used to normalize figure scales to make visual correlation between cores accurate. An example of this interpretive method depicts \(\ln(Ca/Fe)\) from Cores 19538-3, 19513-3, and 19518-3 (Figure 13). Zn and Pb are known sources of anthropogenic pollution in the Gulf of Cadiz (Ruiz, et al., 2014; see Hanebuth et al., 2018 for more references). These metals were normalized to aluminum (Al) since Al is assumed to be entirely sourced from the clay fraction (Delgado et al., 2012) of the terrigenous supply (Martín-Puertas, et al., 2010; Pipper and Perkins, 2004; Nieto-Moreno et al., 2011) and used as a representative of fines in a grain-size distribution (Hanebuth et al., 2018). \(\ln Ti/Zr\) ratio was explained in section 5.4.1 Element Intensity Ratio. \(\ln Ti/Al\) ratio was taken to depict Ti and Al are present in the material at an approximate 1:1 ratio, making them interchangeable (Figure 14). Ti is also known to be mainly sourced from terrigenous material (Richter et al., 2006).

The element ratios (\(\ln Ca/Fe\), \(\ln Ti/Zr\), \(\ln Zn/Al\), and \(\ln Pb/Al\)), and the magnetic susceptibility curves were also used for a robust inter-core correlation. Nine representative coring stations were compared in six transects by proximity to shore (Table 2). The three
coring stations most proximal, central, and distal to shore, were compared in three transects. For example, Sites 19538 (closer to the Tinto-Odial Estuary), 19513, and 19518 (closer to the Guadalquivir River) were compared to each other (Figure 13, locations depicted in Figure 2). Sites were also compared from proximal to distal in three transects. Sites 19534 (closest to the Tinto-Odial Estuary), 19535, 19538 were compared to each other (Figure 15, locations depicted in Figure 2). Once the correlation model was complete, the depths at which each correlation line landed were compiled by depth on a core transect (Figures 16 and 17). This stratigraphic model was used to transfer absolute ages received from $^{210}$Pb profiles (Table 6) and calibrated $^{14}$C dates (Table 5). Due to the coarse material, some of the oldest core sections were could not be XRF scanned. Therefore, some of the oldest ages were transferred from core to core by tracing major reflectors in seismo-acoustic profiles. This framework allowed for detailed sedimentation and accumulation rates to be determined.

Although this approach led to the calculation of detailed sedimentation and accumulation rates, there is error to be considered. There are limitations to $^{14}$C dating and human error associated with picking material. Bioturbation and lateral transport can cause younger material to be located deeper in the sediment succession than its natural depositional depth or older material to be pulled to younger depths. While benthic foraminifera are being picked with great care, older material can accidentally be chosen causing the age to be older than the sample depth. The gravity coring method can also cause compression or expansion of layers, thereby altering the true accumulation rates artificially. Gravity coring can also cause a loss of material of the uppermost 0-15 cm. These reasons alone give all ages a conservative error of ± 15 cm. By using the ratio correlation method, an
additional error is given to those ages depending on how easily or how far ages transpose vertically since this method identifies peaks and trends in the magnetic susceptibility and XRF element distribution curves. Since it is not always straight-forward to patch the related peaks from core to core additional error of ± 1 to 20 cm can be added. For ages transferred by following major reflectors on seismo-acoustic profiles the maximum error was given to the age, thus far (± 35 cm), ± an additional 10 to 40 cm due to limit in vertical echosounding resolution. These errors are considered when calculating average sedimentation rates for each core (Figures 18, 19, and 20).

5.2 Calculation of Material Budgets

To generate volumetric and mass budgets of the Holocene accumulated sediment, porosity and grain density was first calculate by the methods listed in Section 5.3.3 Sediment Sample Properties. Based on coring methods and core penetration, more samples were collected from younger facies than older facies. Instead of using average porosity and grain density values for all of the samples, values were averaged by facies, F & E (combined), D, C, B, A). Facies determination is based off of lithology description and core images. Ages bounding facies are sourced from the stratigraphic age model. Three major time slices were used for volumetric and mass budget calculations: Slice 1 – base of the MDCs to 2.0 cal ka BP (composed of Facies D, E, and F), Slice 2 – 2.0 to 1.0 cal ka BP (composed of Facies C), and Slice 3 – 1.0 cal ka BP to present (composed of Facies A and B). To accurately represent porosity and grain density values in Slice 3, values were averaged from Facies A and B. The same concept was used for Slice 1. This approach for an accurate representation of vertical changes of sediment properties was also applied for the TOC and CaCO$_3$ mass calculations.
6.0 Results

6.1 Age framework

Nine sediment cores with 18 calibrated $^{14}$C ages span from 8.98 cal ka BP, near the Tinto-Odiel Estuary (bottom of core 19521-3), to 0.44 cal ka BP off the Guadalquivir River (bottom of core 19519-3) (Table 5). A resolution of at least an age every millennia was collected, except for time between 4.35 to 2.70 cal ka BP. Reliable $^{210}$Pb ages using model CRS range from 1950 to 2010 CE off the Guadalquivir River (19520-3) and 1930 to 2000 CE near the Tinto-Odiel Estuary (19534-3) (Table 6). Cores 19512-3 and 19535-3, located centrally parallel to shore, contain dependable ages ranging from 1930 to 1990 CE.

6.2 Determination and Timing of Sedimentary Facies

While echosounder data depicts qualitative information about the depositional architecture of the MDCs, gravity cores provide a laterally scattered but temporally/stratigraphically higher resolution insight into depositional patterns and facies composition. Together with the sedimentary facies determination, average sedimentation rates are presented for each facies in the following. For exact and average sedimentation rates for each site refer to Table 7 and Figures 18, 19, and 20.

Using photographic images, lithology descriptions, and element intensity ratios, six main sedimentary facies were identified (Figure 21). In general, grain size fined up core in the MDCs (Figure 22). These facies were moderately to highly bioturbated and contained
monosulfides in Facies F through B. Facies transition from one to another occurred at different times on the shelf, therefore, age ranges at boundaries represent all ages at which transitions occurred in cores. Facies F and E contain the largest grain size and highest marine material content at core bases (Figure 13, 15, 22) with a combined bulk density of 1.32 g cm\(^{-3}\). Facies F and E are distinguishably different from younger facies by the dark greenish to dark grey, slightly sandy silty, stiff mud to muddy silt with abundant shell fragments (Figure 21, 23). Although within the same facies regime, Facies F is composed of siltier material than Facies E. The erosive boundary between Facies F and E formed at approximately 9.0 to 8.4 cal ka BP.

Most of the carbonate material and sediment > 63 μm in Facies E, found while picking \(^{14}\)C samples, is deteriorated, stained and fragmented. Four of the nine sediment cores are old enough to provide sedimentation rates for Facies E ranging from 12 to 30 cm ka\(^{-1}\) with an average rate of 25 cm ka\(^{-1}\) for the time interval 8.98 to 6.67 cal ka BP (Figures 19 and 20). From 6.67 to 5.79 cal ka BP, these cores show extremely low rates of 2 to 6 cm ka\(^{-1}\) for Facies E with an average sedimentation rate of 5 cm ka\(^{-1}\) (Figures 19, 20). Core 19513 shows, in contrast, a significantly higher sedimentation rate of 10 cm ka\(^{-1}\) from 7.41 to 5.79 cal ka BP for Facies E (Figure 19).

The boundary between Facies E and D is a sharp and erosional contact that occurred around 6.7 – 4.3 cal ka BP, distinguished by the beginning of a general decreasing grain size trend and an increasing terrigenous influence (Figure 13, 15, 21, 22, 23). The drastic difference between Facies E and D depict separate regimes (Figure 23). Facies D is composed of dark grey homogeneous mud that is moderately silty with some shell fragments (Figure 21, 23) and a dry bulk density of 1.08 g cm\(^{-3}\). Oldest section
of Facies D (5.79 to 2.70 cal ka BP), contains sedimentation rates of 7 to 24 cm ka\(^{-1}\) with a 15 cm ka\(^{-1}\) average, i.e., four times higher compared to that in Facies E (Figures 19 and 20). Although only spanning from 4.72 to 1.95 cal ka BP, Core 19518 shows a low resolution, sedimentation rate of 14 cm ka\(^{-1}\) (Figure 18). From 2.70 to 1.95 cal ka BP, sedimentation rates vary by core location. A transect perpendicular to shore near the Tinto-Odiel Estuary, Cores 19534, 19535, and 19538 retain sedimentation rates of 104 to 204 cm ka\(^{-1}\) with an average of 147 cm ka\(^{-1}\) from 2.70 to 2.45 cal ka BP. Up core in the same transect, the average rate drops to 72 cm ka\(^{-1}\) (2.45 to 1.95 cal ka BP) (Figure 20). Inversely, Cores along a transect shore-perpendicular (19521, 19512, 19513) indicate low sedimentation rates of 29 to 79 cm ka\(^{-1}\) with a 47 cm ka\(^{-1}\) average from 2.70 to 2.45 cal ka BP. Up core in the same transect, rates increase three and a half times to 116 to 245 cm ka\(^{-1}\) with an average of 163 cm ka\(^{-1}\) (2.45 to 1.95 cal ka BP) (Figure 19). Cores located closest to the Guadalquivir River (19519 and 19520) contain a sedimentation rate of 80 to 163 cm ka\(^{-1}\) during a low age resolution of 4.72 to 1.95 cal ka BP (Figure 18).

At approximately 2.0 – 1.3 cal ka BP, Facies D gradually transitioned to into the less silty Facies C with a lower amount of shell fragments (Figure 21, 23) and a dry bulk density of 0.98 g cm\(^{-3}\). Core 19517-3 (Figure 2) degassed in Facies C and B during opening, destroying any internal lamination that may have existed. Shore-perpendicular sites near the Tinto-Odiel estuary (19534, 19535, and 19538), within the oldest portion of Facies C, show sedimentation rates of 60 to 97 cm ka\(^{-1}\) with a 79 cm ka\(^{-1}\) average from 1.95 to 1.42 cal ka BP. Then from 1.42 to 1.29 cal ka BP, the average rate increases to 88 cm ka\(^{-1}\). Sedimentation rates drastically increase to 118 to 449 cm ka\(^{-1}\) from 1.29 to 1.11 cal ka BP.
At sites shore-perpendicular, (19521, 19512, 19513; Figure 2) the cores contain low sedimentation rates of 58 to 78 cm ka\(^{-1}\) with a 69 cm ka\(^{-1}\) average from 1.95 to 1.42 cal ka BP, oldest portion of Facies C. From 1.42 to 1.29 cal ka BP, rates increased two and a half times to 92 to 237 cm ka\(^{-1}\) with an average of 169 cm ka\(^{-1}\). At Site 19513, rates slightly increase to 261 cm ka\(^{-1}\) from 1.29 to 0.96 cal ka BP (Figure 19). Sedimentation rates at the sites located closest to the Guadalquivir River, 19519 and 19520, are 131 to 376 cm ka\(^{-1}\), respectively, from 1.95 to 0.88 cal ka BP. Core 19518 showed an extremely low sedimentation rate of 23 cm ka\(^{-1}\) from 1.95 to 0.88 cal ka BP (Figure 18).

The gradual transition from Facies C to B, a lighter brown homogeneous mud with decreasing shell fragment quantity, occurring around 1.0 – 0.8 cal ka BP (Figure 21, 23). Facies B contained light olive to dark greyish brown homogeneous mud with few tiny shell fragments (Figure 21, 23) and a dry bulk density of 0.95 g cm\(^{-3}\). Remarkably, Core 19520-3, located closest to the Guadalquivir River, shows impressive preservation of lamination, burrows, and silt lenses (Figure 21).

Shore-perpendicular Cores 19535 and 19538 (Figure 2), show an average sedimentation rate of 37 cm ka\(^{-1}\) from 0.96 to 0.44 cal ka BP at the start of Facies B. Then from 0.44 cal ka BP to 1950 CE, rates increase by two times to 75 to 120 cm ka\(^{-1}\) with a 98 cm ka\(^{-1}\) average. At Site 19534, a low sedimentation rate of 20 cm ka\(^{-1}\) from 1.11 cal ka BP to 1930 CE persisted (Figure 20). Sites 19521 and 19512 (Figure 2), shore-perpendicular, Facies B contains sedimentation rates of 76 and 133 cm ka\(^{-1}\), respectively, with a 104 cm ka\(^{-1}\) average from 1.29 to 0.44 cal ka BP. Core 19512 shows a sedimentation rate increased by two times to 267 cm ka\(^{-1}\) from 0.44 cal ka BP to 1930 CE. Close to shelf edge in the same perpendicular transect, Core 19513 retains a sedimentation rate of 114 cm ka\(^{-1}\).
from 0.96 cal ka BP to 1970 CE (Figure 19). Cores 19518, 19519 and 19520 (Figure 2) show sedimentation rates of 65 to 230 cm ka\(^{-1}\) with a 155 cm ka\(^{-1}\) average from 0.88 to 0.65 cal ka BP. From 0.65 to 0.44 cal ka BP rates decrease to an average of 117 cm ka\(^{-1}\) (57 – 185 cm ka\(^{-1}\)). Then rates increase by four and a half times to an average of 527 cm ka\(^{-1}\) (205 – 759 cm ka\(^{-1}\)) from 0.44 cal ka BP to 1950 CE (Figure 18).

Facies B gradationally changed, based on a decreasing grain size (Figure 21, 22) and light brown homogeneous soft mud, to Facies A (Figure 21, 23) with the lowest dry bulk density of 0.72 g cm\(^{-3}\) (Table 4). All sedimentation rates in the modern (during the Industrial Era: Hanebuth et al., 2018) MDCs increased from 1950 to 2000 CE, except at sites located shore-perpendicular near the Tinto-Odiel estuary where rates minimally decreased after 1970 CE (19535 and 19538) and 1990 CE (19534; Figure 20). Highest sedimentation rates during the modern MDCs are located closest to Guadalquivir River with a rate of 2,800 cm ka\(^{-1}\) from 1990 to 2000 CE, and 3,000 cm ka\(^{-1}\) from 2000 to 2010 CE (Figure 18). Another high sedimentation rate is near the Tinto-Odiel estuary with a rate of 2,400 cm ka\(^{-1}\) from 1960 to 1970 CE (Figure 20). Lowest sedimentation rates are located near the shelf edge off the Guadalquivir River from 1950 to 1990 CE with a rate of 125 cm ka\(^{-1}\) (Figure 18). Similarly low rates (200 cm ka\(^{-1}\)) are closest to the Tinto-Odiel Estuary from 1930 to 1960 CE (Figure 20). A summary of all sedimentation rates can be found in Table 7. Facies A reflects the modern conditions at the seafloor and spans the most recent time interval since 1980-2010 CE.

6.3 Stratigraphic Architecture

Accurately assuming ages of depositional sediment packages based on the stratigraphic architecture of the Holocene transgression is difficult due to high accumulation
rates. Interpretation of the stratigraphic base of the Holocene MDCs, initially depicted as the reflector above the rock-like basement foundation, changed once the age framework allowed for a linkage from one core to another. For instance, the accumulation rate at the bottom of Core 19521-3 is 16 g cm\(^{-2}\) ka\(^{-1}\) from 8.98 to 6.67 cal ka BP, where the age of 8.98 cal ka BP is found at 4.46 m core depth (Table 8, Figure 24). Radiocarbon ages and accumulation rates from sediment cores suggest the base of the Holocene MDCs is 1 ± 0.5 m from the base of the core with an age of 10.0 ± 1.0 cal ka BP. The age of the Holocene mud accumulation on the shelf is important to determine an accurate budget calculation for MDCs in this study area.

It turned out that the boundary, which defines the base of the Holocene MDCs (10.0 ± 1.0 cal ka BP), shows a lateral variety in topographical expressions. The base of the depocenter near the Tinto-Odiel Estuary was found to be on top of a prodelta-like sediment package (Lobo et al., 2004, 2005), sourced by the estuary, which is older than the Holocene MDCs (Figure 25). In the western section of this study area, the base is characterized as a low relief erosional boundary from mid-shelf to shelf edge. The base of the MDCs, mid-shelf position, is underlain by an uneven boundary that trapped sediment between structures during early MDC sediment accumulation. These structures increase in size from northwest to southeast and are commonly interpreted as being associated with exposure (Figure 26 and 27). No sediment cores were recovered in these local deposits, so determining the base of the MDCs remains speculative here. The southeastern portion of the MDCs is acoustically masked, which is commonly associated with free gas present in the sediment (Figures 27 and 28). This phenomenon causes soundwaves to be absorbed, therefore sediment reflector tracing brought limited success near the Guadalquivir River. The careful
extrapolation of the base in this area was established on what was imaged around the acoustically masked areas. In summary, the base of the MDCs coincides with the assumed stratigraphic position of transgressive aged ravinement surfaces that have formed on top of regional transgressive deposits.

The seismo-acoustic profiles show a sediment-rich environment with an overall Holocene sediment thickness increasing in southward direction from off the Tinto-Odiel estuary toward the Guadalquivir River. Shelf-wide, the base of the MDCs stratigraphically coincides with erosional boundaries. The two MDCs are identified as a mud belt, located mid-shelf near the Tinto-Odiel Estuary, and as a sheet-like prodelta, source by the Guadalquivir River (Figure 29). Mud deposition portrays packages of lateral retrogradation, progradation, and aggradation with strata terminating at shelf edge.

A profile stretching from 15 m water depth near the Tinto-Odiel estuary to the shelf break at 120 m water depth, shows a perpendicular view of the mud belt with a maximum thickness of 10 m (Figure 25: acoustic profile; Figure 30 isopach map of MDCs). The central profile (see Figure 2) portrays early sediment deposition propagating around mud entrapments and a thickness of 12 m (Figure 26). The farthest southern profile, closest to the Guadalquivir River mouth, portrays a sediment thickness of 18 m (Figure 28). Through acoustic masking, maximum thickness of the sheet-like prodelta MDC is 21 m, located closest to the Guadalquivir River (Figure 30).

Acoustic masking occurs in all proximal profiles around the Guadalquivir river mouth obscuring internal stratification (Figure 27). At the shelf edge, internal reflectors pinch out or are acoustically obscured, indicating the seaward limit of the depocenter in all seismo-acoustic profiles. Extension faults, as young as $0.03 \pm 0.05$ cal ka BP, i.e., 350 yrs,
within the sheet-like prodelta MDC are identified using the high-resolution seismo-acoustic profiles with the stratigraphic age model from cores (Figure 27, 31). Lower resolution boomer data sets from 1992 and 1986, depict these extension faults and many more that extend deeper throughout the shelf (Figure 31, 32). The boomer data sets show features under the south-southeast portion of the prodelta MDC, identified as salt diapirs (Figure 31, 32; Lobo et al., 2002 Fernández-Puga et al., 2007; Medialdea et al., 2009). Two diapiric locations are distinguished by western and eastern.

Due to the internal stratigraphic architecture of mud accumulation, only two reflectors, aged at 2.0 ± 0.1 cal ka BP and 1.0 ± 0.1 cal ka BP, are traced to the full extent of the study area. Isopach maps portray the general extent and the centers of maximum mud deposition and their formation history in the form of pre-defined time slices from the base of the MDCs to 2.0 cal ka BP (Slice 1), 2.0 to 1.0 cal ka BP (Slice 2), and 1.0 cal ka BP to present (Slice 3). For the time interval of Slice 1, the main deposition area was located close to the mouth of the Guadalquivir River with a thickness of 7 to 14 m (Figure 33). Off the Tinto-Odiel Estuary near the shelf edge, a smaller depositional center which is 5 to 7 m thick. The two tails associated with the pro-delta, deposit sediment around mud entrapments through mid-shelf regions, splitting the accumulation location of the prodelta extent.

For time Slice 2, the central deposition near the Guadalquivir River consistently stayed locally stable but shifted a bit more south and also extended a bit closer to the shelf edge (Figure 34). Sediment deposition from 2.0 cal ka BP to present (combined Slice 2 and 3, referred to as Slice 2.5) of the mud belt MDC (Figure 35) occurred mostly during the time Slice 2 with 2 m of maximum sediment accumulation from 2.0 to 1.0 cal ka BP (Figure 34) and 1 m from 1.0 cal ka BP to present (Figure 36). Deposition during the youngest time
slice was almost entirely confined to the Guadalquivir River region, although isopach maps depict deposition was centrally more spread out than the millennia before.

6.4 Material Budget Calculation

The Holocene sediment accumulation of the MDCs was separated into volumetric sections based on reflectors that travelled the full extent of the study area, Slice 1, Slice 2, and Slice 3, as discussed above. Volumes were produced by time slice of the MDCs (Table 9). Using methods discussed, 1.56 km$^3$ of material remained unaccounted for due to open questions in regards to the lateral shape of Holocene sediment accumulation, acoustic masking of strata portions, and low quality of some seismo-acoustic profiles. This 1.56 km$^3$ of material was included in calculations by assuming it contains the same grain density (2.24 g cm$^{-1}$) and porosity (52.21 %) values as the average MDCs (Table 9). By splitting the MDCs succession into time slices, Slice 1, Slice 2, and Slice 3, dry sediment volumes from IHS Kingdom 2015 are 3.13, 0.99, 0.93 km$^3$ respectively. With the unaccounted material (0.75 km$^3$), the total dry sediment volume for the MDCs is 5.80 km$^3$ with a mass of 12,971 Mt (megatons).

6.5 Carbon Budget Calculation

Select samples were measured for TOC, and CaCO$_3$ content from Cores 19512-3, 19513-3, 19519-3, 19520-3, and 19535-3 (Table 10). TOC ranged from 0.58 to 0.78 % varying by facies (Table 4) and 0.62 to 0.73 % varying by time slice (Table 9). Consistent CaCO$_3$ concentrations ranged from 27.26 to 28.79 % by facies (Table 4) and 27.85 to 28.63 % by time slice of the MDCs (Table 9). Facies B contains the highest CaCO$_3$ content (28.79%), while Facies A contains the highest TOC (0.78 %) (Table 4). Although Facies A and B combine to create Slice 3 (0.693 %), Slice 2 (0.726 %) (composed of Facies C)
contains a higher total organic content (Table 9). These values, when combined with the volumetric and mass calculations lead to a qualitative approximation of the retention of marine and terrigenous carbon by the MDCs. For CaCO$_3$ a total volume of 1.63 km$^3$ and a mass of 3637 Mt is calculated (Table 9). TOC has a total mass of 85 Mt (Table 9).
7.0 Interpretation and Discussion

7.1 Mud Depocenter Evolution: Influences on Accumulation and Stratigraphy

Areas of low sediment accumulation in the early Holocene (> 6.5 cal ka BP) were composed of dark greenish silts with abundant shell fragments, while material younger than 6.5 cal ka BP contained lighter grayish homogenous muds (Figures 21, 23). Muds from a terrigenous material are commonly associated with Fe-enriched material (Hanebuth et al., 2015b) and the color change may potentially point to a change in sediment source: This trend towards a stronger terrigenous contribution is also clearly reflected by a gradual upward shift towards lower \( \ln \text{Ca}/\text{Fe} \) values (Figures 13, 15, 21).

7.1.1 Holocene Transgression to 6.5 cal ka BP

After the last transgression began about 19 cal ka BP (Hernández-Molina et al., 1994; Hanebuth et al., 2009), the base of the MDCs is defined as approximately 10.0 ± 1.0 cal ka BP. The lowermost Facies F and E are composed of muddy silt with chaotic sorting and abundant shell fragments (Figure 21, 23). Most of the carbonate material is deteriorated, stained and fragmented, which points to reworking processes during transgression. The slightly lower \( \text{Ca}/\text{Fe} \) ratio (Figures 13, 15), compared to younger facies, is possibly affected by the larger grain size (Figure 21, 22) of material indicating a less representative increase in Fe. The two Facies show a retrogradational deposition pattern caused by backstepping sedimentation as a results of a material influx which was unable to keep up with a rapidly rising sea level. All strata terminate at the shelf break, making it challenging to distinguish between retrogradational, aggradational, and low angle progradational.
sequences. In combination with absolute dating, the base of the Holocene MDCs is composed of sediment deposited during a transgressive systems tract (TST) (Figures 21, 23), which is normally not well preserved (Lobo et al., 2001, 2004). Mendes et al. (2012) found sedimentation rates in the mud body offshore of the Guadiana River (around 10 cm ka\(^{-1}\)), compared to the variable 17 to 35 cm ka\(^{-1}\) in the mud belt MDC off shore of the Tinto-Odiel Estuary (Figure 29; Table 7). Rates of accumulation (taking into consideration dry bulk density) during this stage were as low as 16 to 46 g cm\(^{-2}\) ka\(^{-1}\) (Figure 24, Table 8).

An erosive boundary was located between and around topographic structures that locally confined the northwestern base of the prodelta MDC (Figure 29), which can be easily seen on the shore-facing side of these elevations (Figures 26, 37). Boomer data sets show that these structures are characterized by chaotic internal reflection at depths 55 to 65 m below modern sea level. This depth suggests that these entrapping structures were once a chain of exposed islands, possibly ca. 8.2 cal ka BP (MWP-2) (Lobo et al., 2001). Distinguishing whether sediment naturally deposited on the landward side of these structures as a kind of lagoonal facies, or whether these depositional packages still experienced deformation due to local uplift of the rocky obstacles, cannot be resolved by the existing data set. Overall, internal clinoform formation inside, illustrates a backstepping pattern consistent with the retrogradation dynamics of a TST. Once the accommodation space between these structures filled, possibly at different times during transgression, the weight of the overbearing sediment may have started to cause subsidence of the structures closest to the Guadalquivir River (Figure 37). Acoustic masking, due to gas presence, near the Gua-
dalquivir River hides most material from the TST (Figures 27, 28, 32, 37). Faulting between structures matched with draping offsets of major reflectors indicates the base of the prodelta MDC has undergone rates of subsidence after material deposited (Figure 37).

7.1.2 Maximum Flooding Surface

A maximum flooding surface (mfs), occurred ca. 6.5 cal ka BP (Dabrio et al., 2000; Lario et al., 2002), i.e., at the boundary between Facies E and D (Figure 21, 23), when sea level reached its most landward point in flooding the continent (Van Wagoner et al., 1988). At times, the boundary-like reflector depicting the mfs is sharp, indicating non-deposition, condensation of time, or even erosion (Figure 21). The sediment deposited just below and above this boundary is characterized by elevated values in the ln Ca/Fe ratio (Figures 13, 15, 21) indicating that the material was dominantly supplied from marine sources (Hanebuth et al., 2015b). This finding underlines the interruption in terrigenous supply during maximum transgression at about 6.5 cal ka BP. At this point, the high sea level has stabilized, creating the widest accommodation space on the continental shelf and inside the estuaries.

7.1.3 Highstand Depositional System

Following the mfs, sea level began to stabilize towards its present day position allowing for a HST to develop with deposits characterized by laterally, expanding aggradational sheets and low-angle progradational clinoforms (Figure 6; Van Wagoner et al., 1988; Lobo et al., 2005). Grain size decrease and a constant increase in terrigenous material continues at a constant rate to present day formation of the MDCs (Figures 13, 15, 22).

While the rate of sea level rise slowed from 6.5 to 3.2 BP (Figure 7), strong long-shore currents displaced large amounts of sediment along the coast and created a sand spit
around the mouth of the Tinto-Odiel Estuary, leading to partial enclosure of the estuary (Lario et al., 2002). During this stage, infilling of the estuary was characterized by massive mud deposition (López-González et al., 2006). The low accumulation rates (3 to 7 g cm\(^{-2}\) ka\(^{-1}\)) between 6.67 and 5.79 cal ka BP found off the Tinto-Odiel Estuary can be caused by the high quantity of riverine mud being captured in the newly formed estuary (Table 8; Figure 23).

Mendes et al. (2012) found sedimentation rates to be lower in the prodeltaic wedge offshore of the Guadiana River (52 cm ka\(^{-1}\) from 3.75 to 1.3 cal ka BP), compared to 55 to 107 cm ka\(^{-1}\) from 4.35 to 1.29 cal ka BP in the mud belt MDC and northwestern portion of the prodelta MDC (Figure 29; Table 7). In summary, the accumulation rates slightly increased shelf wide in this study area from 5 to 38 g cm\(^{-2}\) ka\(^{-1}\) from 5.79 to 2.7 cal ka BP (Table 8; Figure 24). In the middle of this interval, Bond Event 2 occurred as early as 3.0 cal ka BP (drought-resistant vegetation: Jiménez-Moreno et al., 2015) and as late as 2.6 cal ka BP (decline in forest cover: Jiménez-Moreno et al., 2015). Due to this temporal blurring and the given low time resolution between 4.35 and 2.70 cal ka BP, it is hardly possible to identify changes in accumulation rates and link them to Bond Event 2 (Table 8). Seismo-acoustic profiles depict aggradational deposition for this time interval which might be related to the rate of sea level, thus the opening of new accommodation space, may have been comparable to sediment available through fluvial input.

The northwestern portion of the prodelta MDC (Figure 29) is known to undergo subsidence due to the weight of material loading (Lobo et al., 2002), continuously opening new accommodation space. In contrast, a diapiric intrusion (Figures 27, 31, 32) close to shelf edge, observed at the base of the prodelta MDC (Figure 29), leads to a local reduction
in accommodation space. This is due to mud deposition occurring mainly from the bottom nepheloid layer transport (gravity currents stopping to allow for accumulation: Figure 3). Local positive obstacles can lead to a slowing of the bottom, gravity driven, current velocity thus acting as local mud traps (Hanebuth et al., 2015a). Here, deposition is not only controlled by the accumulation space available, but possibly also by local upwelling along the shelf edge (Current N1 in Figure 9; García-Lafuente et al., 2006), hindering sediment deposition or increasing seafloor interaction with currents. Further discussion on the diapiric uplift is provided in Section 7.3 Tectonic Influence on the Geometry of the Mud Depocenter.

A major change in the sedimentary regime occurred after 2.7 cal ka BP when accumulation rates increased by three to 17 times (Figure 24). In comparison, Mendes et al. (2012) found sedimentation rates increasing by up to only 2 times in the prodelta wedge of the Guadiana River. Some of this increase can be attributed to region-wide mining, deforestation, and agriculture activities during the Roman Period, which peaked around 1.9 ± 0.2 cal ka BP (Figure 11; Martín-Puertas et al., 2010; Hanebuth et al., 2018 and references therein). The increase in sediment accumulation can also be related to a regional climatic change into a humid period causing higher lake levels in southern Spain that lasted from 2.6 to 1.6 cal ka BP (Martín-Puertas et al., 2008), increased sedimentation rates in rivers (Goy et al., 1996), and overall increased aridity in the western Saharan region (Hanebuth and Henrich, 2009). Around 1.6 cal ka BP, the depositional pattern of the prodelta MDC (Figure 29) transitioned into a progradational system where clinoforms reached the shelf edge and the rate of accumulation assumedly surpassed the rates in sea level rise and subsidence. The colder and dryer influence related to Bond Event 1 (1.4 cal ka BP), which
occurred during or right after the termination of the Roman Empire, might be reflected by a slight noticeable decrease in accumulation rate from 1.95 to 1.42 cal ka BP (Figure 24).

Slightly elevated accumulation rates around 1.0 cal ka BP, compared to the 600 yrs before, is linked to the extremely high precipitation that occurred throughout the Iberian Peninsula around 0.95 ka BP (Abrantes et al., 2017). In contrast, a locally restricted aridification event around 1.0 cal ka BP was confirmed in cores from Doñana National Park, Spain (Jiménez-Moreno et al., 2015). This conflicting finding may indicate locally restricted precipitation events affecting fluvial sediment influx to the MDCs.

The decreasing and increasing accumulation rate, depending on MDC location, from 0.7 to 0.4 cal ka BP (Table 8; Figure 24) can be attributed to intense, but less frequent precipitation events during the warm and generally dry MCA (1.05 to 0.7 cal ka BP) extending into the LIA (0.65 to 0.15 cal ka BP) (Nieto-Moreno et al., 2011; Wanner et al., 2015; Abrantes et al., 2017). The prodelta MDC (Figure 29) formed larger progradational clinoforms caused by increased flood frequency until about 0.2 cal ka BP (enhanced freshwater input Western Mediterranean Sea: Nieto-Moreno et al., 2011; 0.82 to 0.09 cal ka BP Old Yellow River delta, South China Sea: Liu et al., 2013; 0.28 to 0.25 cal ka BP Rhone River delta, Western Mediterranean Sea: Fanget et al., 2014). Due to core location, accumulation rates collected during the formation of these larger progradational clinoforms is not accurately represented with this data set (Table 8; Figure 24).

Lower accumulation rates between 0.7 to 0.4 cal ka BP (Table 8; Figure 24) of the mud belt MDC (Figure 29) persisted during the LIA due to a dry regional climate regime and infrequent precipitation events (0.65 to 0.15 cal ka BP; Nieto-Moreno et al., 2011;
Abrantes et al., 2017). The ln (Ca/Fe) ratios depict an increase in terrestrial influence (Figures 13, 15, 21). The enhanced terrestrial signal may have been a regional difference between the Tinto-Odiel Estuary, Guadalquivir River, or Guadiana River locations or other local controlling factors affecting accumulation rates that have not been considered such as changes in agriculture or cultivation.

Over the past 200 yrs, accumulation rates remarkably increased up to ninety times (72 to 2,863 g cm\(^{-2}\) ka\(^{-1}\); Table 8, Figure 24) with a high degree of industrial contamination (Figure 11; Martín-Puertas et al., 2010; Hanebuth et al., 2018). This massive increase in material availability is probably caused by the mining and land-use activities at a regional and industrial scale. Yet, increasing sea surface temperatures and pollen records indicate amplified humidity and precipitation events during the past 200 yrs (Fanget et al., 2014; Abrantes et al., 2017), potentially intensifying sediment mobility from source to sink. At this point, the prodelta MDC (Figure 29) depicts a switch towards an aggradational clinoform pattern. The general increase in accumulation rates, during the Industrial Era, might reflect an expansion of the regional land-use, often accompanied with deforestation and soil erosion (Table 8; Figure 24). Although the Guadalquivir River hosts 15 major dams built since the 1960’s (Hanebuth et al., 2018), which significantly interrupt the sediment influx to the shelf, the accumulation rate (Figure 24) at the prodelta MDC (Figure 29) persistently increased. This trend may be owed to the frequent occurrence of flood layers from storms events that eroded additional material from the lower Guadalquivir region (Abrantes et al., 2017; Hanebuth et al., 2018). Cores within the mud belt MDC (Figure 29), however, contained decreased accumulation rates by about 40% over the past 40 yrs (1970 to 1990
CE (Sites 19535 and 19538; Table 8). Close to the Tinto-Odiel Estuary, Site 19534, contains a decrease of 60% from 1990 to 2000 CE (Table 8). This local reduction in sediment availability cannot be explained by the existing data sets. It might be related to increased bottom trawling (Oberle et al., 2014) leading to massive sediment resuspension; or an efficient damming in the small catchment area of the Tinto and Odiel Rivers, or further and larger Guadiana River, trapping sediment inside rivers.

As a summary, the accumulation rates of the MDC increase substantially at about 2.7 ± 0.2 ka BP (Table 8; Figure 24). In contrast, the Holocene accumulation rates reconstructed from southwestern Spanish estuaries (Lario et al., 2002) showed that early sediment accumulation occurred at a high rate of 5 mm yr⁻¹ between 10 to 6.5 cal ka BP, while it substantially lowers to 1.5 mm yr⁻¹ afterwards (6.5 cal ka BP to present). This transition occurred around 6.5 cal ka BP when the accumulation rate surpassed the rate a decelerating sea level rise (Figures 11, 24; Lario et al., 2002; Lantzsch et al., 2009, 2014). When comparing the general rising and accelerating trend of sedimentation rates extracted from the MDCs with estuary rates from Lario et al. (2002), there is almost an inverse correlation (Figure 38). During the TST, as sea level rose rapidly and shoreline retrograded, sediment was initially being trapped inside the newly formed estuaries.

Lario et al. (2002) indicated a definite change in sediment accumulation between 7 and 6 cal ka BP, whereas accumulation rates in the MDC did not depict a major increase until 3 to 2 cal ka BP (Figure 38). This apparent delay can be due a variety of factors which are unrelated to sea level history, such as the increase in deforestation, mining, coastal land-use (Hanebuth et al., 2018 and references therein), but also a humid climatic event (Martín-Puertas et al., 2008; Goy et al., 1996); all increasing the sediment flux to the shelf. Another
reason, although speculative, could be that the current oceanographic circulation patterns may not have been well established before 2.7 cal ka BP, limiting regional-scale sediment movement. Even after taking these scenarios into consideration, the time delay could be due to a gap in data coverage between the modern coastline and the 20 m mark in water depth. The inner shelf zone may have accumulated material before the mid-shelf region received sediment, i.e., until the accommodation space on the inner shelf was filled (around 2.7 cal ka BP).

7.2 Sediment Budget Calculation

By splitting the MDC into time slices and adding them together with the unaccounted portion of material (an extra 0.75 km$^3$ and 1,672 Mt of sediment), the total dry sediment sums up to a volume of 5.80 km$^3$ and a mass of 12,980 Mt (with an error of at least +7%, if the TWT velocity of 1,500 m/s is underestimating the real acoustic velocity in surficial soft sediment; see Oberle et al., 2014), covering an overall area of 1,900 km$^2$. This time slice approach also led to the calculation of 3,637 Mt for CaCO$_3$ and to 85 Mt for TOC (Table 9). To place these numbers into a context, they are compared to two other siliciclastic shelf systems which contain sediment budget calculations.

The Galicia mudbelt system off Northwest Spain contains 3.9 km$^3$ of sediment with a total mass of 4,035 Mt (similar uncertainty as mentioned above) over an area of 4,490 km$^2$ (Oberle et al., 2014). Its total organic and carbonate contents sum up to 40 Mt and 174 Mt, respectively. This shelf mud depositional system started to form around 5.3 cal ka BP (Lantzsch et al., 2009), i.e., about a millennium later than the establishment of the modern MDC in the Gulf of Cadiz. The advantage the Oberle et al (2014) study had was that the fluvial sediment discharge for the Galician region was roughly known. With these two
parameters, the primary input, and the storage on the shelf, it was possible to calculate that about 65% of the fluvially supplied mud bypasses extent of the shelf eventually depositing in the deep ocean.

The Adria mudbelt system to the east of Italy assumed that no sediment ever left this semi-enclosed basin (Brommer et al., 2009). The study could then be used to reconstruct the volume of later Holocene sediment discharge of various rivers draining from the Italian Peninsula into the Adriatic Sea. The budget calculation resulted in 254,000 Mt ± 15% for the highstand MDC over a larger area of ca. 35,000 km². This depocenter also formed over the past 5.5 thousand yrs when sea level stabilized.

By comparing the three systems it turns out that each individual MDC is inherently different (Table 11). In terms of initiation age, these three systems are close to each other and underline the important role sea level can play in open accommodation space. However, the early initiation of the transgressive Facies F and E in the Cadiz MDC corresponds to other examples, as compiled by Hanebuth et al. (2015b and worldwide references therein), where the shelf was inundated enough at the beginning of the Holocene to allow for early mud accumulation. The Galician shelf is characterized by an overall exceptionally steep shelf gradient and the Adriatic shelf shows two steps in bathymetry, therefore both did not favor an early accumulation.

In terms of composition, the Gulf of Cadiz depocenters contain a much higher content of carbonate and organic matter than the Galician depocenter (Table 11). The average carbonate content in the Cadiz depocenter is 28% while it is only 4% off Galicia; the average TOC in the Cadiz depocenter is 0.5%, but nearly 1% off Galicia. This difference indicates that proportion of fluvial input in the mid-shelf MDC off Galicia is significantly
higher compared to the Cadiz system. Thus, the role of MDCs as sinks and possible secondary sources for carbon as a component in the regional and global carbon cycle needs to be individually considered. This makes a global calculation of med depocenter carbon retention a challenge.

In terms of sediment retention, the lack in sediment supply data in the Gulf of Cadiz does not allow for a full budget calculation or a comparison. Since the sediment export from muddy shelf systems can vary from 0 to 90% (see Oberle et al., 2014, for worldwide references) it is not further possible to calculate either fluvial input or export across the shelf edge based on this new data.

7.3 Tectonic Influence on the Geometry of the Mud Depocenter

The central depositional location of the prodelta MDC (Figure 29) shows an unusual stratigraphic pattern during early Holocene. Boomer data illustrates a diapiric structure below the MDC (Figures 31, 32), which confirms the finding of salt diapirism by previous studies (Fernández-Puga et al., 2007; Rodero et al., 1999; Lobo et al., 2002). This diapiric (western diapir) structure caused spectacular deformation of the MDC during early Holocene and led to a concentration of deposition to other areas of the shelf (Figure 32). Extension faulting is conceptually associated with diapir tectonics (Rodero et al., 1999; Lobo et al., 2014). Initially during this study, only a few isolated faults were found and were expected to be caused by local subsidence due to compaction. After the discovery of two diapiric intrusions, however, it became obvious that the boomer data sets show numerous faults vertically extending far into the MDC from at least as deep as 150 m below seafloor (Figure 31, 32).
Extensional faulting is found between the western salt diapir and Guadalquivir River, where depocenter thickness is greatest (Figures 31, 39). Salt diapirism is a widespread phenomenon in the eastern part of the Gulf of Cadiz (Fernández-Puga et al., 2007; Medialdea et al., 2009). The loading by the MDC may additionally be pushing on evaporitic deposits located deeply below the shelf. These evaporitic deposits flow along a pressure gradient by the overburden until it reaches a fault line where the evaporite elastically migrates upward into an elevation of less pressure, creating the two identified diapir locations (Figures 31, 32; Fernández-Puga et al., 2007). These diapiric structures are composed of salt or a marly salt from the regional so-called Allochthonous Unit of Triassic age (Medialdea et al., 2009).

As the evaporitic material moves towards the diapir, the sediment cover around the diaper tends to subside to balance the mass lost in the subbottom, accompanied by extension fault lines (Figure 39). Surprisingly, these faults extend up into MDC strata as young as $0.03 \pm 0.05$ cal ka BP, i.e., 350 yrs ago, meaning they are still active in sub-recent times (Figure 39), with an increasing age trend towards the west. Overall, these basement structures seem to be subsiding in relation to the large sheet-like prodelta MDC (Figure 29).

The eastern diapir location contains three small diapir peaks, where the formation capping the eastern most diapir, of the three small peaks, has penetrated into the base of the MDC (Figure 31). Local extension faults associated with this penetration are also as young as $0.03 \pm 0.05$ cal ka BP, i.e. again 350 yrs ago.

Perpendicular to the shelf edge in the southern-most seismo-acoustic profiles, an extensional fault, which even deforms the modern seafloor was detected (Figure 39). Based on fault orientation, the shore-side of the fault, extending inland as far as to Site 19519, has
undergone subsidence related to local block tectonics (Figure 39). Due to the acoustic masking caused by gas, it is not possible to trace the full movement of this fault (Figure 27).

Gas deposits commonly formed in relation to diapirism due to faults, often provides both a pathway of least resistance for the gas to travel and a cap stone by upward bending strata. Within the Gulf of Cadiz, the Allochthonous Unit and overlaying units are known to contain a mixture of thermogenic and biogenic gas (Medialdea et al., 2009). Past the shelf break, Boomer acoustic images depict gaseous sediment along the flank of the western diapir (Figure 40) and pockmarks caused by gas expulsion below the gaseous sediment (Casas et al., 2003). If thermogenic gas off the Guadalquivir River travels upward through extension faults (fault locations in relation to acoustic masking Figure 27), a capping fine-grained sediment body would have the potential to trap and thus concentrate the gas. The top of the gas correlates with an internal reflector, which dates at about 0.88 ± 0.05 cal ka BP and represents the boundary between Facies C and B (Figures 21, 23).

However as a commonly found alternative to explain the shallow gas blob in front of major river systems, the gas might simply be associated to the thick Holocene prodeltaic sediment wedge which was sourced by the Guadalquivir River over time (Figures 27, 28). Locations of organic rich fluvial material are favorable for microbial shallow-gas formation as described in many other regions (Senegal shelf: Nizou et al., 2010).

7.4 Differentiation of Sediment Sources

Using the newly generated data sets, a differentiation in the influence of the various fluvial sediment sources could not be determined and therefore remains speculative. Looking at the isopach maps, Slice 3 (1.0 cal ka BP to present: Figure 36) has a larger area
(1,130 km²) than Slice 2 (2.0 to 1.0 cal ka BP: Figure 34) (1,030 km²) but a smaller volume and mass (Table 7). Maximum MDC thicknesses from Slice 3 is 5 m (Figure 36), while Slice 2 max thickness is 7 m (Figure 34).

After 2.0 cal ka BP, sediment deposition specifically in the Tinto-Odiel portion of the depocenter occurred mostly during Slice 2 with maximum, 2 m of sediment, (Figure 34) and 1 m, i.e., 50 % from Slice 3 (Figure 36). Deposition post-1 cal ka BP (Slice3) was almost entirely confined to the Guadalquivir River region, although isopach maps depict deposition was laterally more extent than the millennia before (Figure 36).

This observation can be explained by several mechanisms that influence growth dynamics of the MDC. Current circulation patterns on the shelf may have been different from 2.0 to 1.0 cal ka BP than modern day circulation. On the anthropogenic side, an increase in river damming, (small Tinto and Odiel Rivers, or further and larger Guadiana River) trapping sediment inside rivers (González-Ortegón et al., 2010), may have limited sediment input. To verify this assumption, high resolution grain size measurements of cores through central shelf, parallel to shore, should be performed. If the seemingly detached lobe near the Tinto-Odiel Estuary is not fed by the Guadalquivir, grain size distribution stemming from the Guadalquivir to this lobe, will depict decreasing grain size followed by an increase. An increase in grain size can indicate a different source, as speculated, the Guadiana River. Sediment from the Guadiana River can be transported to this location by the NASW current (Mauritzen et al., 2001; García-Lafuente et al., 2006).
8.0 Conclusions

Mud accumulation between the Tinto-Odiel Estuary and the Guadalquivir River has previously been described as taking place in separate MDCs (Figure 4; Lobo et al., 2004), where the outer-shelf deposits are mainly sourced by the Guadiana and mixed with Guadalquivir-sourced material. For the mid- to inner-shelf, a prodelta wedge MDC is identified off the Guadalquivir River mouth (Figures 11, 29; Lobo et al., 2004). Due to the lateral continuity of major internal stratigraphic reflectors across the shelf and based on the accumulation rate reconstruction, the southeastern two thirds of this study area seem to be sourced mainly by the Guadalquivir River. The deposit, however, also contains a mixed heavy metal signature from the Tinto-Odiel Estuary (Hanebuth et al., 2018). The remaining northwestern third of the study area is determined to be a portion of a mud belt MDC sourced mainly by the Guadiana River (Figures 11, 29; Lobo et al., 2004). The closer Tinto-Odiel Estuary may also provide material to the mud belt MDC (heavy metal signature presence: Hanebuth et al., 2018).

While the prodelta MDC (Figure 29) seems relatively unchanged over the past 2.0 cal ka BP (Figures 34, 36), the mud belt MDC (Figure 29) showed a 50% decrease in accumulation when splitting the 2.0 cal ka BP-to-present time interval in a phase prior to and after 1.0 cal ka BP (and particularly during the past 200 yrs). Although this assumption remains speculative, recent damming of the Tinto and Odiel Rivers, or further and larger Guadiana River, may have instigated a lower sediment output to the shelf causing lower accumulation rates in the northwest sector (Figure 24, Table 8).
Through accumulation rates and early Holocene ages, the base of the MDCs is estimated to be around 10.0 ± 1.0 cal ka BP, i.e., in earliest Holocene times. Six major successive sedimentary facies comprise the MDC with the oldest two (F and E) depicting retrogradational deposits linked to the last transgression until 6.5 cal ka BP, when sea level stabilized close to the present day level (Figures 21, 23). The modern appearance of the MDCs started to develop at that time, which indicates a major change in sediment availability and accumulation associated with a stable and high sea level. Accumulation rates stayed relatively low until around 2.7 cal ka BP (Figure 24, Table 8). The following increase in sediment accumulation can be linked to agricultural and mining activities during the Roman Period on the southern Iberian Peninsula (Hanebuth et al., 2018 and references therein) and also to a humid climatic period, which lasted from 2.6 to 1.6 cal ka BP in southern Spain (Martín-Puertas et al., 2008; Goy et al., 1996). A drop in accumulation rates (Figure 24, Table 8) occurred around Bond Event 1 (1.4 cal ka BP) from 1.8 to 1.4 cal ka BP. Intense precipitation events during an arid and dry MCA (1.05 to 0.7 cal ka BP) (Nieto-Moreno et al., 2011; Wanner et al., 2015), with extreme occurrences around 950 cal ka BP (Abrantes et al., 2017), probably attributed to higher accumulation rates around 1.0 cal ka BP and slightly lower, variable accumulation rates extending within the LIA (Figure 24, Table 8). In contrast, localized decline in forest cover in Doñana National Park, Spain (Jiménez-Moreno et al., 2015) indicates these intense precipitation events may differ on regional scale by watershed basin. Variable accumulation rates in the mud belt MDC and northwestern prodelta MDC (Figure 29) occur due to frequent, yet less extreme, precipitation events with an arid climate persisting into the LIA (0.65 to 0.15 cal ka BP) (Abrantes et al., 2017) until about 0.44 cal ka BP (Nieto-Moreno et al., 2011). From 0.44 to present,
accumulation rates have been heavily influenced by urbanization and industrialization, mining, river damming, possibly offshore and inshore dredging, and chronic bottom trawling (Hanebuth et al., 2018 and references therein; Figure 24, Table 8).

An increase in the terrigenous input signal (Figures 13, 15, 21: ln Ca/Fa), a fining grain size (Figure 21, 22: ln Ti/Zr), and increasing sedimentation (Figure 18, 19, 20; Table 7) and accumulation rates (Figure 24; Table 8) all correlate to a generally more humid and increased anthropogenic modified present day shelf.

From the base of the MDCs to 2.0 cal ka BP, 3.13 km$^3$ weighing 6,939 Mt of sediment accumulated. After the start of the humid period, while the Roman Empire expanded over the Iberian Peninsula, i.e., during time slice 2.0 to 1.0 cal ka BP, the depocenter accumulated 0.99 km$^3$ of sediment with a mass of 2,222 Mt. Since the MCA (1.0 cal ka BP to present), 0.93 km$^3$ of dry sediment accumulated with a weight of 2,138 Mt. The time slice method used to produce the volumetric and mass budget calculations accounted for an additional 0.27 km$^3$ and 566 Mt of material (Table 9: synopsis of calculations). These calculations combined with the carbon contents provided a TOC mass of 85 Mt, and a CaCO$_3$ mass of 3637 Mt with a total volume of 1.63 km$^3$.

Surprising findings, depict extension faults persist into the modern MDC. Salt diapirs, originating from the Triassic Era (Fernández-Puga et al., 2007; Medialdea et al., 2009) are rising along older extension faults caused by compression in the NE-SW orientation (Fernández-Puga et al., 2007; Medialdea et al., 2009). As the material is displaced, salt diapir uplift has caused localized extension faults and controlled the location and thickness of mud deposition on local scale (Figures 32, 33). This tectonic influence was active until
0.03 ± 0.05 cal ka BP (Figures 39). As a result of this displacement, the sedimentary succession of the prodelta MDC (Figure 29) has undergone and continues to undergo subsidence in correlation with other extension faults. Commonly associated with diapirs, gaseous sediment have been found close to extension faults, evident by acoustic-masking (Figure 28) and core expansion while opening (Figure 21: Core 19517-3). However, the gaseous sediments can be related to a high organic content present in the Guadalquivir prodelta depocenter (Senegal shelf: Nizou et al., 2010).

There are some studies that can be conducted to bring to light some speculation discussed or confirm proxies used. Grain size data should be collected at a future time to corroborate the grain size proxy using ln (Ti/Zr) ratios (Figures 21, 22) and confirm or deny source differentiation between the mud belt MDC and prodelta MDC (Figure 29). If age resolution can be increased, climatic variability can be found on a smaller scale than what has been presented. A closer look into the extension faults can produce rates at which the fault has been moving, at least during the Holocene. Further study of the gas may be able to determine if its origin is thermogenic or biogenic fueled (Medialdea et al., 2009). If further studies of the suspended sediment and sediment bedload for all fluvial sources are conducted, a retention budget can be complied for the shelf.
## 9.0 Tables

Table 1. Justification to use specific data for each Thesis Objective.

<table>
<thead>
<tr>
<th>Data</th>
<th>Objectives</th>
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<tbody>
<tr>
<td></td>
<td>Chrono- &amp; Litho-Stratigraphy of MDCs</td>
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<tr>
<td><strong>Seismo-acoustic Echosounder Data CADISED cruise</strong></td>
<td>Geometric Formation, Stratigraphic Correlation</td>
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<tr>
<td><strong>Boomer Data Sets 1992, 1986</strong></td>
<td>Geometric Formation</td>
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<tr>
<td><strong>High-Resolution Core Images</strong></td>
<td>Detailed Facies Determination</td>
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<tr>
<td><strong>Lithology Descriptions</strong></td>
<td>Detailed Facies Determination</td>
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<tr>
<td><strong>Magnetic Susceptibility Scans</strong></td>
<td>Stratigraphic Correlation, Source Differentiation</td>
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<td>Facies Boundary Identification</td>
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<td><strong>Dry Bulk Sediment Density Data</strong></td>
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<td><strong>Grain Density Data</strong></td>
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<td><strong>XRF Scanner Element Intensities</strong></td>
<td>Stratigraphic Correlation, Source Differentiation</td>
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<td><strong>XRF Powder Element Concentrations</strong></td>
<td>Source Differentiation</td>
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<td><strong>Carbonate Content / TOC</strong></td>
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<tr>
<td><strong>Grain Size Distribution (GSD) Data</strong></td>
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<td><strong>Radiography Images</strong></td>
<td>Detailed Facies Determination</td>
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<td><strong>$^{14}$C Dates / $^{210}$Pb Profiles / $^{137}$Cs Peaks</strong></td>
<td>Age Control</td>
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MDC = Mud Depocenter

TOC = Total Organic Content
Table 2. Justification for stations selected in the study area based on preliminary interpretation of acoustic data. *(1)*Representative stations used for correlating element intensity ratios to create a robust age framework for MDCs.

<table>
<thead>
<tr>
<th>Station</th>
<th>Gravity Core Coordinates</th>
<th>Water Depth (m)</th>
<th>Gravity Core Recovery (cm)</th>
<th>Reason for selection</th>
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<td>19512(1)</td>
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<td>58</td>
<td>452</td>
<td>Mud depocenter, central</td>
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<td>19513(1)</td>
<td>36°46.721’N 6°52.267’W</td>
<td>91</td>
<td>432</td>
<td>Mud depocenter, distal</td>
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<td>19514</td>
<td>36°40.580’N 6°46.150’W</td>
<td>90</td>
<td>358</td>
<td>Mud depocenter, distal</td>
</tr>
<tr>
<td>19515</td>
<td>36°52.743’N 6°58.506’W</td>
<td>90</td>
<td>457</td>
<td>Mud depocenter, distal</td>
</tr>
<tr>
<td>19516</td>
<td>36°53.994’N 6°56.121’W</td>
<td>70</td>
<td>479</td>
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<td>485</td>
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<td>235</td>
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Table 3. Data sets collected at coring stations within study area.

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<sup>(1)</sup> Total Organic Content
Table 4. Summary of MDCs facies characterization by sediment properties.

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<td>A</td>
<td>B</td>
<td>C</td>
<td>D</td>
<td>E &amp; F</td>
</tr>
<tr>
<td>Avg. Thickness (cm)</td>
<td>21</td>
<td>182</td>
<td>141</td>
<td>178</td>
<td>229</td>
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<tr>
<td>Porosity (%)</td>
<td>66.54</td>
<td>56.06</td>
<td>54.98</td>
<td>50.22</td>
<td>40.00</td>
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<td>Dry Bulk Sediment Density (g cm⁻³)</td>
<td>0.72</td>
<td>0.95</td>
<td>0.98</td>
<td>1.08</td>
<td>1.31</td>
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<tr>
<td>Grain Density (g cm⁻³)</td>
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<td>Total Carbon (%)</td>
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<td>4.09</td>
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<tr>
<td>Total Organic Carbon (%)</td>
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<td>0.68</td>
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<tr>
<td>CaCO₃ (%)</td>
<td>27.26</td>
<td>28.79</td>
<td>28.03</td>
<td>28.34</td>
<td>27.47</td>
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Table 5. Sediment cores with coordinates, water depth taken, sediment sample depth in core, measured conventional radiocarbon ages (+1σ error), calibrated radiocarbon ages (+1σ error, calibrated with CALIB software version 7.10 with data set "marine13.14c") (Stuiver and Reimer, 1993; Reimer et al. 2013).

<table>
<thead>
<tr>
<th>Gravity Cores</th>
<th>Sample Depth (cm)</th>
<th>Conventional $^{14}$C Age (yr BP)</th>
<th>Calibrated $^{14}$C Age (yr BP)</th>
<th>Material</th>
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<tr>
<td>POS482 GeoB Gravity Cores</td>
<td>Sample Depth (cm)</td>
<td>Conventional $^{14}$C Age (yr BP)</td>
<td>Calibrated $^{14}$C Age (yr BP)</td>
<td>Material</td>
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<tr>
<td>19512-3</td>
<td>318.5-320.0</td>
<td>1875 ± 35</td>
<td>1425 ± 55</td>
<td>Foraminfera, echinoderm spines, ostracods</td>
</tr>
<tr>
<td>19513-3</td>
<td>418.0-719.5</td>
<td>2755 ± 40</td>
<td>2460 ± 85</td>
<td>Foraminfera, echinoderm spines, ostracods</td>
</tr>
<tr>
<td>19518-3</td>
<td>197.0-197.5</td>
<td>2905 ± 30</td>
<td>2700 ± 30</td>
<td>Delicate in-situ bivalve shell</td>
</tr>
<tr>
<td>19519-3</td>
<td>224.0-255.5</td>
<td>4500 ± 35</td>
<td>4715 ± 70</td>
<td>Delicate in-situ bivalve shell</td>
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<tr>
<td>19520-3</td>
<td>365.0-366.5</td>
<td>0785 ± 30</td>
<td>0440 ± 40</td>
<td>Foraminfera, echinoderm spines, ostracods</td>
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<tr>
<td>19521-3</td>
<td>426.0-427.5</td>
<td>1335 ± 30</td>
<td>0880 ± 45</td>
<td>Foraminfera, echinoderm spines, ostracods</td>
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<td>19534-3</td>
<td>505.0-505.5</td>
<td>1545 ± 30</td>
<td>1075 ± 30</td>
<td>Delicate bivalve shell frags</td>
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<tr>
<td>19535-3</td>
<td>1740 ± 30</td>
<td>1290 ± 30</td>
<td>0960 ± 40</td>
<td>Delicate bivalve shell frags</td>
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<tr>
<td>19538-3</td>
<td>5410 ± 35</td>
<td>5790 ± 55</td>
<td>510.0-511.5</td>
<td>8050 ± 40</td>
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<tr>
<td>Benthic forams</td>
<td>6211 ± 33</td>
<td>6665 ± 50</td>
<td>Benthic forams</td>
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<td>510.0-511.5</td>
<td>8050 ± 40</td>
<td>Foraminfera, echinoderm spines, ostracods</td>
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<tr>
<td>Foraminfera, ostracods</td>
<td>1420 ± 30</td>
<td>0960 ± 40</td>
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<td>5410 ± 35</td>
<td>5790 ± 55</td>
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Table 6. Age models for Cores 19534-3, 19520-3, 19512-3, and 19535-3, using $^{210}$Pb and $^{137}$Cs dating methods. All ages are given in Common Era (CE). Constant Rate of Supply (CRS) and Constant Initial Concentration (CIC) models were used for $^{210}$Pb ages.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
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<th>$^{137}$Cs ages (CE)</th>
<th>Depth (cm)</th>
<th>$^{210}$Pb ages (CE)</th>
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a Samples not dated with the CRS model.
b Sample beyond the method’s determination limit.
Table 7. Sedimentation rates (cm ka⁻¹) calculated between two age points using ²¹⁰Pb profiles and ¹⁴C dating. Listed by coring site. Example of how to read the table: The lowermost part of Core 19521 has a sedimentation rate of 12 cm ka⁻¹ from 8.98 to 6.67 cal ka BP.

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<td>92 82 119 62</td>
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<td>1.42</td>
<td>78 72</td>
<td>58 80 97 60</td>
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<td>1.95</td>
<td>116 129</td>
<td>245 84 94 39</td>
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<td>2.45</td>
<td>79 29</td>
<td>80* 163*</td>
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<tr>
<td>2.70</td>
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<td>33 133 204 104</td>
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<td>17* 24</td>
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<td>7.5*</td>
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</table>
* Age or sedimentation rate extrapolated from seismio-acoustic profiles
Table 8. Accumulation rates (g cm\(^{-2}\) ka\(^{-1}\)) based on \(^{210}\)Pb profiles and \(^{14}\)C dating. Listed by stations. Example how to read this table: The base of 19521 has an accumulation rate of 16 g cm\(^{-2}\) ka\(^{-1}\) from 8.98 to 6.67 cal ka BP.

<table>
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<th>Mud Belt</th>
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<th>MDCs</th>
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<td>19520</td>
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<td>7.41</td>
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Dry Bulk Density (g cm\(^{-3}\)) by Facies: A 0.72 B 0.95 C 0.98 D 1.08 E & F 1.31 unavailable

* Age or sedimentation rate extrapolated from seismio-acoustic profiles
Table 9. Summary of MDCs sediment properties by time slice as defined from seismo-acoustic profile analysis.

<table>
<thead>
<tr>
<th>Property</th>
<th>Slice 1</th>
<th>Slice 2</th>
<th>Slice 3</th>
<th>Unaccounted Material</th>
<th>Totaled (timeslices)</th>
<th>Total MD Calculated</th>
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<tbody>
<tr>
<td>Porosity (%)</td>
<td>44.47</td>
<td>54.98</td>
<td>57.17</td>
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<td>52.21</td>
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<tr>
<td>Area (km²)</td>
<td>1270</td>
<td>1030</td>
<td>1130</td>
<td>-</td>
<td>-</td>
<td>1900</td>
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<tr>
<td>Max Thickness (m)</td>
<td>13.7</td>
<td>7.1</td>
<td>5.0</td>
<td>-</td>
<td>-</td>
<td>21.2</td>
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<tr>
<td>Volume (km³)</td>
<td>5.64</td>
<td>2.21</td>
<td>2.17</td>
<td>1.56</td>
<td>-</td>
<td>11.58</td>
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<tr>
<td>Grain Density (g cm⁻³)</td>
<td>2.22</td>
<td>2.24</td>
<td>2.30</td>
<td>2.24</td>
<td>-</td>
<td>2.24</td>
</tr>
<tr>
<td>Dry Sediment Vol. (km³)</td>
<td>3.13</td>
<td>0.99</td>
<td>0.93</td>
<td>0.75</td>
<td>5.80</td>
<td>5.53</td>
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<tr>
<td>Dry Sediment Weight (Mt)</td>
<td>6939</td>
<td>2222</td>
<td>2138</td>
<td>1672</td>
<td>12971</td>
<td>12405</td>
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<tr>
<td>TC (%)</td>
<td>3.96</td>
<td>4.09</td>
<td>4.13</td>
<td>4.03</td>
<td>-</td>
<td>4.03</td>
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<td>0.041</td>
<td>0.038</td>
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<td>TC Weight (Mt)</td>
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<td>91</td>
<td>88</td>
<td>67</td>
<td>521</td>
<td>500</td>
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<tr>
<td>TOC (%)</td>
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<td>0.726</td>
<td>0.693</td>
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<td>TOC Vol. (km³)</td>
<td>0.019</td>
<td>0.007</td>
<td>0.006</td>
<td>0.005</td>
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<td>0.036</td>
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<td>TOC Weight (Mt)</td>
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<td>16</td>
<td>15</td>
<td>11</td>
<td>85</td>
<td>82</td>
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<td>CaCO₃ (%)</td>
<td>27.85</td>
<td>28.03</td>
<td>28.63</td>
<td>28.09</td>
<td>-</td>
<td>28.09</td>
</tr>
<tr>
<td>CaCO₃ Vol. (km³)</td>
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<td>0.28</td>
<td>0.27</td>
<td>0.21</td>
<td>1.63</td>
<td>1.55</td>
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<td>CaCO₃ Weight (Mt)</td>
<td>1932</td>
<td>623</td>
<td>612</td>
<td>470</td>
<td>3637</td>
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Table 10. Representative total carbon content (TC), total organic content (TOC), and calcium carbonate content (CaCO3) for MDCs.

<table>
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<tr>
<th>Core</th>
<th>Depth (cm)</th>
<th>TC%</th>
<th>TOC%</th>
<th>CaCO3%</th>
<th>Core</th>
<th>Depth (cm)</th>
<th>TC%</th>
<th>TOC%</th>
<th>CaCO3%</th>
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<td>19520-3</td>
<td>25.0-26.5</td>
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<td>0.69</td>
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<td>0.73</td>
<td>27.09</td>
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<td>55.0-56.5</td>
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<td>110.0-111.5</td>
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<td>0.78</td>
<td>28.47</td>
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<td>150.0-151.5</td>
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</table>
Table 11: Comparison of three shelf systems with a confined MDCs, for which a high-resolution budget analysis was performed. (1) This study; (2) Lantzsch et al., 2009; (3) Brommer et al., 2009. Although the base of the MDCs from the Gulf of Cadiz are dated at 10.0 ± 1.0 cal ka BP, the regime change occurred at 6.5 cal ka BP (comparable to the other systems). (*) Calculated number.

<table>
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<tr>
<th>Shelf region</th>
<th>Basal age (cal ka BP)</th>
<th>Average thickness (m)</th>
<th>Total area (km²)</th>
<th>Total weight (Mt)</th>
<th>Total weight/area (Mt/km²)</th>
<th>Total Volume (km³)</th>
<th>Total CaCO₃ (Mt)</th>
<th>TOC (Mt)</th>
<th>Fluvial import (Mt/yr)</th>
<th>Shelf export (%)</th>
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<td>(10.0) 6.5</td>
<td>10.5</td>
<td>1,900</td>
<td>12,980</td>
<td>6.83</td>
<td>5.8</td>
<td>3,637</td>
<td>85</td>
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<td>?</td>
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<td>3.89</td>
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</tr>
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<td>ca. 15</td>
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<td>254,000</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>4.62(*)</td>
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</tr>
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</table>
Figure 1. The Guadalquivir River in southeastern Spain pushing a sediment filled plume into the northern Gulf of Cadiz on 13 November 2012 (Schmaltz, 2012). The red circle represents the study area for this study.
Figure 2. (A.) Location map of Iberian Peninsula in relation to study area. (B.) Zoomed in to track lines of POS482 echosounder data (black lines). (C.) Study area between the Tinto-Odiel Estuary and Guadalquivir River. Due to map size, Station names were reduced to their representative last two digits: Station 19513 is location 13, etc. Station location numbers that are focused on have a pink background. Figure locations of seismo-acoustic profiles are depicted.
Figure 3. Suspended sediment discharges from a freshwater plume forming a bottom layer that is driven by gravity and bottom currents. This bottom layer either deposits forming MDCs or bypasses the system off the shelf edge (Hanebuth et al., 2015).

Figure 4. Surface distribution of sediment. (A) Faro-Tavira wedge; (B) inner wedges; (C) shelf aggradational deposits (C1: undifferentiated shelf aggradational deposits, C2: shelf muddy belts, or shelf aggradational deposits with elongated patterns; C3: main MDCs of shelf muddy belts); (D) Guadalquivir wedge (Lobo et al., 2004).

Figure 6 (A). A high-resolution seismo-acoustic profile off the Guadalquivir River. (B). Interpretations of the high-resolution profile depict a TST and the repetition of progradational and aggradational deposition units during the Holocene HST (Lobo et al., 2005; modified from Fernández-Salas et al., 2003). Location of this profile is depicted on Figure 2.
Figure 7. Relative mean sea level curve since 9.0 cal ka BP from the Quarteira coast, in the Gulf of Cadiz, Portugal. Each box is error represented for one sample from lagoon and estuarine sediments. Image modified by Zazo et al. (2008) from Teixeira et al. (2005).
Figure 9. Surface circulation patterns of the southwest Iberian Peninsula. N2 and N1 are described by García-Lafuente et al., 2006 as cores of eastward flowing water. N2 is a portion of large-scale circulation current that drives the geostrophic flow around the southeastern Iberian Peninsula from the Portuguese Current, also referred to simply as the NASW (Lobo et al., 2004). N2 flows east through the Strait of Gibraltar into the Mediterranean or veers south becoming part of the Canary current. N2 is warmer and saltier than N1, suggesting N1 contains water from another body. The dashed line at the southeast indicates closure of core N1 with the Coastal Counter Current (CCC). The CCC feeds core N1 in the west, however, under favorable conditions can bypass Cape Santa Maria westward feeding the Cape San Vicente cyclonic eddy (SVE) (García-Lafuente et al., 2006).
Figure 10. Basic Geologic Map of Spain depicting the location of the Guadalquivir basin and insert (a.) depicting in detail the Iberian Pyrite Belt (IPB) composed of three lithological groups: the Phyllite-Quartzite Group, Volcano-Sedimentary Complex (VS), and the Culm Group (Spanish Geological Survey IGME 1998; (a.) Onézime et al., 2003).
Figure 11. Pb/Al ratio concentrations with overlapping human impact time periods that have caused chronological markers as early as the Bronze Age in the Alboran Sea and Zoñar Lake in Spain (Martín-Puertas et al., 2010).
Figure 12. Ln Ti/Fe ratio, comparing two proxy elements used in identifying terrigenous material from cores that include all facies (19535-3, 19538-3, and 19513-3). The $^{14}$C ages presented are those collected from the depth portrayed. See Figure 2 for coring station locations.
Figure 13. Interpretive stratigraphic core correlation represented by orange lines of ln (Ca/Fe) from the Tinto-Odiel Estuary to the Guadalquivir River (distal to shore) Cores 19538-3, 19513-3, and 19518-3. The red lines indicate calibrated $^{14}$C ages collected from the core. For location of core transect see Figure 2.
Figure 14. Ln Ti/Al ratio, comparing two proxy elements used in identifying terrigenous material from cores that include all facies (19535-3, 19538-3, and 19513-3). The $^{14}$C ages presented are those collected from the depth portrayed. See Figure 2 for coring station locations.
Figure 15. Interpretive stratigraphic core correlation represented by orange lines of ln (Ca/Fe) in cores 19534-3, 19535-3, and 19538-3 located perpendicular to shore from the Tinto – Odiel Estuary. The red lines indicate calibrated $^{14}$C ages collected from the core.
Figure 16. Combined stratigraphic correlation of element intensity ratios and magnetic susceptibility from stations perpendicular to shore from Tinto-Odiel region to Guadalquivir. Numbers above red lines on cores are radiocarbon samples dated in cal ka BP. The same interpretive correlation in Figure 15 of ln Ca/Fe is also represented here by orange lines in correlation 19534-19535-19538. The multi-color grey and white boxes indicate different facies interpretations represented within the cores (Figure 21). Core lengths are indicated by the extent of the facies boxes.
Figure 17. Combined stratigraphic correlation of element intensity ratios and magnetic susceptibility from stations parallel to shore from proximal to distal. Numbers above red lines on cores are radiocarbon samples dated in cal ka BP. The same interpretive correlation in Figure 13 of ln Ca/Fe is also represented here by orange lines in correlation 19538-19513-19518. The multi-color grey and white boxes indicate different facies interpretations represented within the cores (Figure 21). Core lengths are indicated by the extent of the facies boxes.
Figure 18. Depth – Age representation of sedimentation rates given in thousands of years (cm/ka) for transect near the Guadalquivir River (Site locations: Figure 2). Ages from $^{210}$Pb located at tops of cores are given in Common Era (CE). Ages with an asterisk (*) indicate data was extrapolated from seismio-acoustic profiles. For a complete list of sedimentation rates refer to Table 7. Note that depth profiles are not the same size due to differences in rates of sedimentation.
Figure 19. Depth – Age representation of sedimentation rates given in thousands of years (cm/ka) for transect shore-perpendicular through the central portion of the study area (Site locations: Figure 2). Ages from $^{210}$Pb located at tops of cores are given in Common Era (CE). For a complete list of sedimentation rates refer to Table 7.
Figure 20. Depth – Age visual representation of sedimentation rates given in thousands of years (cm/ka) for transect shore-perpendicular near the Tinto-Odiel Estuary (Site locations: Figure 2). Ages from $^{210}$Pb located at tops of cores are given in Common Era (CE). Ages with an asterisk (*) indicate data was extrapolated from seismio-acoustic profiles. For a complete list of sedimentation rates refer to Table 7. Note that depth profiles are not the same size due to differences in rates of sedimentation.
Figure 21. Idealized profile and lithology descriptions of the successive sedimentary facies units (A – F) synthesized from the sediment cores collected. Yellow ages are the range at which the facies boundaries are present in cores, depending on core location and accumulation rate. Ages listed next to the core image of 19538-3 were amassed through the age model created for site 19538 and fall within facies boundary age ranges. Ln Ti/Zr ratio depicts a fining upward of sediment. Ln Ca/Fe ratio shows a general increasing trend of terrigenous material up core. Sequence stratigraphic interpretation includes transgressive systems tract (TST), maximum flooding surface (mfs), and highstand systems tract (HST).
Figure 22. Ln Ti/Zr ratio used as a grain size proxy. Depth axis are not depicted by the same scale to clearly show similar grain size trends from cores that include all facies (19535-3, 19538-3, and 19513-3). The $^{14}$C ages presented are those collected from the depth portrayed. See Figure 2 for coring station locations.
Figure 23. Photos from selected cores illustrating sedimentary facies of mud accumulation of MDCs on the continental shelf in the Gulf of Cadiz, Southwestern Spain.
Figure 24. Compilation of the 98 accumulation rates from MDCs. The green background envelope includes accumulation rates from the prodelta MDC and the purple of the mud belt MDC. Three high accumulation rates from modern deposition are not shown to depict in greater detail older accumulation rates. Two rates from 4.72 to 1.95 cal ka BP and one rate from 1.95 to 0.88 cal ka BP were not used in the prodelta MDC envelope due to the higher error associated with the seismio-acoustic extrapolated ages. Low accumulation rates were persistent until 2.7 to 0.4 cal ka BP when the rates increased to about 1.4 g mm$^{-2}$ ka$^{-1}$. From 0.4 cal ka BP to present, accumulation rates increased exponentially to as high as 29 g mm$^{-2}$ ka$^{-1}$. 
Figure 25. (A.) Seismo-acoustic profile and (B.) with interpretations, depicting Holocene mud accumulation near the Tinto-Odiel estuary. The zoomed-in section shows in high-resolution the internal stratification of the mud belt MDC. Major horizons are traced and correspond to the age model collected from $^{14}$C dates. Location of this profile is depicted on Figure 2.
Figure 26. (A.) Seismo-acoustic profile and (B.) with interpretations, depicting Holocene mud accumulation of the northwestern portion of the prodelta MDC, shore-perpendicular. The zoomed-in section shows in high-resolution the internal stratification around mud entrapments. Major horizons are traced and correspond to the age model collected from $^{14}$C dates. Location of this profile is depicted on Figure 2.
Figure 27. Notable features relating to the MDCs overlain on ship track lines and station locations. The faults labeled are found only within the Holocene sediment. Faults associated with Structures are speculative. The prodelta MDC is centrally located near two acoustically masked locations. The southwestern acoustically masked area is below the Holocene sediment. There are deeper extension faults located in correlation with diapirs.
Figure 28. (A.) Seismo-acoustic profile and (B.) with interpretations, depicting Holocene mud accumulation of the southeastern portion of the prodelta MDC, shore-perpendicular. The zoomed-in section shows in high-resolution the internal stratification are traced and correspond to the age model collected from $^{14}$C dates. Horizons stop at acoustic masking locations. Location of this profile is depicted on Figure 2.
Figure 29. Mud Belt MDC (coring sites 19534, 19535, 19538) and Prodelta MDC (coring sites 19512, 19513, 19518, 19519, 19520, 19521) central depositional locations outlined by contour thickness of 6 m. Coring sites are distinguished by blue dots.
Figure 30. Isopach map of the MDCs from stratigraphic base to modern seafloor. Blue dots are coring locations for reference.
Figure 31. (Profile A) One lobe of the eastern diapiric uplift, close to the Guadalquivir River, 40 m from mean sea level. (Profile B) The cap rock of the diapir has penetrated the base of the prodelta MDC, 3 m from seafloor. Location of seismo-acoustic profiles in Figure 2.
Figure 32. Western diapir with related extension faults, located near shelf edge below the base of the prodelta MDC. Location of seismio-acoustic profile in Figure 2.
Figure 33. Isopach map from the base of the MDCs to sediment horizon dated at 2.0 ± 0.1 cal ka BP (Slice 1). Blue dots are coring locations for reference.
Figure 34. Isopach map from sediment reflector dated at 2.0 ± 0.1 cal ka BP to sediment reflector dated at 1.0 ± 0.1 cal ka BP (Slice 2). Blue dots are coring locations for reference.
Figure 35. Isopach map from sediment reflector dated at 2.0 ± 0.1 cal ka BP to modern seafloor (Slice 2.5). Blue dots are coring locations for reference.
Figure 36. Isopach map from sediment reflector dated at 1.0 ± 0.1 cal ka BP to modern seafloor (Slice 3). Blue dots are coring locations for reference.
Figure 37. Entrapping structures subsiding as a result of overbearing sediment weight causing major horizons and prodelta MDC base to dip towards the central accumulation center of the depocenter. Location of seismio-acoustic profile in Figure 2.
Figure 38. Comparison of sedimentation rate trend from the MDCs (orange line), based on sediment cores in this study, with an idealized sedimentation rate trend from estuaries (blue line), modified from Lario et al. (2002). (For accumulation rates for this study, see Figure 23).
Figure 39. Evidence of block-like subsidence occurring between the two main diapir locations affecting the prodelta MDC. Location of seismio-acoustic profile in Figure 2.
Figure 40. Acoustic masking due to the presence of gaseous sediments near the western diapir along the shelf edge. Location of seismo-acoustic profile in Figure 2.
11.0 References


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12.0 Appendix

Hazard potential of widespread but hidden historic offshore heavy metal (Pb, Zn) contamination (Gulf of Cadiz, Spain)

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HIGHLIGHTS

- Heavy metal contamination is not restricted to coastal zones but is found in the whole shelf system.
- Dispersal of heavy metals across a continental shelf happens instantaneously.
- Thin surface sediments may hide shallow-buried high heavy metal concentrations.
- Natural and human disturbances may form shelf deposits into a source of heavy metals.

GRAPHICAL ABSTRACT

ABSTRACT

Natural and human-induced scaled sediment disturbances affect wide areas of the global coastal ocean. These recurrent to chronic disturbances mobilize significant amounts of material, including substances that have the potential to significantly harm the environment once re-released. This very challenging issue is difficult to deal with if sub-surface contaminant concentrations are unknown. Based on the analysis of 11 new, up to 5 m long sediment cores taken offshore in the Gulf of Cadiz, the contamination history (using the trace elements lead and zinc) is well documented over major parts of the Gulf. The mining and metal processing industries on the southwestern Iberian Peninsula started five thousand years ago and experienced a first peak during the Roman Period, which can be detected over the entire Gulf. The Industrial Era added a massive, shelf-wide heavy metal excursion of unprecedented dimension. This metal contamination to the coastal ocean decreased in the 1990s and appears to be today limited to larger areas off the Tinto-Odiel and Guadiana River mouths. The unforeseen, significant finding of this study is that the Gulf-wide, peak heavy metal concentration stemming from the industrial era, is widely overlain by a modern sediment veneer just thick enough to cover the