ENVIRONMENTAL CONTROLS ON THE SAND-MUD TRANSITION AND APPLICATION TO HEAVY METALS DISTRIBUTION

by
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Submitted in partial fulfillment of the requirements for the degree of Master of Science

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This thesis is dedicated to my family and my Jeep. Without the love and bolstering of the first and sacrifice of the second, I wouldn’t be here to deliver this effort.
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Abstract

The sand-mud transition (SMT) is one of the major environmental boundaries on Earth. The seafloor transition separates distinct benthic habitats, causes a significant change in acoustic backscatter, represents a key facies change and delineates more surface-reactive mud from less surface-reactive sand. With the goal of improving dynamical understanding of the sand-mud transition, or mudline, several properties of surficial sediments straddling the SMT on the Apennine coast of Italy were measured: geometric mean diameter (GMD), specific surface area (SSA), mud fraction (<63 µm), heavy metals concentrations, calcium carbonate content and clay mineralogy. The SMT on the Tronto River is identified between 15 – 20 m while the SMT associated with the Pescara River varies between 15 – 25 m. Several sediment properties highly correlate with water depth (GMD, SSA, mud fraction). Depositional dynamics were examined with a sedimentological parameter, floc fraction in sediments, $f_s$, which also correlates with depth, GMD, SSA, and mud fraction. These correlations suggest that floc dynamics exert strong influence over sediment properties and that wave energy is a dominant control on the depth of the SMT. The concentration of three metals (Cu, Pb, Zn) clearly indicate sharp increases across the Apennine SMTs but do not show anthropogenic enrichment. The metals also correlate significantly with $f_s$, a finding that supports the link between flocs and the transport of contaminants.

Sand-mud transitions occur in a range of water depths around the globe. Similar behavior in $f_s$ was observed for other identified SMTs in diverse oceanic climates. A dimensional analysis based on a simple flux balance at the sand-mud transition was carried out in an effort to identify the key variables for determining the depth on an SMT. This analysis exposed significant wave height as the critical factor to determine the depth of the SMT.
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CHAPTER 1

Introduction

The sand-mud transition (SMT) is a nearshore boundary on the seafloor where the dominant sediment changes from sand (63 – 2000 μm) to silts and clays (0.24 – 63 μm), hereafter called mud. Mud, known as fine-grain sediment, possesses higher surface-area-to-volume ratios, is less sorted and is more cohesive than sand. These significant differences in sediment character make the SMT an important biological, physical, geological and chemical boundary in the sea. Through this study, ‘SMT’ and ‘mudline’ are used interchangeably. SMTs associated with rivers have been identified around the world. The Yangtze mudline has been observed at 5 m (Wright and Nittrouer, 1995) while the Mississippi SMT was described at 20 m by Stanley et al., (1983). Other SMTs include the Ebro at 30 m (Palanques and Drake, 1990), the Eel at 55 m (Wheatcroft and Borgeld, 2000) and the Kunene at 60 m (Brenmer and Willis, 1993). Besides these
episodic explorations of the mudline, surprisingly little research has been dedicated to understanding the dynamic controls of this unique boundary.

Biologically, mudlines represent a change in benthic habitat structure. Traditionally, benthic communities were generalized into deposit- or suspension-feeding depending on the sediment size (i.e., mud or sand). Recently, to better describe the animal-sediment relationship, Snelgrove and Butman (1994) suggested incorporating hydrodynamics and sediment transport processes into habitat classification. This idea arises from observations of varied communities in different bottom sediments. Particle flux was invoked to help explain species distribution, emphasizing that grain size affects flux. Other research has focused on the level of productivity in sand and mud environments. Oxygen demand was found to be 2.7 times higher and carbon consumption ~1.5 times higher in fine sediments than in coarser ones on the Scotian Shelf, Canada (Grant et al., 1991). These differences demonstrate that grain size and productivity are linked, which implies that the SMT is a significant boundary in habitat structure.

The effects of grain size on acoustic returns are well documented. Urick (1983) compiled research that showed mud causes 2 – 4 times more decibel loss than sand. Differences between fine and coarse sand were also identifiable. This knowledge is frequently exploited during acoustic surveys. For example, in a study in the northeastern Gulf of Mexico, larger amplitude sound returns were attributed to coarse-grained sand and less reflection was ascribed to fine-grained sand (Davis et al., 1996). Therefore, abrupt shifts during an acoustic survey can correlate to changes in bottom sediment.
Understanding where and why these shifts occur would benefit military search and recovery operations, hydrocarbon explorations and marine archaeology expeditions.

The SMT is also a major sediment facies change. Approximately 75% of the Earth’s exposed rocks are sedimentary and three sub-categories dominate: mudstone, sandstone and limestone. Press and Siever (1994) note that mudstone accounts for ~75% of the sedimentary category while sandstone accounts for ~11% and limestone for ~14%. Recent Earth history is recorded in rocks formed from mud, and this history can be interpreted more fully by developing better understanding of the depositional dynamics of mud. Key to this broader understanding is specific understanding of the environmental controls on facies transitions, such as the SMT.

Finally, the SMT marks a shift in heavy metal accumulation. Heavy metals, which are potentially toxic, show an affinity for mud particles, and where fine-grained sediments deposit, these bound metals accumulate. Evidence of this process can be found in a wide variety of marine systems: the Southern California Bight (Schiff, 2000), eastern Canada (Milligan and Loring, 1997), the northwest Mediterranean (Puig et al., 1999) and the Adriatic Sea (Giani et al., 1994; Boldrin et al., 1989).

Stanley et al., (1983), using the term mudline, suggested that the SMT is an energy level marker with higher energy areas corresponding to coarser benthic sediments. In the nearshore, McCave (1972) proposed that the mudline occurs where the deposition of suspended sediment exceeds erosional removal by waves and tides. These simple conceptual models are sound, yet it has been difficult to formalize them into explicit predictive tools because of the complex depositional dynamics of mud. Mud particles tend to form clumps of many particles called “flocs” that sink many times faster than the
component grains (e.g., Sternberg et al., 1999). Therefore, the dynamics that lead to the formation of an SMT likely are linked to the dynamics of flocs.

The goal of this project is to investigate dynamic controls on the SMT and on heavy metal loading in the vicinity of the SMT. Two hypotheses are to be investigated. Hypothesis A is the SMT reflects a boundary in the net depositional flux of flocs. Hypothesis B states flocs are the primary transport mechanism for heavy metals. The first step to analyze these hypotheses involves linking seabed grain size distributions to the inferred extent of flocculation in surficial sediment at the time of deposition. The second step is to correlate seabed grain size distributions with concentration of selected metals. The third step is to relate, by inference, accumulation of metals to accumulation of flocs. The final step is to assess the causes of global variability in the water depths of mudlines and link these causes to the environmental controls on accumulation of flocculated sediment.
CHAPTER 2

Background

2.1 – Fine-grain Sediment Transport
The SMT is produced by a change in accumulation rate of fine-grained sediments (McCave, 1972). Particle settling is the primary mechanism for sediment flux to the seabed with flux as the product of settling velocity and sediment concentration. Stokes Law of settling typically applies to unflocculated particles of mud (e.g., Dietrich, 1982) and therefore, settling velocities of single particles scale with the square of particle diameter. As a result, single clay-sized particles (0.2 – 4 µm) fall at extremely slow rates. For example, a 40-µm diameter silt grain falls at 1 mm s⁻¹ while a 4-µm clay particle settles at only 0.01 mm s⁻¹, 100 times slower. In one day, this clay particle would fall only about 1 m and hence, single grain settling cannot produce a significant depositional flux of muds in most environments (Kranck, 1980a). Particle aggregation has therefore been invoked to explain observed accumulation rates of mud.
The extent of flocculation in a suspension is dependent on many factors. The principal ones are particle concentration, turbulence and material composition. A simplified set of equations for partitioning between single grains and flocs is (Curran et al., 2002):

\[
\frac{dN_s(i)}{dt} = -k_a(i)N_s(i)M_f + k_oN_f(i) - \frac{w_s(i)}{h} N_s(i) \tag{2.1.1}
\]

\[
\frac{dN_f(i)}{dt} = k_a(i)N_s(i)M_f - k_bN_f(i) - \frac{w_f}{h} N_f(i) \tag{2.1.2}
\]

where \(N_s(i)\) is the number concentration of single grains in size class \(i\) (m\(^{-3}\)), \(N_f(i)\) is the number concentration of size \(i\) particles within flocs (m\(^{-3}\)), \(k_a(i)\) is the aggregation rate coefficient between flocs and particles in size class \(i\) (m\(^3\) s\(^{-1}\)), \(\mu_f\) is the number concentration of flocs (m\(^{-3}\)), \(k_b\) is the breakup rate for flocs (s\(^{-1}\)), \(w_s(i)\) is the settling velocity for single grains of size class \(i\) (m s\(^{-1}\)), \(w_f\) is the floc settling velocity (m s\(^{-1}\)), and \(h\) is the flow depth (m). A box model illustrates this simple characterization of floc dynamics (Figure 2.1). Aggregation (the first term on the right hand sides of (2.1.1) and (2.1.2)) is a second-order process, meaning that the aggregation rate, \(k_a(i)N_s(i)M_f\), increases approximately as the square of concentration. For example, if energy is held constant and sediment concentration is doubled, the production rate of flocs quadruples. Conversely, floc disaggregation (the second term in (2.1.1) and (2.1.2)) is a first-order process where the breakup rate, \(k_bN_f(i)\), scales linearly with concentration. So, if energy is constant and concentration doubles, floc breakup is only twice as fast. The final term in (2.1.1) and (2.1.2) removes sediment from the water column to the seafloor by sinking.
Figure 2.1: Box model of floc dynamics. $N_s(i)$ is the number concentration of single grains at size class $i$ (m$^{-3}$), $N_f(i)$ is the number concentration of size class $i$ within flocs (m$^{-3}$), $k_a(i)$ is the aggregation rate coefficient between flocs and particles in size class $i$ (m$^3$ s$^{-1}$), $N_f$ is the number concentration of flocs (m$^{-3}$), $k_b$ is the breakup rate for flocs (s$^{-1}$), $w_s(i)$ is the settling velocity for single grains of size class $i$ (m s$^{-1}$), $w_f$ is the floc settling velocity (m s$^{-1}$), and $h$ is the flow depth (m). Aggregation, the production of flocs, is a second order rate process, so the aggregation rate, $k_a(i)N_s(i)N_f$, increases approximately as the square of concentration. Disaggregation is a first-order process where the breakup rate, $k_bN_f$, scales linearly with concentration.
The first two terms in (2.1.1) and (2.1.2) interact to produce a distribution of mass between flocs and single grains. An indicator of the interaction is floc fraction, $f$, which is defined as the proportion of sediment mass in the water column bound as flocs. Floc fraction, according to (2.1.1) and (2.1.2), depends on concentration and energy. An increase in concentration leads to aggregation rates increasing more than disaggregation rates, resulting in a higher floc fraction. Turbulent kinetic energy dissipation rate ($\varepsilon$) may have a negative correlation to floc fraction, although the form of the relationship remains unclear (Hill et al., 2001). Presumably, as $\varepsilon$ increases, floc breakup increases (Hunt, 1986) and consequently, floc fraction drops. This hypothesized role of turbulence is supported by observations of small flocs in high-energy conditions (Kranck and Milligan, 1991) and laboratory experiments showing that floc size decreases as $\varepsilon$ increases (Hunt, 1986). Hill et al., (2001) question the link between floc breakup and $\varepsilon$ at low energy but show dramatic floc size reductions when bottom stresses exceed 0.1 Pa.

Although concentration and energy are suspected to be the dominant controls on floc fraction, quantification of their influence is minimal (Dyer and Manning, 1999). As a result, a firm understanding of in situ controls on floc fraction is lacking. This is unfortunate as floc fraction is vital to determining the downward flux of sediment to the seabed. Kranck (1973), while investigating water column floc fraction, found that the component grain sizes in suspended flocs show a poorly sorted size distribution characteristic of seafloor muds. High floc fraction in the water should correspond to increases in mud accumulation because flocs are the main vertical transport vehicles for mud (Kranck, 1973). Consequently, the SMT likely marks a boundary in the net depositional flux of flocs. One way to quantify the importance of flocculation to
accumulation of seabed sediments is with a recently redefined parameter based on the findings of Kranck (1973) that here will be called “floc fraction in the sediments” and assigned the symbol \( f_s \).

The parameter \( f_s \) is determined by applying an inverse model based on equations 2.1.1 and 2.1.2 to the Disaggregated Inorganic Grain Size (DIGS) distribution of a seabed sediment sample. Details of the method are provided in Chapter 3. In general, however, the inverse model compares the shapes of the coarser and finer portions of the distribution to extract an estimate of floc fraction. A DIGS distribution with a well-defined coarse mode (or modes) and a fine tail has a low floc fraction, whereas poorly sorted sediment with no distinct mode has a large floc fraction (Figure 2.2). This methodology is useful for describing surficial sediments in terms relevant to the depositional dynamics of the sediment. For this reason, it was selected as a primary descriptor of sediments on the Apennine margin.

2.2 – Metals Transport
A vast amount of research has been conducted on the movement of elements and contaminants through the water column and to the benthos (Fowler and Knauer, 1986; Ongley et al., 1992; Droppo et al., 2002). The affinity metals exhibit for fine-grained sediments is well documented and has been used to account for transport in various environments (Zhang et al., 1992) and laboratory experiments (Brassard et al., 1994). Lead was shown to arrive on North Atlantic sediments as part of large biogenic particles (Lambert et al., 1991). Puig et al., (1999) show a strong connection between decreasing sediment size and higher concentrations of Cr, Cu, Ni and Zn off the Barcelona, Spain, continental margin.
Figure 2.2: Comparison of $f_s$ from a sandy (a) and muddy (b) seafloor. Data in (a) is from station 15011 and in (b) from station 34 in this thesis (station details provided in Chapter 3). The Disaggregated Inorganic Grain Size (DIGS) distribution was produced with a Coulter Multisizer Ile (see Chapter 3 for details) and is plotted as relative volume versus diameter ($\mu$m). The portion of the total sample deposited as single grains is plotted with open squares (□) and the portion deposited as flocs is plotted with open circles (○). The area found under the floc curve divided by the area under the total curve is $f_s$. The bimodal distribution and small $f_s$ in (a) indicate a coarse-grained sample where higher energy results in transport as bedload and suspended load. The unimodal distribution with a significant fine tail and large $f_s$ in (b) indicates a highly flocculated, muddy sample.
The fundamental process behind these observations is the binding of negatively charged mud particles with positively charged metals, or cations. Some suggested sediment properties for control of cation adsorption are mineralogical and chemical composition, specific surface area and amount of organic material (Horowitz and Elrick, 1988). Most adsorption occurs in estuaries as salinity and alkalinity increase (Libes, 1992) and the products are transported offshore as metal-mud colloids. As the colloids encounter conditions conducive to flocculation, the metal-mud complexes can become part of larger flocs. Zwolsman et al., (1997) used this process to account for removal of Cd, Cu and Zn in the Scheldt estuary, Netherlands. Similar processes were invoked for the Po River (Pettine et al., 1994) and the northern Adriatic Sea (Giani et al., 1994).

The potential for accumulation of contaminants via floc deposition is significant, yet direct links between floc deposition and contaminant concentration are rare (Milligan and Loring, 1997). By comparing estimated floc fractions with measured concentrations of several metals, this thesis will examine the association between flocs and metals.
CHAPTER 3

Study Area and Methods

3.1 – Study Site
The nearshore region of Abruzzi-Marches in eastern Italy was chosen for this research (Figure 3.1). This area of the western Adriatic Sea experiences tides of ~0.5 m and a dominant southerly current (Passega et al., 1967). Significant wave height occurrence frequencies, calculated from three years (1999 –2002) of data at the Ortona buoy (42.4011° N, 14.5339° E, http://www.envirtech.org/ron.asp, Italian Sea WAve Network), are 53.2% less than 0.5 m, 27.9% between 0.5 and 1.0 m, 10.4% between 1.0 and 1.5 m and 8.5% greater than 1.5 m.

The geology of the region is dominated by the actively uplifting Apennine Mountains. The range falls steeply to the Adriatic Sea and is drained by dozens of small fast-flowing rivers. Rainfall varies greatly from the wet high elevations, which can receive more than 1500 mm yr\(^{-1}\), to the drier coastal zone (<1000 mm yr\(^{-1}\)). Surficial
Figure 3.1: Study site and sampling transects. Grab samples (●) were collected from the M/n Erimone and box corer samples (■) were acquired on the R/V Urania. A total of 101 samples were gathered from the five Tronto (Tc1 – Tc5) and 16 Pescara (Pc1 – Pc16) transects in April and May 2002.
Seabed sediments were characterised near the mouth of two rivers: the Pescara and the Tronto. Milliman and Syvitski (1992) reported that these discharge similar amounts of suspended sediment to the sea (0.9 and \(1.1 \times 10^6\) t yr\(^{-1}\), respectively). The Pescara watershed consists of Mesozoic carbonate sequences, Upper Miocene sandstone turbidites and Quaternary clay and calcareous deposits. The Tronto watershed is mainly carbonate sequences and calcareous deposits (Farroni et al., 2002). Both have been dammed extensively for hydroelectric power generation and flood control, affecting the volume and size distribution of sediment carried by the rivers. Farroni et al., (2002) identify seven hydraulic structures on the Pescara River that cumulatively have a significant trapping effect. In addition, sand and clay deposits are removed from the rivers for industrial and commercial use. Data from Aquater (1982) indicate that sediment loads in the region’s rivers have dropped 30 – 70% since 1965 due to human activities. Patterns of offshore sediment dispersion have also been changed by human endeavours, especially from breakwaters, jetties and sea walls. Although heavy industry along the rivers is limited, the human impact from the ~3 million people (Italian Census, 1998) living in the two states is evident both on land and at sea.

### 3.2 – Sample Collection and Pre-treatment

In April and May 2002, surficial sediment was collected from the Italian ships \textit{R/V Urania} and \textit{M/n Ermione} at 101 stations: 75 centred on the Pescara River and 26 on the Tronto River. The sampling strategy relied on bathymetry, namely the 6-, 10-, 15-, 20- and 25-m isobaths, although five stations were noted to be greater than \(\pm 2.5\) m from the intended depth. In addition, thirteen samples were collected from depths greater than 25 m on nine of the 21 transects. Sixteen shore normal cross-shelf transects for the Pescara
River and five cross-shelf transects for the Tronto River were completed. The fraction of samples at identical depths (6, 10, 15 and 20 m) is the same for both shelves. For example, the five 6-m stations on the Tronto represent ¼ of the 20 samples from 20 m and shallower; on the Pescara, the 16 6-m stations also represent ¼ of the 64 samples from the same depth range. Spacing between the Pescara stations was ~1000 m, creating a high-resolution grid of surficial sediment samples similar to one assembled by Passega et al., (1967). Stations at the Tronto were generally farther apart (~1.5 – 2 km). A clamshell grab was deployed in water depths of 6 – 25 m and an Ocean Instruments box corer was used for depths of 30 m and deeper. Several hundred grams of sediment were sub-sampled with plastic spoons from the top centimetres of the sample. The bagged sub-samples were kept in freezer storage at the Bedford Institute of Oceanography (BIO) in Dartmouth, Nova Scotia, Canada. Preparation for analyses consisted of room temperature thawing and oven drying at 50°C. The dry sediment was then homogenized with a mortar and pestle before storage in plastic vials. Grain size, clay mineralogy and carbonate content analyses were conducted at BIO; specific surface area was analyzed at the Darling Marine Center, University of Maine, Walpole, Maine, United States. Samples for metals analysis were sent to ALS Chemex laboratories in Mississauga, Ontario, Canada and in North Vancouver, British Columbia, Canada.

3.3 – Grain Size
Disaggregated inorganic grain size (DIGS) distributions of the prepared sediment were determined using a Coulter Multisizer IIe electro resistance particle size analyzer (Milligan and Kranck, 1991). Results were plotted as $\log_{10}$ concentration of component grains against $\log_{10}$ particle diameters. The instrument determines the relative number
and size of grains suspended in an electrolyte by measuring voltage changes in an electric current across a known aperture. The instrument measures particles 2 – 50 % of the aperture size. The distributions were processed with a customized software package that removed the background noise from the electrolyte before plotting the results.

Less than 0.05 g of dry, homogenized sediment from each sample was treated with 5 – 10 ml of 35% H₂O₂ to remove organic material. The sample was then placed in a 1% NaCl electrolyte solution and dispersed with a sapphire-tipped ultrasonic probe. A sub-sample was removed from this initial stock and sized using a 200-µm-aperture tube, counting particles 4 – 100 µm in diameter. Dilution was necessary for some samples to prevent particle coincidence in the aperture. The remaining suspension was re-sonified and filtered with a 25-µm-mesh screen to remove particles that would block a 30-µm aperture tube. The filtered suspension was counted and sized using this smaller tube, measuring particles 0.6 – 15 µm.

The initial stock solution was then prepared for either a 400- or 1000-µm aperture tube. If the sample was observed to be mud-dominated, the 400-µm tube (sizing particles 8 – 200 µm) was used. However, the presence of large silt or sand particles required the 1000-µm tube to measure grains 20 – 500 µm in diameter. For the 400-µm tube samples, the stock was passed through a 16-µm-mesh screen to reduce coincidence caused by small particles. The sediment trapped on the screen was resuspended in 1% NaCl electrolyte and sonified before processing on the Multisizer. Coarse samples requiring the 1000-µm tube were screened using a 25-µm-mesh as above, and the trapped sediment was resuspended in a 35% glycerine solution (glycerine, water and 3.3% NaCl, Milligan and Kranck, 1991). The glycerine solution increases the viscosity of the electrolyte so
that large particles remain in suspension. Samples processed with one tube were not processed on the other. The counts from the 200-, 30- and 400- or 1000-µm tubes were combined with a customized computer program that allows removal of overlapping sections of the three distributions. The result is a complete DIGS distribution for each sample.

### 3.3.1 – DIGS parameterization

Initial size distributions of natural sediments that have undergone no sorting by transport can usually be described with the equation (Kranck et al., 1996)

\[
C(i; 0) = Q \left( \frac{d_i}{d_0} \right)^m
\]  

(3.3.1)

where \( C(i; 0) \) is the concentration of size class \( i \) at time 0 (i.e., before any sorting has taken place) (kg m\(^{-3}\)), \( Q \) is the concentration of a reference size class (kg m\(^{-3}\)), \( d_0 \) is the reference diameter (m), \( d_i \) is the size class of interest (m), and \( m \) is an exponent describing the “source slope” of this parent distribution on a log-log plot of mass concentration versus diameter. Decay from sedimentation in a well-mixed suspension is a first-order loss process described by the equation

\[
\frac{dC(i)}{dt} = -\frac{w_s(i)}{h} C(i)
\]  

(3.3.2)

where \( h \) is the suspension thickness (m), and \( w_s(i) \) is the Stokes settling velocity of particles in size class \( i \) (m s\(^{-1}\)). Integrating (3.3.2) yields

\[
C(i; t) = C(i; 0)e^{-\left(\frac{w_s(i)}{h}\right)t}.
\]  

(3.3.3)
Let $d$ be the grain size diameter whose concentration has fallen to $e^{-1}$ of its value in the initial distribution

$$\frac{C(d_\infty)}{C(d;0)} = e^{-1}. \quad (3.3.4)$$

Inserting (3.3.4) into (3.3.3) leads to the expression

$$w_i(d) = \frac{h}{t} \quad (3.3.5)$$

Noting that

$$\frac{w_i(i)}{w_i(d)} = \left( \frac{d_i}{d} \right)^2 \quad (3.3.6)$$

leads to an expression for concentration in suspension of the form

$$C(i) = C(i;0) e^{-\left( \frac{d_i}{d} \right)^2}. \quad (3.3.7)$$

Substituting (3.3.1) into (3.3.7) produces a working concentration expression that describes many fine sediment suspensions (Kranck and Milligan, 1991; Curran et al., 2003):

$$C(i) = Q \left( \frac{d_i}{d_o} \right)^m e^{-\left( \frac{d_i}{d} \right)^2}. \quad (3.3.8)$$

The floc fraction in the seabed can be back-calculated by performing disaggregated inorganic grain size (DIGS) analysis on bottom sediments. The distribution of individual size classes represents the flux of the classes from the water column. Under the assumption that particles exist either as single grains or within flocs of a single size and settling velocity, the total concentration of particles can be divided into a floc pool and a single grain pool as

$$C_f(i) = f(i)C_i \quad (3.3.9)$$
\[ C_i(i) = (1 - f(i))C_i. \] (3.3.10)

Although formally \( f \) is a function of \( i \), it is assumed here to remain constant with changing \( i \). This assumption follows from aggregation theory (McCave, 1984) that shows that the aggregation rate between typical flocs and suspended mud particles is insensitive to the size of the mud grains. Fluxes as flocs and single grains follow as

\[ J_f(i) = w_f C_i(i) \] (3.3.11)

\[ J_s(i) = w_s(i) C_i(i). \] (3.3.12)

Substituting (3.3.9) into (3.3.11) and (3.3.10) into (3.3.12) and summing them gives the total flux of size class \( i \) as

\[ J(i) = w_f (fC_i(i)) + w_s(i)[(1 - f)C_i(i)]. \] (3.3.13)

Replacing \( C_i \) with (3.3.8) yields total flux as

\[ J(i) = \left\{ w_f f + w_s(1 - f) \right\} Q \left( \frac{d_i}{d_o} \right)^m e^{- \left( \frac{d_i}{d_o} \right)^{\gamma}}. \] (3.3.14)

Within the sediment distribution, there exists a particle size class for which floc flux and single grain flux are equal. The nominal diameter of this size class is called the “floc limit,” \( (d_f) \), where grain sizes larger than \( d_f \) predominately fall as single grains and those smaller settle mostly within flocs. The flux of particles of size \( d_f \) can be written as (3.3.13)

\[ J(d_f) = w_f (C(d_f)) f + w_s(d_f)(C(d_f)(1 - f)) \] (3.3.15)

Because, by definition,

\[ w_f (C(d_f)) f = w_s(d_f)(C(d_f)(1 - f)) , \] (3.3.16)

\[ \frac{w_s(d_f)}{w_f} = \frac{f}{1 - f}. \] (3.3.17)
Rewriting Stokes Law with \( w_s(d_f) \) as before gives

\[
\frac{w_s(d_f)}{w_s(i)} = \left( \frac{d_f}{d_i} \right)^2
\]  
(3.3.18)

or

\[
w_s(d_f) = w_s(i) \left( \frac{d_f}{d_i} \right)^2.
\]  
(3.3.19)

Substitution of (3.3.19) into (3.3.17) yields

\[
w_s(i) = w_f \left( \frac{d_i}{d_f} \right)^2 \left( \frac{f}{1-f} \right)
\]  
(3.3.20)

which, when inserted into a rearranged (3.3.14), gives a flux equation that incorporates \( d_f, d_i, \) and \( d_0 \)

\[
J(i) = w_f f Q \left( \frac{d_i}{d_o} \right)^m e^{-\frac{d_i}{m}} \left( 1 + \left( \frac{d_i}{d_f} \right)^2 \right).
\]  
(3.3.21)

Assigning \( B=w_f Q \), which is the floc flux of the reference diameter, (3.3.20) becomes

\[
J(i) = B \left( \frac{d_i}{d_o} \right)^m e^{-\frac{d_i}{m}} \left( 1 + \left( \frac{d_i}{d_f} \right)^2 \right).
\]  
(3.3.22)

Nonlinear regression can be used to estimate \( B, d_i, d_f \) and \( m \). To estimate the floc fraction in the sediment, the total floc flux \( (J_f) \) across all size classes \((n\text{class})\) is summed and then divided by the total flux:

\[
f_i = \frac{\sum_{i=1}^{n\text{class}} w_f C(i)}{\sum_{i=1}^{n\text{class}} w_s(i)(1-f)C(i) + w_f C(i)}.
\]  
(3.3.23)
By substituting (3.3.20), (3.3.23) simplifies to

\[ f_i = \frac{\sum_{i=1}^{nclass} C(i)}{\sum_{i=1}^{nclass} \left(1 + \left(\frac{d_i}{d_f}\right)^2\right) C(i)}. \]  

(3.3.24)

The parameter \( f_i \) is dimensionless and ranges from 0 – 1 with larger values corresponding to higher percentages of floc deposited sediment.

### 3.4 – Clay Mineralogy

Preparation of the samples followed methods outlined by Moore and Reynolds (1997).

Test X-ray diffractometry (XRD) runs indicated that three steps were required to characterise the clay mineralogy in the < 2\( \mu \)m fraction: carbonate removal, organic removal and clay separation. Carbonate removal is necessary both to reduce calcium ion activity, which can prevent full dispersion of clay particles, and to prevent calcite from masking the signal from less abundant minerals. Organic material was removed because biogenic matter can also prevent dispersion, broaden X-ray peaks and generate random variability in the data.

The majority of larger particles were assumed to be quartz (Abuodha, 2003), so clay separation was required to isolate and identify clay mineralogy. Only samples from 15 m and deeper were analyzed for mineralogy, with one exception. The exclusion of shallower stations is due to the absence of a significant clay fraction, although one 10 m station, near the mouth of the Tronto River, was muddy and therefore included in the analysis.

Carbonate removal was performed first by treating 0.5 g of dry, homogenized sediment with 2 – 3 ml of 0.3 M acetic acid in glass beakers. By using a low
concentration of a weak acid, damage to the mixed-layer clays was avoided (Moore and Reynolds, 1997). The beakers were placed on a hot plate set on low heat to encourage complete dissolution. After the sediment was dry, organic material was removed by addition of 5 ml of 35% H₂O₂ and exposure to low heat. The treated sediment was washed into 50-ml heavy-duty Nalgene centrifuge tubes with reagent grade water. The tubes were spun at 2000 rpm for 10 min in an International Equipment Company Centra-8 centrifuge. If the supernatant was clear, flocculation had occurred from salts, and the water was decanted. The rinse was repeated until the supernatant was cloudy, indicating that the sample was free of flocculation promoting salts and ready for extraction of the clay fraction. The sample was dispersed with 1 – 2 mg of purified sodium metaphosphate and allowed to stand for several minutes. To expedite the separation process, the sample was centrifuged at 700 rpm for 4 min, according to a table in the Moore and Reynolds (1997) protocol. The supernatant was assumed to contain only <2 µm particles and was collected for further analysis (for some coarse samples, dispersion with water and centrifugation was repeated to extract as much clay as possible). The supernatant was centrifuged to concentrate the clays in a Beckman J2-21 ultra-centrifuge at 15,000 rpm for 20 min; the new supernatant was discarded carefully so as to not resuspend and lose clay particles. The clay paste was then homogenized by mortar and pestle in ACS-grade methanol. A Pasteur pipette was used to deposit the slurry onto a 2-cm square glass slide, which when uniformly covered, was dried at 50°C.

The sample was loaded into a Siemens Diffraktometer and exposed to X-rays at angles of incidence (measured from the horizontal) from 2 – 52° in 0.02° steps. This range of angles encompasses all known diffraction patterns for clay minerals. The
mineral composition was identified with the DiffracPlus computer program, which matches the sample diffraction pattern with documented diffraction patterns. Percentages of the identified minerals were quantified with ProfPlus, a profiling program that calculates the area beneath a selected peak on the mineral distribution. For those minerals identifiable by several peaks, a sum of the areas was used as the value for percentage calculations.

3.5 – Carbonate Content

The percentage of CaCO₃ in all samples was determined by direct exposure of the sediment to HCl in accordance to Loring and Rantala (1992). Approximately 1 g of dry, homogenized sediment was placed in a 250-ml conical glass flask. A 6-ml glass cuvette with 4 M (33%) HCl was placed upright in the flask and a rubber stopper with a desiccating plastic tube of CaCl₂ inserted through the centre was placed on the flask. The assembly was weighed in grams to the fourth decimal place for high precision. A second tube containing CaCl₂ was attached by Tygon plastic tubing to the exposed end of the first tube to prevent moisture from entering the main chamber. The flask was tilted until the cuvette emptied the acid onto the sediment and was allowed to stand for two hours to ensure complete acid exposure. The top tube was removed and the assembly reweighed to calculate the change in weight. Samples were run as duplicates. An identical procedure was performed with 100 mg of CaCO₃ instead of sediment for use as a standard. A standard was run at the same time as 19 sediment samples (38 flasks). The percent CaCO₃ was calculated as

\[
CaCO₃ \, (\%) = \frac{\Delta P}{\Delta S} \times 0.100 \times 100 \quad (3.5.1)
\]
where $\Delta P$ is the change in the sample weight, $\Delta S$ is the change in the standard weight and $R$ is the dry weight of the sample. A mean was calculated as a final value of CaCO$_3$% for the samples.

### 3.6 – Specific Surface Area

Specific surface area of the sediment was quantified using the single-point BET (Brunauer-Emmett-Teller) method where an SSA value on an adsorption isotherm is determined (Mayer, 1994). A Quantachrome Corporation Monosorb Surface Area Analyzer was used for this analysis. When using this instrument, sediment is exposed to a stream of nitrogen gas (30 mole percent nitrogen in helium) and adsorption of the gas onto the sediment surface is forced by oversaturation. The instrument detector compares the gas passing through the sample cell to that passing through a reference cell. A cold trap (an empty cell) cools the gas and this cooled gas flows into a cell containing sediment where gas condensation occurs. Cooling is accomplished by submergence of specially designed Pyrex glass U-tubes for the Monosorb instrument in dewars of liquid nitrogen. Desorption is induced by replacing the dewar of liquid nitrogen with a beaker of room temperature water that spikes the temperature of the sediment. The desorption process occurs rapidly, as all of the nitrogen is vaporized within minutes compared to the slower process of condensation during adsorption. As a result, the amount of desorbed gas is counted and recorded for calculation of surface area instead of the adsorbed value. During adsorption, the conductivity signal from the sample cell is lower than the reference cell so the polarity on the detector is adjusted to receive a positive value. Conversely, during desorption, the sample cell has a higher conductivity than the reference cell and the polarity is reversed to maintain a positive signal. Essentially, the
polarity determines if the instrument is recording adsorption or desorption. An attenuation value related to the gas counts is also needed for the calculation.

Specific surface area was determined for all samples. Approximately 1.5 g of dry, homogenized sediment was dispersed in 30 ml of distilled water and spun at 15,000 rpm for 20 min on a Sorvall centrifuge with a SS-34 rotor. The supernatant was decanted and the sediment redispersed with 10% ACS-grade acetone to remove water. After a second centrifuge spin, the supernatant was discarded and the sample frozen overnight. Once frozen, the sample was freeze dried to remove residual water. A muffle furnace set at 350°C was used to combust organic compounds in the freeze-dried sediment. Sample preparation was complete at this point. The only contaminating factor remaining was water acquired from ambient air, so to ensure a dry sample, the sediment was stored in a vacuum oven set at 150°C for at least 12 hours. The U-tubes were placed in a dessicator for cooling.

The instrument was calibrated by injection of 1 cc of room air to establish an ambient baseline. A U-tube with sediment sample was placed in the second position on the gas route. Room air was allowed to purge from the tube before re-zeroing the counter and submersion in the liquid nitrogen dewar. When the counter was no longer changing, adsorption was complete. The counter was then re-zeroed, the polarity switched and desorption induced with the beaker of water. Runs were performed on each sample until two consecutive desorption counts were within 1% of each other, and the mean was calculated. The sample U-tube was immediately weighed after the final run for the dry weight of the sediment. The SSA calculation is

\[
SSA \ (m^2 \ g^{-1}) = \frac{\bar{C} \times A}{m}\quad (3.6.1)
\]
where $\overline{C}$ is the average count, $A$ is the attenuation setting and $m$ is the mass of the dry sediment.

**3.7 – Heavy Metals**

Assuming metal concentrations were negligible in sand-dominated samples (Tim Milligan, pers. comm.), only fine-grained samples were analyzed for heavy metals. Approximately 10 – 15 g of dried, homogenized sediment was sub-sampled with plastic spoons and separated using an ASTM E-11 No. 80 (180 µm) sieve. The fraction of sediment caught on the sieve was discarded, and the portion that passed through was placed in plastic vials to be sent to ALS Chemex laboratories. The 180-µm sieve was selected to conform to the company’s protocol. The sieved samples were digested with a HF-HNO$_3$-HClO$_4$ acid mixture followed by an HCl leach, releasing both labile and refractory metals. Forty-seven elements were identified by a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Mercury was quantified by Atomic Absorption Spectrometry (AAS).
CHAPTER 4

The Apennine Margin Sand-Mud Transition

4.1 – Sediment Character and Deposition

Several different parameters can be estimated from the disaggregated inorganic grain size (DIGS) distribution of a sediment sample. In this study, geometric mean diameter (GMD), floc fraction in the sediment ($f_s$) and the sand, silt and clay fractions are calculated at each station. GMD is calculated as

$$GMD \, (\mu m) = 2 \times 1000 \times \left[ - \sum_{i=1}^{n_{class}} \Phi(i) C(i) \right]$$

where $\Phi(i) = \frac{-\log d_{med}(i)}{\log 2}$ with $d_{med}(i)$ as the nominal diameter of Coulter class $i$, which is taken as the equivalent spherical diameter of midpoint of size bin $i$, and $C(i)$ is the concentration in class $i$. Floc fraction in the sediment is a process-based parameterization that describes how sediments were deposited rather than what sizes are present (3.3.12;
Kranck and Milligan, 1985; Curran et al., 2003). Because \( f_s \) characterises how the sediment was deposited (as flocs or as single grains), this variable is a more direct measure of the sediment transport dynamics in a region than GMD. This dynamical characterisation of seabed deposits should be useful in building insight into the mechanisms of formation of SMTs. The three size class fractions (sand, silt, clay) are calculated by summing the concentrations across all size classes, summing the concentrations across the range of each fraction and then dividing the fractional concentration by the total or

\[
sand (\%) = \frac{\sum_{d=0.75}^{256} C(d)}{\sum_{d=0.75}^{256} C(d)} \times 100
\]

\[
silt (\%) = \frac{\sum_{d=4}^{64} C(d)}{\sum_{d=0.75}^{256} C(d)} \times 100
\]

\[
clay (\%) = \frac{\sum_{d=0.75}^{4} C(d)}{\sum_{d=0.75}^{256} C(d)} \times 100
\]

where \( C(d) \) is the concentration of particles at diameter \( d \). The mud fraction is the sum of the silt and clay fractions. Size fractions provide an overview of the study area based on bulk sediment properties and allow an SMT to be defined by the percentage of sand or mud on the seafloor.

On the Apennine Margin, GMD ranges and means for 20 m and shallower on the Tronto and Pescara river shelves can be compared based on the identical representative
fractions of each depth category. The Tronto values (13 – 115 µm, \( \text{GMD} = 56.43 \pm 28.15 \) µm, at one standard deviation) indicate a siltier seafloor than the Pescara (14 – 149 µm, \( \text{GMD} = 73.11 \pm 26.32 \) µm). The largest cross-shelf decreases in GMD occur between 15 and 20 m for the Tronto and between 15 and 25 for the Pescara (Figure 4.1). The 10-m station on transects Pc2 and Pc16 (see Figure 3.1 for transect lines) show anomalously low values of GMD when compared to surrounding stations. Pc2 is directly offshore of the Saline River while Pc16 is in the vicinity of actively eroding cliffs and possibly a submerged sewage outlet from the town of Ortona. The GMD distribution shows a strong negative correlation with depth (\( R_z = -0.75; \alpha=0.95, p<0.001 \)), indicating that shallower depths have larger GMD, which correspond to beach sands. The sediment size decreases as depth and distance from the shore increase, with the smallest GMDs found at the deepest stations.

Floc deposition on the shelves is nearly identical for the 20 m and shallower stations with the Tronto region (0.02 – 0.34; \( \bar{f}_s = 0.12 \pm 0.11 \)) slightly more than the Pescara (0.01 – 0.32; \( \bar{f}_s = 0.09 \pm 0.08 \)). The correlation with depth is significant (\( R_z = 0.76; p<0.001 \)), which shows that increasing depth is associated with larger \( f_s \) (Figure 4.2). Both river systems show a noticeable increase in \( f_s \) at 20 m where 0.16 – 0.45 of the sediment has been deposited as flocs. The majority of the shallow stations’ sediment is 0.01 – 0.15 floc-deposited; all of the deep stations’ sediment is greater than 0.30 floc-deposited. The 10-m stations on Pc2 and Pc16, identified before, show anomalously high values of \( f_s \). All of the Tronto transects show a seaward increase in \( f_s \) by 20 m, but sediment at six of the Pescara transects remains below 0.15 at the 20 m isobath. Two of
Figure 4.1: Distribution of geometric mean diameter (GMD). The GMD at a station is categorized by established sediment classifications (very fine – fine silt (5 – 15), medium silt (16 – 31), coarse silt (32 – 63), very fine sand (64 – 125) and fine sand (126 – 150)). These classifications are indicated by the size of each black circle. Bathymetry is in meters and black dots (*) represent station locations. Stations with the largest GMD are in shallow water while those with the smallest GMD are located in deep water offshore.
Figure 4.2: Distribution of floc fraction in sediment ($f_s$). Bathymetry is in meters and black dots ($•$) represent station locations. Stations with the smallest $f_s$ are found in shallow water. The largest $f_s$ values are deeper with an intermediary zone along the 20 m isobath. The Tronto $f_s$ distribution shows a more consistent seaward increase than the Pescara.
those six are near the mouth of the Pescara River, suggesting that proximity to the mouth may affect $f_s$ in this system.

The mud fraction at each station generally increases seaward and with depth for both rivers – deeper than 25 m, all stations are 76 – 100% mud (Figure 4.3). The Tronto area 20 m and shallower is muddier ($\bar{\text{mud}}\% = 41.05 \pm 29.80\%$) than the Pescara ($\bar{\text{mud}}\% = 24.54 \pm 22.26\%$). At 20 m, the sediment at all of the Tronto stations is 51% or more mud. This occurs by the 25-m isobath for the Pescara. Five shallow stations on the Pescara shelf show anomalously high mud fractions: the 10 m Pc2 (35%), 6 m Pc8 (39%), 10 m Pc13 (31%), 6 m Pc16 (26%) and 10 m Pc16 (62%). While the Pc2 and Pc16 stations continue to be different, the other sites have not shown notable variation before. The significant positive correlation with depth ($R_z = 0.79; p<0.001$) confirms the observed bathymetric increases in mud fraction.

4.2 – Specific Surface Area

Similar to GMD, SSA data are free from calculation and subjectivity errors in the $f_s$ analysis and can be considered highly accurate descriptions of bottom sediment. Larger SSA corresponds to smaller grain size (Mayer and Rossi, 1982). The Tronto stations 20 m and shallower ($1.74 - 23.69 \text{ m}^2\text{ g}^{-1}$; $\overline{\text{SSA}} = 9.89 \pm 8.44$) have slightly larger SSA than the Pescara ($1.69 - 20.96 \text{ m}^2\text{ g}^{-1}$; $\overline{\text{SSA}} = 6.42 \pm 5.96$). SSAs are $2 - 8 \text{ m}^2\text{ g}^{-1}$ for 60% (12 of 20) of the Tronto stations 20 m or shallower (Figure 4.4). This contrasts with the 73% (47 out of 64) of Pescara stations that have the smallest surface, indicating the Tronto seafloor has more SSA available than the Pescara. Overall, SSA increases with depth ($R_z = 0.84; p<0.001$). Sediment from most of the stations in water depths of 15 m and shallower has SSAs of $2 - 15 \text{ m}^2\text{ g}^{-1}$ while sediment from 20 m and deeper has SSAs
Figure 4.3: Distribution of mud fraction. Bathymetry is in meters and black dots (•) represent station locations. Sediment from the deeper stations has mud fractions of $\geq 51\%$ while the shallow stations have fractions $<50\%$. The Tronto sediment is muddier than the Pescara and shows a more consistent seaward increase.
Figure 4.4: Distribution of specific surface area (SSA). Bathymetry is in meters and black dots (•) represent station locations. Sediment with the largest SSA is found ≥20 m. The Pescara has a less consistent seaward increase than the Tronto. Two anomalies to the seaward trend are near the mouth of the Tronto River (10 m on Tc3, see Figure 3.1) and close to a suspected sewage outlet from the town of Ortona (10 m on Pc16, see Figure 3.1).
larger than 16 m$^2$g$^{-1}$. Two notable exceptions are the 10 m Pc16 station (20.93 m$^2$g$^{-1}$) and the 10 m Tc3 (16.13 m$^2$g$^{-1}$), which is near the mouth of the Tronto River. For both rivers, the largest increase in SSA occurs between 15 and 20 m.

**4.3 – Heavy Metals**  
Heavy metals concentrations were analyzed for trends and anthropogenic enrichment. When exploring metals for anthropogenic enrichment, a major complication arises from the grain size itself. Metals do not appear to accumulate on large grains, such as sand, because the ratio of the weight of a metal to the weight of the sediment decreases with increasing grain size. If metal concentrations are determined with respect to sediment classifications within a full size distribution, concentrations from small particles (clays and fine silts) appear erroneously as enrichment (Campbell *et al.*, 1988). To remove this obstacle, metals with documented associations with human activities are often compared to metals without significant anthropogenic sources to establish a background metal-metal relationship (Loring, 1990; Horowitz and Elrick, 1988). Positive deviations outside the upper confidence bounds of the relationship are assumed to originate from pollution. Aluminum and lithium (Li) are commonly used to determine the relationship between reactive and biologically harmful metals, such as cadmium (Cd) or mercury (Hg), and other metals in an environment. Several metals, including Cd, Hg, nickel, silver, magnesium, chromium, iron, copper (Cu), lead (Pb) and zinc (Zn) were plotted against Li and this revealed that none of the metals were anthropogenically enriched. Of the 48 metals tested, Cu, Pb and Zn showed the largest $r^2$ values during Li-normalization plotting. These three metals are known to track with fine-grained sediment through particle scavenging (Libes, 1992) and therefore were investigated further.
sedimentologically. During the laboratory analysis, the detectable range was 0.2 – 10,000 ppm for Cu, 0.5 – 10,000 ppm for Pb and 2 – 10,000 ppm for Zn. For the remainder of this thesis, ‘metals’ refers only to Cu, Pb and Zn. The largest change in metals concentration in the sediments on the margin off both the Tronto and Pescara rivers occurs between 15 and 20 metres water depth. The [Cu] (Figure 4.5) and [Pb] (Figure 4.6) show similar concentrations (3 – 45 ppm and 8 – 37 ppm, respectively) while [Zn] (Figure 4.7) ranges from 10 – 96 ppm. Cu and Zn increase more than Pb, and the Tronto river changes are larger than those off the Pescara. The Tronto means are higher ([Cu] = 18.38 ± 6.49 ppm, [Pb] = 22.04 ± 8.57 ppm, [Zn] = 57.73 ± 23.57 ppm) than the Pescara ([Cu] = 10.55 ± 5.47 ppm, [Pb] = 14.20 ± 3.86 ppm, [Zn] = 36.30 ± 18.29 ppm). There is also a more evident connection to depth for the Tronto than the Pescara, where the metal concentrations are patchy. Cu and Zn show similar distributions of steadily increasing with depth along each transect ($R_z = 0.57, 0.72; \ p<0.001, <0.001$, respectively), with the highest concentrations found at the deepest depths. Pb ($R_z = 0.49$, $p<0.001$), on the other hand, varies only slightly throughout the entire Pescara region and peaks along the 20-m isobath in the Tronto area. The 10 m Tc3 station shows some of the higher concentrations (Cu = 20.8, Pb = 15.4, Zn = 61.0) while the two anomalous Pescara stations (10 m at Pc2 and Pc16) were not analyzed for metals.

4.4 – Calcium Carbonate
Calcium carbonate was analyzed for two reasons. First, carbonate analysis is a standard procedure in Karst-dominated systems, such as the Apennines. Second, Hesse et al., (1997) have hypothesized that flocculation may be suppressed by high levels of calcium carbonate in suspension. On the Apennine Margin, the carbonate distribution varies
Figure 4.5: Distribution of copper ([Cu]). Bathymetry is in meters and black dots (•) represent station locations. Only stations 15 m or deeper were analyzed for [Cu] except for a 10-m station (Tc3) and a 6-m station (Pc16). Cu increases sharply between 15 – 20 m with the largest concentrations in deep water. The 10-m Tc3 station shows an elevated value compared to the surrounding stations. The Tronto exhibits higher concentrations and more consistent seaward increases than the Pescara.
Figure 4.6: Distribution of lead ([Pb]). Bathymetry is in meters and black dots (•) represent station locations. Only stations 15 m or deeper were analyzed for [Pb] except for a 10-m station (Tc3) and a 6-m station (Pc16). Lead is relatively homogeneous, with a slight seaward increasing trend. The largest increase occurs between 15 – 20 for the Tronto while the Pescara does not show a region of rapid increase.
Figure 4.7: Distribution of zinc ([Zn]). Bathymetry is in meters and black dots (•) represent station locations. Only stations 15 m or deeper were analyzed for [Zn] except for a 10-m station (Tc3) and a 6-m station (Pc16). Zn increases rapidly between 15 – 20 m for both rivers. The 10-m Tc3 station shows an anomalously high concentration. The seaward increases are more consistent for the Tronto than the Pescara.
Figure 4.8: Distribution of calcium carbonate (CaCO$_3$). Bathymetry is in meters and black dots (•) represent station locations. CaCO$_3$ shows no depth-related trends. On the Tronto, carbonate content peaks at 15 m then decreases in deeper water, while on the Pescara, the highest concentrations are found north and south of the mouth of the Pescara River. The lowest CaCO$_3$ are deeper than 25 m for both rivers.
spatially and differs from the previous parameters (Figure 4.8). Percentage in the sediment from stations 20 m and shallower ranges from 19 – 31% for the Tronto (CaCO₃ = 24.12 ± 3.56%) and from 18 – 28% for the Pescara (CaCO₃ = 22.53 ± 2.65%). Despite the similar ranges and means, the distributions differ for the two rivers. On the Tronto transects, CaCO₃ percentage increases seaward from 6 – 15 m then falls in deeper waters. In the Pescara region, most of the larger CaCO₃ measurements are to the north and south of the mouth of the Pescara River. The CaCO₃ percent peaks at 15 m for every Tronto transect while six Pescara transects show almost no variability. However, the smallest percentages are found at the deepest stations – one of the few spatial similarities between the rivers. Previously noted stations (10 m at Tc3 and Pc16) do not show any discernable anomalous behavior for carbonate.

4.5 – Clay Mineralogy

Five minerals dominate clay mineralogy after removal of calcite. For both rivers, in order of decreasing percentage, illite, quartz, kaolinite, dickite, and gypsum were identified. Illite and quartz make up ~70% of the mineral content. Variation between the rivers is slight (Figure 4.9). No discernable cross-shelf variation is evident, indicating the homogeneity of the mineralogy in this area (Figure 4.10). The homogeneity likely arises from lack of distinctiveness between the rivers’ watersheds combined with blending of sediments emanating from the two rivers during transport.
Figure 4.9: Mean percent of identified minerals after calcite removal. Only stations 15 m or deeper were analyzed for mineralogy except for two 10-m stations (Tc3, Pc16). White bars (Tronto) and gray bars (Pescara) represent the mean percentage of each mineral across all samples. Little variation between the rivers indicates that the minerals produced by erosion in each system do not differ markedly and/or that the clay minerals emanating from the rivers are blended during transport. Error bars one standard deviation.
Figure 4.10: Cross-shelf average mineralogy profiles. Only stations 15 m or deeper were analyzed for mineralogy except for two 10-m stations (Tc3, Pc16). Illite (◊), quartz (□), kaolinite (△), dickite (★) and gypsum (○) do not show any significant variation across 15 – 20 m. Error bars one standard deviation where there is more than one sample at the identical depth.
4.6 – Correlation Investigations

4.6.1 – Sediment character and $f_s$

Sediment size, surface area, floc fraction and metals all correlate with depth, suggesting that they are inter-linked. To investigate these possible connections, analysis of correlation between the variables was conducted (Tables 4.1, 4.2, 4.3). First, the relationships between $f_s$ and the sediment parameters of GMD and SSA were examined. Second, correlation between $f_s$ and the mud fraction was analyzed to identify a broader relationship between depositional dynamics and sediment classification.

GMD and $f_s$ show a significant negative correlation of $R = -0.86$ ($\alpha=0.95$, $p <0.001$), meaning sediment with large GMD (coarse silts and sands) shows low values for $f_s$. Conversely, sediment with the smallest GMDs (clays and fine silts) has high $f_s$ values. An upward trend in the semi-log scatter plot supports the correlation (Figure 4.10); an exponential fit quantifies the relationship according to

$$y = 0.51^{(-0.030)x} \quad (4.6.1)$$

SSA and $f_s$ have a significant positive correlation ($R = 0.89$; $p <0.001$), demonstrating that increasing SSA corresponds to high $f_s$ values. Because large SSA is associated with clay and fine silts, the correlation means these size classes deposit more frequently as flocs while larger size classes are more likely to deposit as single grains (Figure 4.11). This plot indicates a wide spread of data in the smaller SSA region but this is a result of the log-scaled y-axis. An exponential fit of

$$y = 0.041^{(0.086)x} \quad (4.6.2)$$

quantifies the positive trend with the largest SSA points having the highest $f_s$ values.
Table 4.1: Correlation coefficients for SMT parameters (Tronto and Pescara). All have $p < 0.001$.

<table>
<thead>
<tr>
<th></th>
<th>$z$</th>
<th>$f_s$</th>
<th>GMD</th>
<th>SSA</th>
<th>CaCO$_3$</th>
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<th>Pb</th>
<th>Zn</th>
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$z$ = depth (m); $f_s$ = floc fraction in sediments; GMD = geometric mean diameter ($\mu$m); SSA = specific surface area ($m^2g^{-1}$); CaCO$_3$ = calcium carbonate (%); Cu = copper (ppm); Pb = lead (ppm); Zn = zinc (ppm); d = distance from river mouth (m); mud = mud fraction (%).
Table 4.2: Correlation coefficients for SMT parameters (Tronto only). All have p < 0.001.

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z = depth (m); f_5 = floc fraction in sediments; GMD = geometric mean diameter (µm); SSA = specific surface area (m^2 g^-1); CaCO\textsubscript{3} = calcium carbonate (%); Cu = copper (ppm); Pb = lead (ppm); Zn = zinc (ppm); d = distance from river mouth (m); mud = mud fraction (%).
### Table 4.3: Correlation coefficients for SMT parameters (Pescara only). All have $p < 0.001$.

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<td>0.94</td>
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$z$ = depth (m); $f_s$ = floc fraction in sediments; GMD = geometric mean diameter ($\mu$m); SSA = specific surface area ($m^2g^{-1}$); CaCO$_3$ = calcium carbonate (%); Cu = copper (ppm); Pb = lead (ppm); Zn = zinc (ppm); d = distance from river mouth (m); mud = mud fraction (%).
Figure 4.11: GMD-fs correlation according to $y = 0.51^{(0.030)x}$. Tronto stations are represented by circles (○) and Pescara stations by stars (★). Increasing GMD is associated with lower $f_s$, suggesting fine-grain sediment is deposited as flocs.
Figure 4.12: SSA-fs correlation according to $y = 0.041^{(0.086)^x}$. Tronto stations are represented by circles (○) and Pescara stations by stars (★). Larger SSA is linked to increasing fs, indicating sediment with high SSA is more likely to be floc deposited.
Exponential dependence of floc fraction on GMD and SSA better describes the data than linear dependence. This observation reveals the difficulty in sorting small, highly flocculated sediments compared to large, unflocculated grains. Flocs are unbiased samplers of the water column meaning they incorporate a range of sediment sizes. Sorting arises partially from the differential settling velocities of these various particles. Individual small particles have small single-grain settling velocities so they must arrive at the bed predominantly within flocs, regardless of the overlying suspension’s flocculation state. This produces a seafloor distribution comprised of many different small particles with varied settling velocities. Because flocs contain a size distribution resembling the parent suspension, flocculated suspensions populated by small particles tend to produce deposits with the same GMD and SSA as the parent suspension. Thus, high values of $f_s$ beget relatively constant values of SSA and GMD.

The relationship between the mud fraction and $f_s$ simplifies the GMD and SSA trends. A significant positive correlation of $R = 0.93$ ($p < 0.001$) shows that as the percentage of mud increases, the sediment is more likely to be floc deposited (Figure 4.13). The increasing mud %-higher $f_s$ trend is described with the linear fit

$$y = 0.0040x - 0.010.$$  \hspace{1cm} (4.6.3)

All of the stations determined to be 80% or more mud show the largest $f_s$ values while those with 20% or less mud reside in the smallest $f_s$ region. A higher percentage of mud in a sample arises from deposition as flocs.
Figure 4.13: Mud-fs correlation according to $y = 0.0040x - 0.010$. Tronto stations are represented by circles (○) and Pescara stations by stars (★). As the percentage of mud in the sediment increases, $f_s$ also increases.
4.6.2 – CaCO₃ and fₛ
As an exploratory exercise for the carbonate effect on flocculation and floc deposition, CaCO₃% was plotted against fₛ (Figure 4.14). The data are widely scattered and weakly correlated with depth (R = -0.28; p=0.040). The concentration decreases with depth after 15 m, which yields the weak correlation, but also exhibits cross-shelf structure not observed in any other parameters. This suggests that carbonate does not enhance or inhibit floc deposition in this study area.

4.6.3 – Metals and deposition
Many contaminants are hydrophobic, so their concentrations in sediments are tied closely to sediment surface area. Given the link between sediment surface area and floc fraction documented above, metals concentration in the sediment should increase as floc fraction increases. These expected behaviours emerge from the analysis of correlation.

SSA and concentrations of Cu, Pb, and Zn are positively correlated (RₐCu = 0.91; p<0.001; RₐPb = 0.81; p<0.001; RₐZn = 0.98; p<0.001) (Figure 4.15). Linear least squares regression was used to characterize the relationships between SSA and metals with

\[ y_{Cu} = 0.86x + 3.1, \]  \hspace{1cm} (4.6.4)
\[ y_{Pb} = 0.51x + 9.7, \]  \hspace{1cm} (4.6.5)
\[ y_{Zn} = 3.01x + 8.4. \]  \hspace{1cm} (4.6.6)

Copper and zinc show a stronger relation to SSA than lead, which has more variability. Most of this variability comes from four Tronto stations that have elevated Pb levels when compared to other stations. Copper and zinc do not show elevated levels at these stations. With this exception, both rivers show nearly identical behavior for SSA and metal concentration.
Figure 4.14: CaCO₃-fₜ correlation. Tronto stations are represented by circles (○) and Pescara stations by stars (★). A weak correlation exists between CaCO₃ and fₜ (R = -0.28; p=0.040). The absence of an association suggests that calcium carbonate does not directly affect floc deposition.
Figure 4.15: SSA-metals correlation. Tronto stations are represented by circles (○) and Pescara stations by stars (★). All three metals show increasing concentrations with larger SSA according to $y_{\text{Cu}} = 0.86x + 3.1$, $y_{\text{Pb}} = 0.51x + 9.7$ and $y_{\text{Zn}} = 3.01x + 8.4$. 
As a result of the strong connection between $f_s$ and SSA, a positive correlation emerges between $f_s$ and the metals (Figure 4.16). All three metals show significant correlations ($R_{Cu} = 0.76; p < 0.001; R_{Pb} = 0.71; p < 0.001; R_{Zn} = 0.84; p < 0.001$). As $f_s$ increases, metal concentrations rise although the scatter around the robust linear fits is wider for $f_s$ than for SSA. The fits are

$$y_{Cu} = 45.92x + 6.5,$$

(4.6.7)

$$y_{Pb} = 31.39x + 11.0,$$

(4.6.8)

$$y_{Zn} = 193.80x + 16.9.$$

(4.6.9)

The slightly weaker correlations between $f_s$ and the metals could be due to the nature of $f_s$. Recall that SSA is a direct observation from an instrument while $f_s$ is produced from an inverse model based on a set of simplifying assumptions.

### 4.7 – Results Summary

Of the six parameters examined for determining the environmental controls in the vicinity of the SMT, four show similar depth-dependent trends ($f_s$, GMD, SSA, mud fraction), one shows no change (mineralogy) and one varies with a weak correlation ($CaCO_3$). Surficial sediments at the 10-m Tronto River mouth station are finer than neighbouring stations from the same depth. However, with only three river mouths (Tronto, Pescara, Saline) and a suspected sewage outlet (functioning as a river mouth), there are not enough data to explore the observed local fining more completely. Hence, depth-related dynamics apparently dominate in this study area for floc deposition on the seafloor. The most significant increases in $f_s$, GMD, SSA and mud fraction occur around 15 m for the Tronto and 20 m for the Pescara, although the differences between the two shelves are relatively slight.
Figure 4.16: $f_s$-metals correlation. Tronto stations are represented by circles (○) and Pescara stations by stars (★). The metals show a loose association with $f_s$ according to $y_{\text{Cu}} = 45.92x + 6.5$, $y_{\text{Pb}} = 31.39x + 11.0$ and $y_{\text{Zn}} = 193.80x + 16.9$ but maintain an increasing trend with higher $f_s$. This suggests that metals are deposited primarily by flocs.
Results relating to the investigation on metal deposition show strong correlations of both SSA and $f_s$ with the metal concentrations for copper, lead and zinc. No significant anthropogenic enrichment is evident for Cu or Zn while four Tronto stations show increased Pb.

### 4.8 – The Tronto and Pescara SMTs
Several parameters indicated depth-related changes around 15 m for the Tronto and 20 m for the Pescara. These changes mark each river’s SMT. Isobathic averages of GMD, $f_s$ and SSA plotted against depth clarify the depth of the SMT (Figure 4.17). In these cross-shelf profiles, the rapid increases in $f_s$ and SSA and sharp decrease in GMD clearly show the mudlines between 15 and 20 m for the Tronto and 15 and 25 m for the Pescara. These changes fit the mudline definition as the depth where silt and clay account for the majority of flux to the seafloor (Figure 4.17; Stanley et al., 1983). The cross-shelf profiles of sand-silt-clay fractions indicate the mud fraction begins to dominate in the same depth range as the largest GMD, $f_s$ and SSA changes, corroborating the depth of the Tronto SMT as 15 – 20 m and of the Pescara SMT as 20 – 25 m. The slight difference between the two depth ranges indicates the Tronto SMT is more abrupt than the Pescara SMT possibly due to differing sediment concentration, energy or bathymetry.

One goal of this research was to explore how an SMT is produced. The SMT can be considered a transition in nearbed fine-grained sediment flux instead of in terms of sediment character. The correlations between high $f_s$ and GMD, SSA and mud fraction indicate that the change in fine-grained sediment flux at the SMT arises from increases in nearbed flux of flocculated sediment. Several SMTs have been defined based on a
Figure 4.17: Cross-shelf averages of GMD, $f_s$, SSA and sediment classifications. In the first three panels, Tronto stations are represented by circles (○) and Pescara stations by stars (★). The bottom two panels show sediment classifications as sand (solid line), silt (dotted line), clay (dashed line) and mud (solid line with circles). All four parameters exhibit a significant shift from coarse grain to fine grain at 15 – 20 m (Tronto) and 15 – 25 m (Pescara), defining these depths as the depths of the SMTs. Error bars represent one standard deviation. Standard deviation was not calculated for the silt and clay fractions.
transition to mud fractions of 25 – 50% (Demirplot, 1991; Kachel and Smith, 1989; Chough and Kim, 1981). A definition of \( f_s > 0.2 \) is proposed for the landward edge of the SMT based on several observations involving mud fraction and \( f_s \). The first is a statistical exploitation of the high significant correlation between \( f_s \) and mud fraction. For the second, the mean \( f_s \) when the mud fraction is 25% or greater is calculated to be \( 0.25 \pm 0.15 \), providing a numerical basis for the definition. Finally, according to a graphical examination, \( f_s > 0.2 \) where the mud fraction ranges from 26 – 50%. To analyze the suitability of this definition of the SMT, an interpolated surface of \( f_s \) was produced by a kriging algorithm in ArcGIS 8.0. Several interpolation methods were attempted and compared to the direct observations of \( f_s \) before the kriging algorithm was selected. This interpolation method assumes that the distance or direction between sample points reflects a spatial correlation that can be used to explain variation in the surface. Kriging fits a mathematical function to a specified number of points, or all points within a specified radius, to determine the output value for each location. The resulting surface was overlaid with GMD and SSA values (Figures 4.18 and 4.19, respectively). The third shade of gray represents \( f_s \) between 0.21 and 0.30. This zone occurs between 15 – 20 m water depth for the Tronto and between 20 – 25 m for the Pescara. Both GMD and SSA indicate rapid fining of the sediment at the same depths. Hence, the depth at which \( f_s \) equals 0.2 is a useful, process-based definition of the SMT.

With the SMT explained as a change in the deposition of flocs, the next step is to investigate why floc deposition should increase across this boundary. The two factors that were suggested as reasons for the change (Chapter 2) are low energy, which allows fragile flocs to settle to the seafloor, and high suspended sediment concentrations, which
Figure 4.18: Interpolated $f_s$ (kriging algorithm) and GMD distribution. Bathymetry is in meters, black dots ($\bullet$) represent station locations and the SMT is defined where $f_s > 0.2$ (third shade of gray). GMD shows a rapid shift to smaller sediment classifications (see Figure 4.1) where the $f_s$-defined SMT occurs.
Figure 4.19: Interpolated $f_s$ (kriging algorithm) and SSA distribution. Bathymetry is in meters, black dots (•) represent station locations and the SMT is defined where $f_s > 0.2$ (third shade of gray). SSA shows a rapid increase where the $f_s$-defined SMT occurs.
provide the necessary concentration of fine-grain material for rapid floc formation. Two proxies are chosen for the proposed factors: depth as a proxy for energy and distance from river mouth as a proxy for concentration. Of these two proxies, depth showed a strong correlation with \( f_s \) for both rivers (Table 4.1) while distance was correlated only for the Tronto (Table 4.2). This leads to the hypothesis that energy is the primary control on floc deposition for the Apennine Margin. Although several studies claim that sediment concentration plays a vital role in creation of mudlines and deposits (McCave, 1972; Wells, 1981; Wright and Nittrouer, 1995), the absence of a distance correlation for the Pescara could indicate the two SMTs may be controlled differently. The minor difference in the SMT depths, however, suggests that the common energy correlation relates to the primary control.

As noted earlier, the sediment loads of both the Tronto and Pescara rivers have been extensively altered by damming and aggregate extraction. As these activities reduced the supply of sediment to the margin, cross-shelf position of the SMT may have changed. One way to examine the effect of changing sediment supply on depth of the SMT is to compare SMT depths before and after large changes to the sediment supply.

Passega et al., (1967) described the grain size distribution of the Pescara shelf in the mid-1960s, the decade when dams were erected on the river. Benthic sediment was sampled from 15 cross-shelf transects at the 10-, 15-, 20-, 25-, 30-, 40- and 50-m isobaths. They concluded that the SMT occurred at 30 – 40 m based on median grain size \( M \) from each station. By design, this current project reoccupied and sampled the same region. Published \( M \) from the 1967 study was compared to \( M \) calculated from the sediment collected in 2002. Isobathic averages were generated and cross-shelf profiles
from 1967 and 2002 were compared (Figure 4.20). Both have large variations in $M$ but two differences are evident. First, the 2002 SMT is more abrupt based on the steeper slope between 15 and 20 m. Second, the 1967 SMT appears to occur between 20 and 30, although the authors concluded that 30 – 40 m was the mudline depth. From the profiles, transgression of the SMT transpired during 35 years of reduced sediment supply. To clearly portray the SMT movement, interpolations for both data sets were generated and overlapping sections were subtracted, creating a difference surface (Figure 4.21). The majority of the area shows minimal coarsening or fining but the largest changes occur along the 20- and 25-m isobaths where the seabed sediment has become finer-grained. While no uniform SMT migration is seen, drops of up to 60 $\mu$m in $M$ do indicate increasing mud deposition and therefore floc fraction in the sediment. One caveat to over-interpreting the drop in $M$ is the isolation of the changes. Four individual areas are clearly identifiable as having the largest decreases and coincide with the transgressive behavior of the 2002 SMT. Migration may be occurring but at a much longer time scale than 35 years and the current study captured the SMT partway through the move. However, migration can be refuted on several grounds. First, although Passega et al., (1967) assumed wave energy was the primary dynamic factor for benthic sediment distribution, a comparison between the Passega et al., (1967) and 2002 wave observations shows the wave climate has not changed in the region. This eliminates the possibility that changes to the SMT are caused by a more or less energetic system. Second, the decrease of suspended sediment input from the Pescara is so considerable (Aquater, 1982) that if the SMT depended largely on sediment concentration, a stronger response would be expected. However, the sediment supply has effectively been removed without much
Figure 4.20: Comparison of two Pescara mudline studies. Cross-shelf isobathic averages of median grain size from Passega et al., (1967) are shown by the dotted line while data from this thesis are represented by the solid line. The 2002 profile is noticeably steeper than the 1967 profile, indicating a more rapid transition. The 1967 study identifies the SMT at 30 – 40 m although from the profile, the transition appears to occur at 20 – 30 m. The 2002 study suggests the SMT to be at 15 – 25 m. Depending on which depth range is used for the 1967 mudline, the SMT has transgressed somewhat in 35 years. Error bars represent one standard deviation.
Figure 4.21: Spatial comparison of two Pescara mudline studies. Median grain size was interpolated (kriging algorithm) for the overlapping region of Passega et al., (1967) and this thesis (a, b respectively). The SMT occurs at the boundary between the two darkest shades of gray. Although Passega et al., (1967) define the mudline at 30 – 40 m, this interpolation of their data shows the historical mudline paralleling the 20-m isobath. The 2002 mudline undulates around the 20-m isobath. The two interpolated surfaces were subtracted to identify areas of change (c). Most of the region remains slightly unchanged except for along the 20-m isobath where the sediment became finer grained in 35 years.
change to the observed SMT in 1967 and 2002. As a result, a reasonable conclusion is that energy is and was the dominant control for the Pescara SMT and sediment concentration, while part of the equation, remains secondary. By extension then, energy is the primary factor for floc deposition to the seafloor on the Apennine Margin.

4.9 – Metal Concentrations and Floc Deposition

The high correlation between SSA and the metals confirms conclusions from many studies that high metal concentration in sediments relies on large SSA (Mayer and Rossi, 1982; Buckley and Cranston, 1991; Horowitz and Elrick, 1988). While the effect of grain size has also been widely cited as a determining factor for metal concentration (Kranck, 1980b; Campbell, et al., 1988; Lick, 1994), Mayer and Rossi (1982) explicitly connect large SSA with smaller grain size. Therefore, the strong link between high SSA and large metal concentrations is expected for the sediment from the Apennine Margin. Cross-shelf profiles of the isobathic averages for SSA and the metals clearly indicate the SSA effect on metal concentrations (Figure 4.22). The steepest increases in metal concentrations occur across 15 – 20 m for both rivers, which is at the identified Tronto SMT and within the first half of the Pescara SMT. The observation that the transition in metals concentration coincides with the SMT is key to connecting the transport and dispersal of flocs and particle reactive metals.

Low $f_s$ values and small metal concentrations are found at shallow depths, and high values of $f_s$ and metals concentration are found in deeper water (Figure 4.22). The slopes for the cross-shelf transects of metal concentrations and $f_s$ are steepest at the same depths, which indicates why $f_s$ correlates so strongly with the metal concentrations.
Figure 4.22: Cross-shelf average profiles for SSA, metals and $f_s$. Tronto stations are represented by circles (○) and Pescara stations by stars (★). Only stations 15 m or deeper were analyzed for metals except for a 10-m station (Tc3) and a 6-m station (Pc16). Larger SSA clearly indicates a correlation with higher metal concentrations across the SMT for both rivers. The $f_s$ profile is steepest at the same depths as the metals, indicating that deposition of metals by flocs is occurring. Error bars represent one standard deviation.
Maps of the interpolated $f_s$ surface and $[\text{Cu}]$, $[\text{Pb}]$ and $[\text{Zn}]$ provide a higher level of spatial association among these parameters. With the SMT defined as the zone where $f_s > 0.2$, there is clear evidence that metals accumulate where flocs deposit. For example, Cu first reaches the median range of 21 – 30 ppm along the 20-m Tronto isobath, beyond which $f_s > 0.2$ (Figure 4.23). On the Pescara, this same concentration range is dependent on the $f_s$ boundary rather than the depth. In fact, the association of $f_s$ is more obvious from the Pescara as 28 out of 29 stations with $[\text{Cu}] < 21$ ppm register $f_s \leq 0.2$. Zinc can be described almost identically for both river shelves (Figure 4.24). The first peaks in $[\text{Zn}]$ occur along the 20-m Tronto isobath and are associated with the $f_s > 0.2$ boundary for the Pescara. Similar to copper, the biggest $[\text{Zn}]$ at the deepest depths show a loose connection with large $f_s$. The Pb distribution shows a similar trend to Cu and Zn for the Tronto but is less correlated for the Pescara (Figure 4.25). On the Tronto, the 20-m stations exhibit the previously observed rapid increase within the $f_s > 0.2$ zone. Yet, the deeper stations do not show increasing concentration, despite changing $f_s$. The Pescara distribution appears to complicate the Pb situation further by varying only slightly across all $f_s$ zones. One possible explanation for the noticeably different Pb behavior is the input vector to the ocean. In a study on the Adige River in northern Italy, Boldrin et al., (1989) observe that high discharge events transport 80 times more Pb than normal, which is a larger amplification than Cu (50 times more) and Zn (40 times more). They conjecture that atmospheric Pb from combustion of leaded gasoline deposits within the watershed and augments the Pb already present in the water and soil. In 1993, Italy consumed $19 \times 10^9$ L of gasoline, 76% of which contained 0.15 g L$^{-1}$ of Pb (Thomas, 1995). Lambert et al., (1991) show that transport of atmospheric pollutant Pb to North Atlantic sediments is
Figure 4.23: Interpolated \( f_s \) (kriging algorithm) and Cu distribution. Bathymetry is in meters, black dots (•) represent station locations and the SMT is defined where \( f_s > 0.2 \) (third shade of gray). The highest concentrations of Cu occur where \( f_s > 0.2 \). The Tronto distribution runs parallel to the \( f_s \)-defined SMT while the Pescara distribution follows the curving behavior of the SMT, with only the Tronto mouth sample deviating from this trend. This suggests Cu is transported to the seafloor by flocs.
Figure 4.24: Interpolated $f_s$ (kriging algorithm) and Zn distribution. Bathymetry is in meters, black dots (•) represent station locations and the SMT is defined where $f_s>0.2$ (third shade of gray). The highest concentrations of Zn occur where $f_s>0.2$. The Tronto distribution runs parallel to the $f_s$-defined SMT while the Pescara distribution follows the curving behavior of the SMT. Only the Tronto mouth sample deviates from this trend. This suggests Zn is transported to the seafloor by flocs.
Figure 4.25: Interpolated $f_s$ (kriging algorithm) and Pb distribution. Bathymetry is in meters, black dots (•) represent station locations and the SMT is defined where $f_s>$0.2 (third shade of gray). Lead concentrations do not increase rapidly across $f_s$ zones. The more homogeneous distribution of lead suggests a weaker connection to $f_s$. 
linked to biogenic particles larger than 10 µm. Atmospheric Pb could arguably be depositing onto the Adriatic Sea and accumulating where flocs deposit. Hence, the irregular spatial distribution across the SMT and weaker correlation with increased \( f_s \) could be due partially to an aeolian source for Pb.

Milligan and Loring (1997) presented an explicit connection of contaminated sediment and floc deposition in Ship Harbour, Nova Scotia. A key element of evaluating quantities of cadmium (Cd) and Zn was defining the bottom sediment as “floc deposited” rather than using the traditional categories of <63 µm or <16 µm. This was necessary as the majority of bottom sediments in Ship Harbour are <63 µm but an additional benefit was formalizing the metal-floc association. Data from the Apennine Margin supports the Milligan and Loring approach to parameterization of bottom sediment size distributions.

The clear correlations between SSA and metal concentrations as well as between \( f_s \) and SSA lead to the strong link observed between \( f_s \) and metals. As the primary control on \( f_s \) has been identified as energy, a logical extrapolation can be made as follows: particles with large SSA provide adsorption sites for metals and when these particles enter lower energy zones, net floc deposition increases, which leads to the deposition of metals on the seafloor. To strengthen the \( f_s \) and metal link, future work should focus on metal concentrations in suspended flocs before benthic diagenesis has an opportunity to alter distributions. Other physical and chemical aspects of flocs, such as the amount of organic material, size, density and porosity, should be examined with respect to metals as these floc properties will have an effect on site availability for metals adsorption (Pettine et al., 1994; Ongley et al., 1992; Dyer and Manning, 1999).
4.10 – Carbonates and Mineralogy on the Apennine Margin

The distributions of calcium carbonate and clay minerals on the Apennine Margin are perplexing for several reasons. Many studies in this region have quantified both carbonate content and mineralogy (Miserocchi et al., 2000; Boldrin et al., 1989; Mantovan et al., 1985). Other bottom sediment undertakings also report both parameters for the Namibian shelf (Bremner and Willis, 1993) and the Aegean-Black Sea conduit (Bayhan et al., 2001). In this limited selection of studies, carbonate content was used to explain the presence or absence of certain metal species. Hesse et al., (1997) explained long-distance transport of fine particles in the Labrador Sea by suppression of flocculation by detrital CaCO₃. All emphasize changes to mineralogical content and quantities as a function of grain size.

However, the data produced during this study diverge from documented trends and assumptions. Carbonates show a mid-shelf maximum off the Tronto and depth-independent maxima for the southern region of the Pescara site, both of which are unique among all the investigated parameters. CaCO₃ correlates weakly with the sedimentological parameters (GMD, fₛ, SSA, mud fraction). This indicates that transport of carbonate occurs differently than for sediment. Although the mechanism is unknown, floc transport can be eliminated as the mode for seafloor delivery of CaCO₃ (Figure 4.26). Extrapolating the observations further, the presence of CaCO₃ does not appear to affect flocculation. This counters the Hesse et al., (1997) proposition regarding suppression of flocculation. The only conclusion to be drawn from the carbonate data set is that no connection exists between CaCO₃ and flocculation, which implies calcium
Figure 4.26: Interpolated $f_s$ (kriging algorithm) and CaCO$_3$ distribution. Bathymetry is in meters, black dots (•) represent station locations and the SMT is defined where $f_s$>0.2 (third shade of gray). No connection to the $f_s$-defined SMT is observed, leading to the conclusion that calcium carbonate content does not affect flocculation or floc deposition.
carbonate content does not affect bulk textural properties of seafloor sediments on the Apennine Margin.

The cross-shelf mineralogy profiles show almost no variation with depth, regardless of the grain size. While the suite of identified minerals is in agreement with other Adriatic Sea studies (Miserocchi et al., 2000; Boldrin et al., 1989; Sondi et al., 1994), the homogeneous behavior suggests some points regarding mineralogy in this region. The clay mineralogy of the source material for the two river shelves is similar. Alternatively, or perhaps in addition to the source material similarity, differences could be lessened by other factors in the ocean as the sediment enters the nearshore zone. Longshore currents, for example, may homogenize different mineralogical signatures of the rivers, resulting in the appearance of similar source material. One improvement to the analysis that may expose differences between river systems would be to examine the mineralogy of samples in which calcite has not been removed.

4.11 – Apennine Margin SMT Summary
Mudlines were identified through fining grain size in GMD and SSA and increasing mud fraction. The Tronto SMT occurs between 15 – 20 m and occurs more abruptly than the Pescara SMT, which varies between 15 – 25 m. Exploiting the high correlations $f_s$ exhibited with the other parameters and numerically calculating the mean $f_s$ where the mud fraction is 25% or greater, both SMTs were successfully redefined as the boundary where $f_s > 0.2$. The relatively uniform cross-shelf position of the SMT in space and time leads to the hypothesis that energy, with depth as a proxy, is the dominant factor for $f_s$ and the SMT on the Apennine Margin. Increased metal concentrations were linked with high values of $f_s$, supporting previous assertions that flocs provide transport for metals.
CHAPTER 5

Assessment of General Environmental Controls on the Depth of Sand-Mud Transitions

5.1 – Towards a Predictive Model of SMT Depth
Mudlines occur in different water depths on different margins (Table 5.1), yet, at present, a simple predictive model for the depth of the SMT does not exist. Two steps are required to develop such a model. First, a small variety of watersheds and coastal zones with detailed cross-shelf surveys of grain size are used to examine the behaviour of a mudline with respect to depositional dynamics by comparing f_s observations. Second, a larger selection of more generally defined SMTs can be employed to generalize the environmental controls on the depth of the mudline through dimensional analysis.
5.2 – Comparison of SMTs in Three Different Environments

GMD and $f_s$ data were acquired for SMTs associated with two rivers significantly different from the Tronto and Pescara: the Eel River, in northern California and the Po River, in northern Italy. The Eel River ($24.0 \times 10^6$ t yr$^{-1}$ suspended sediment, $7.3 \times 10^9$ m$^3$ yr$^{-1}$ discharge) empties into the Pacific Ocean along the exposed Eel margin. The river is prone to devastating floods in winter when the majority of the annual sediment discharge is delivered to the ocean. The shelf is wave-dominated with a 30-year average $H_{1/3} = 2.66$ m (U.S. National Buoy Data Center, Buoy # 46022); a mudline was identified at ~55 m by Wheatcroft and Borgeld (2000). By contrast, the Po River ($17.0 \times 10^6$ t yr$^{-1}$ suspended sediment, $36.2 \times 10^9$ m$^3$ yr$^{-1}$ discharge) flows into the closed basin of the northwestern Adriatic Sea, where $H_{1/3} = 0.73$ m (University of Washington Po River tripod I, Annika Fain and Andrea Ogston, pers. comm.). The depth of the SMT on the Po prodelta is in much shallower water at 8 – 10 m depth (Fox et al., 2003).

The isobathic averaged cross-shelf Apennine profiles were combined with single cross-shelf transects from the Eel and Po rivers to compare SMTs from these three diverse environments (Figure 5.1). Each river’s SMT is defined by a drop in GMD accompanied by an increase in $f_s$ across a small depth range. The Eel and Po SMTs are the most abrupt, followed by the Tronto and then the Pescara. The cross-shelf changes in GMD are similar for the four systems. Shoreward of the transitions, GMDs are approximately 80 µm. Seaward of the transitions, GMDs fall to 10 µm. Remarkably, these changes occur across depth ranges of 5 – 10 m for all three systems.

Floc fraction in the sediment changes rapidly across the same depths over which GMDs change. Landward of the transitions, floc fractions are all below 0.05. At the transitions, $f_s$ increases rapidly. On the Eel margin, floc fraction in the sediments levels
Figure 5.1: Cross-shelf profiles of GMD and $f_s$ for four rivers: Po (✓), Tronto (◇), Pescara (□) and Eel (○). The Po and Eel profiles are from one transect only while the Tronto and Pescara profiles are isobathic averages. Error bars on the Tronto and Pescara represent one standard deviation. Wave energy increases from the Po through the Apennine rivers to the Eel. GMD shows similar behavior for all four SMTs by decreasing abruptly across a small depth range. Floc fraction in the sediment increases rapidly across the same depths where GMD decreases. Both parameters stabilize at deeper depths. These observations suggest increasing energy shifts the SMT to deeper water.
near unity. In contrast, Po floc fractions rise only to about 0.3. On the Pescara and Tronto margins, floc fractions asymptote to values just under 0.5. In summary, each of these margins has a similar cross-shelf evolution in grain size. Each margin also has a similar sigmoidal cross-shelf evolution in floc fraction in the sediments. The margins differ in the extent to which sediment is floc-deposited seaward of the sand-mud transition.

Each progressively deeper SMT reflects a more wave-dominated system. This finding reinforces the hypothesis that energy controls the position of an SMT. The observation that the floc fraction in the sediments seaward of the SMTs increases with increasing depth of the SMT suggests that factors other than energy level determine the extent of change in floc fraction beyond the transition itself. Dimensional analysis of net depositional flux at an SMT offers one mechanism of exploring the controls on the depth of the transition.

**5.3 – Dimensional Analysis of Controls on the Depth of the SMT**

Initially, sediment concentration and energy were assumed to be the primary controls on the SMT. These assumptions were based on a combination of observations regarding both the mudline and flocculation. Stanley *et al.*, (1983) propose that the mudline is an energy marker with coarser sediments found in higher energy zones. Curran *et al.*, (2002) consolidated earlier work to arrive at a flocculation model that incorporates sediment concentration and kinetic energy (see 2.1.1 and 2.1.2). Higher levels of energy promote floc disaggregation while higher sediment concentrations encourage floc production. Merging the findings of these two studies leads to the interesting point that if energy decreases across a shelf faster than concentration, then floc disaggregation would
decrease and floc fraction in the sediment would increase. This implies that a mudline could form where energy has reached a low threshold level.

The Apennine SMT investigation showed energy predominates over sediment concentration on this margin. Dimensional analysis can be used to investigate whether this holds true for other SMTs and to reveal the primary elements needed for constructing an SMT model.

5.3.1 – Flux balance analysis
At the simplest level, the depth of the SMT records a seabed change from erosional to depositional flux of mud (McCave, 1972). Mathematically, this deposition-erosion relationship can be stated (Hill and McCave, 2001)

\[- j_e = j_d \]  \hspace{1cm} (5.3.1)

where \(j_e\) is the erosion flux and \(j_d\) is the deposition flux. The components of (5.3.1) are

\[ j_d = -w_f C_o \]  \hspace{1cm} (5.3.2)

\[ j_e = C_e S \]  \hspace{1cm} (5.3.3)

where \(w_f\) is the floc settling velocity (m s\(^{-1}\)), \(C_o\) is the concentration of suspended sediment (kg m\(^{-3}\)) and \(C_e\) is the erosion rate coefficient (kg m\(^{-2}\) s\(^{-1}\)). Nondimensional excess shear stress, \(S\), is defined as

\[ S = \left( \frac{\tau_b - \tau_e}{\tau_c} \right) \]  \hspace{1cm} (5.3.4)

with \(\tau_b\) as bottom shear stress and \(\tau_e\) as critical erosion shear stress. Equations (5.3.2) and (5.3.3) can be further dissected to simplify the dimensional analysis by reducing the number of terms that may affect the depth of the SMT. For (5.3.2), Hill (1998) shows that \(w_f\) is relatively constant in different environments, allowing the assumption that floc
settling velocity is a constant. The concentration of suspended sediment, \( C_0 \), has been observed to be a function primarily of wave stress and river discharge (Cacchione et al., 1999; Ogston et al., 1999). Based on the similar evolution in grain size across SMTs in a range of environments (Figure 5.1), an argument can be made that the concentration of mud in the seabed at an SMT does not vary greatly among environments. Critical erosion shear stress of muds is not well known, but models typically find that values of order 0.1 Pa reproduce observed distributions of mud in the seabed and in suspension (Harris and Wiberg, 2002). Therefore, \( C_c \) and \( \tau_c \) in equation 5.3.3 are assumed constant. Finally, wave energy is assumed to control the boundary shear stress, \( \tau_b \). From linear wave theory, \( \tau_b \) is controlled by density \( (\rho) \), significant wave height \( (H_{1/3}) \), water depth \( (h) \), wave frequency \( (\omega_{1/3}) \), and gravitational acceleration \( (g) \). Assuming gravity is a constant and assigning water depth as the depth of the SMT \( (h_{SMT}) \),

\[
\tau_b = \mathcal{A}(\rho, H_{1/3}, \omega_{1/3}, h_{SMT}). \tag{5.3.5}
\]

Removing the variables that are assumed constant,

\[
j_d = \mathcal{A}(Q_s, \rho, H_{1/3}, \omega_{1/3}, h_{SMT}) \tag{5.3.6}
\]

\[
j_e = \mathcal{A}(\rho, H_{1/3}, \omega_{1/3}, h_{SMT}). \tag{5.3.7}
\]

Thus, the five remaining variables are \( Q_s, H_{1/3}, \omega_{1/3}, h_{SMT} \) and \( \rho \), or

\[
h_{SMT} = \mathcal{A}(Q_s, \rho, H_{1/3}, \omega_{1/3}). \tag{5.3.8}
\]

Identification of the dimensions (mass, time and length) of these variables is the next step in the analysis, which yields \( Q_s \) \( (M \, T^{-1}) \), \( H_{1/3} \) \( (L) \), \( \omega_{1/3} \) \( (T^{-1}) \), \( h_{SMT} \) \( (L) \) and \( \rho \) \( (M \, L^{-3}) \).

The analysis itself is performed using the Buckingham Pi Theorem. This technique states that a system with \( m \) variables in \( n \) dimensions can be described with \( n-\)
\( m \) dimensionless variables (Buckingham, 1914, Buckingham, 1915). In this exercise, \( m = 5 \) and \( n = 3 \), giving two dimensionless variables. Application of the theorem produces

\[
\Pi_1 = \frac{h_{\text{SMT}}}{H_{1/3}} \tag{5.3.9}
\]

\[
\Pi_2 = \frac{\rho H_{1/3}^3 \alpha_{1/3}}{Q_s}. \tag{5.3.10}
\]

\( \Pi_1 \) is a relationship between the depth of the SMT and significant wave height of a shelf. \( \Pi_2 \) describes the relationship between sediment transport rate by wave energy (the numerator) and by rivers (the denominator). If sediment concentration is significantly involved in determining \( h_{\text{SMT}} \), then a trend of increasing \( \Pi_1 \) with increasing \( \Pi_2 \) is expected. Wave climate and river data for eight SMTs and the Apennine mudlines were compiled (Table 5.1). The systems represent a broad spectrum of environments from open ocean (Eel, Columbia, Russian, Kunene), semi-enclosed seas (Yangtze, Mississippi, Ebro) and small basins (Tronto, Pescara, Po). However, as Figure 5.2 shows, the expected relationship does not emerge. Only the Yangtze, with the largest sediment load, appears to experience reduced SMT depth in response to heavy sediment discharges. This result suggests that river sediment concentrations do not have a vital role in defining the depth of the SMT. In fact, it suggests that wave-derived stresses at the seabed account for most of the observed variability in SMT depths around the globe.

**5.3.2 – Significant wave height and the SMT**

The dimensional analysis indicates that \( H_{1/3} \) is the dominant variable for defining the depth, \( h_{\text{SMT}} \). The next logical step is to scrutinize the relationship between these two variables. Using relative wave height \( (H_{1/3} h_{\text{SMT}}^{-1}) \) across the shelf, GMD and \( f_s \) profiles
Figure 5.2: Dimensionless relationship. Represented river SMTs are the Tronto (□), Pescara (◊), Eel (○), Yangtze (△), Ebro (▽), Kunene (<), Mississippi (★), Columbia (×), and Russian (+). The plot indicates that $h_{SMT}$ does not depend on river discharge ($Q_s$) and suggests that $H_{1/3}$ is the controlling factor for $h_{SMT}$. 
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<th>$Q_s \times 10^6$ t yr$^{-1}$</th>
<th>SMT (m)</th>
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Report of Hydrological Survey from Zhejiang Province Islands; Wright and Nittrouer (1995)
Annika Fain and Andrea Ogston, UW Po River tripod I, pers. comm; Fox et al., (2003)
Ortona Buoy; Current study
Ortona Buoy; Current study
Report of Hydrological Survey from Zhejiang Province Islands; Wright and Nittrouer (1995)
Annika Fain and Andrea Ogston, UW Po River tripod I, pers. comm; Fox et al., (2003)
Ortona Buoy; Current study
Ortona Buoy; Current study
were produced for the Tronto, Pescara, Po and Eel margins to examine how $H_{1/3}$ affects mudlines (Figure 5.3). The GMD profiles show similar shapes as in Figure 5.1 with less energetic realms corresponding to fine-grained sediment. The range of relative wave heights at the various sand-mud transitions is small (~0.03 – 0.09). Ideally, if significant wave height was the only control on depth of the SMT, all four systems would collapse onto a particular relative wave height. Also, the order of the SMTs does not follow the trend in wave climate or $h_{SMT}$. The Po, with the shallowest SMT, has the largest relative wave height while the Eel, with the deepest SMT, settles in the middle. The Tronto and Pescara also switch positions with the deeper Pescara SMT ahead of the shallower Tronto. The GMD observations can be extended for $f_s$, although the SMT appears less prominently.

When the connection between wave height and SMT depth is expanded to the 10 previously mentioned SMTs, a linear trend emerges (Figure 5.4). In general, increasing $H_{1/3}$ corresponds to a deeper SMT. A linear fit of depth of the sand-mud transition to significant wave height yields

$$h_{SMT} = 20.3H_{1/3} + 1.7.$$  \hspace{1cm} (5.3.11)

Equation 5.3.11 has wide prediction intervals. For example, the Po, Tronto, Pescara and Ebro have similar $H_{1/3}$ but a wide range of $h_{SMT}$. The mean significant wave height for the four rivers ($H_{1/3} = 0.7$ m) produces $18.0 \pm 17.5$ m as possible $h_{SMT}$. The same calculation for the Eel, Columbia and Russian ($H_{1/3} = 2.6$ m) generates $54.3 \pm 20.1$ m. Table 5.2 shows observed $h_{SMT}$ and the prediction interval for each river. Only the observed $h_{SMT}$ from the Eel, Columbia and Russian fall within 10% of the mean predicted value. The larger scatter for the other SMTs could arise from different methods of determining a
Figure 5.3: Cross-shelf characterization by relative wave height ($H_{1/3}$) for GMD and $f_s$ on the Po (★), Tronto (▽), Pescara (□) and Eel (○). The Po and Eel profiles are from one transect only while the Tronto and Pescara profiles are isobathic averages. Error bars on the Tronto and Pescara represent one standard deviation. For less energetic realms, GMD is small and $f_s$ high. The SMT occurs for these systems over a relatively small range in the ratio of water depth to significant wave height. These four systems do not all collapse to a single ratio for depth of the SMT to significant wave height. The Po shelf has the deepest SMT relative to significant wave height, while the Pescara and Tronto have the shallowest.
Figure 5.4: $H_{1/3}$ vs. $h_{SMT}$ according to $h_{SMT} = 20.3H_{1/3} + 1.7$. Represented river SMTs are the Tronto (□), Pescara (◊), Eel (○), Yangtze (△), Ebro (▽), Kunene (<), Po (>), Mississippi (●), Columbia (×), and Russian (+). Increasing significant wave height correlates with deeper SMT ($R = 0.85; \alpha = 0.95, p < 0.001$). This simple relationship suggests that an easily measured property ($H_{1/3}$) can be used to roughly predict the depth of the mudline. See Table 5.2 for prediction intervals.
Table 5.2: Observed h$_{SMT}$ and prediction intervals ($\alpha=0.95$) based on (5.3.11).

<table>
<thead>
<tr>
<th>River</th>
<th>Observed h$_{SMT}$</th>
<th>Prediction interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yangtze*</td>
<td>5.0</td>
<td>25.5 ± 14.0</td>
</tr>
<tr>
<td>Po</td>
<td>8.0</td>
<td>18.5 ± 17.2</td>
</tr>
<tr>
<td>Tronto</td>
<td>15.0</td>
<td>17.1 ± 18.0</td>
</tr>
<tr>
<td>Pescara</td>
<td>20.0</td>
<td>17.1 ± 18.0</td>
</tr>
<tr>
<td>Mississippi</td>
<td>20.0</td>
<td>23.6 ± 14.7</td>
</tr>
<tr>
<td>Ebro</td>
<td>30.0</td>
<td>19.5 ± 16.7</td>
</tr>
<tr>
<td>Columbia†</td>
<td>50.0</td>
<td>52.4 ± 19.0</td>
</tr>
<tr>
<td>Russian†</td>
<td>50.0</td>
<td>55.1 ± 20.6</td>
</tr>
<tr>
<td>Eel†</td>
<td>55.0</td>
<td>55.4 ± 20.8</td>
</tr>
<tr>
<td>Kunene*</td>
<td>60.0</td>
<td>39.5 ± 13.1</td>
</tr>
</tbody>
</table>

* – observed h$_{SMT}$ outside of prediction interval; † – observed h$_{SMT}$ falls within 10% of mean prediction value

mudline in addition to along margin variability within an SMT. For example, the mean h$_{SMT}$ for the Kunene is 60 m but varies from as shallow as 15 m to as deep as 105 m (Bremner and Willis, 1993). Standardization of the mudline definition could alleviate these sources of variance and this should be examined in the future.

### 5.3.3 – Depth of Closure and h$_{SMT}$

Coastal engineering research has developed the concept of the depth of closure, D$_c$, or the depth that is the seaward limit for significant profile changes to seafloor elevation (Hallermeier, 1981). Interestingly, efforts to link estimated depths of closure to environmental variables produced a nearly linear dependence of depth of closure to effective wave height, which is the significant wave height which is exceeded only 12 h $\text{yr}^{-1}$. The nearly linear dependence of depth of closure on wave height and the linear dependence of the depth of the sand-mud transition on significant wave height suggests that similar physics may underlie determination of the positions of these features.
Hallermeier (1981) invoked linear wave theory and combined it with the concept that the depth of closure corresponds to a constant value of the Shields parameter to produce a working formulation for $D_c$:

$$D_c (m) = 2.28 H_e - 68.5 \left( \frac{H_e^2}{g T_e^2} \right)$$  \hspace{1cm} (5.3.12)$$

$H_e$ is the effective wave height and $T_e$ is the associated effective wave period. The model relies primarily on a linear scaling of wave height for sediment transport with a correction for wave steepness. Nicholls et al., (1998) conducted an evaluation of $D_e$ in which $H_e$ was found to be a more appropriate value than peak significant wave height. The effects of tides and wind-induced currents are ignored.

To explore the strength of the relationship between depth of closure and depth of the sand-mud transition, $D_c$ was calculated for nine of the aforementioned rivers (the Po was excluded because wave period data were unavailable) by an online Applet called Depth of Closure (Robert Dalrymple, http://www.coastal.udel.edu/faculty/rad/depth.html, Center for Applied Coastal Research, University of Delaware) that required input of $H$, $T$ and specific gravity of sand, which was assumed to be constant (2.65, unitless). Four options for $H$ existed and “Offshore Height” was selected. The $D_c$ results and $h_{SMT}$ have a significant correlation of $R = 0.86 (\alpha=0.95, p < 0.001)$. The two variables increase together (Figure 5.5) according to

$$h_{SMT} = 8.0D_c + 5.7 .$$  \hspace{1cm} (5.3.13)$$

The mudline therefore may be controlled by similar physics as the depth of closure.

Although primarily controlled by $H$, $D_c$ also depends on wave steepness. To investigate if this is true for $h_{SMT}$, stepwise linear regression was conducted. This analysis
Figure 5.5: Depth of closure and $h_{\text{SMT}}$ according to $h_{\text{SMT}} = 8.0D_c + 5.7$. Represented river SMTs are the Tronto (□), Pescara (◊), Eel (○), Yangtze (△), Ebro (▽), Kunene (<), Mississippi (★), Columbia (×), and Russian (+). $D_c$ and $h_{\text{SMT}}$ increase together, indicating that the fundamental processes that define $D_c$ may also determine $h_{\text{SMT}}$. 
examines the statistical contribution of a set of variables to an unknown function based on observations. Each step places another variable into the regression equation, which reduces the degrees of freedom for the function but does not necessarily improve the $r^2$ or p values. Addition of variables stops when the statistics cease to improve or begin to degrade. Conducting this type of analysis assists in maintaining the simplest regression while investigating a relationship. Wave steepness ($\zeta$) was calculated for the nine rivers used in the $D_c$ relationship. Significant wave height and steepness were provided as input variables and observed $h_{SMT}$ as output from the unknown regression as

$$h_{SMT} = aH_{1/3} + b\zeta + C$$  \hspace{1cm} (5.3.14)

with $a$ and $b$ as coefficients and $C$ as a constant. The two rounds of input show that inclusion of $\zeta$ degrades rather than improves the p value while not affecting $r^2$ (Table 5.3). This leads to the conclusion that $h_{SMT}$ depends primarily on $H_{1/3}$ according to

$$h_{SMT} = aH_{1/3} + C$$  \hspace{1cm} (5.3.15)

<table>
<thead>
<tr>
<th>Round</th>
<th>Equation</th>
<th>Lower a/b</th>
<th>Upper a/b</th>
<th>$r^2$</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$h_{SMT} = 16.7H_{1/3} + C$</td>
<td>4.7/none</td>
<td>28.7/none</td>
<td>0.69</td>
<td>0.005</td>
</tr>
<tr>
<td>2</td>
<td>$h_{SMT} = 15.1H_{1/3} - 2.5\zeta + C$</td>
<td>-2.4/-19.9</td>
<td>32.6/15.0</td>
<td>0.70</td>
<td>0.028</td>
</tr>
</tbody>
</table>

where $a = 16.7$ and ranges from 4.7 to 28.7. While the $a$ coefficient varies from that in (5.3.11), the difference is slight and could be due to the omission of the Po data. The physics that control the depth of closure appear likely to control the depth of the mudline. This broadens the scope of literature and expertise available for SMT research by
opening the vast quantity of coastal engineering and sand transport modeling information. Factors such as slope and non-wave induced currents should be considered in subsequent investigations (Nicholls et al., 1998, Pilkey et al., 1993). With this in mind, continued efforts toward formalizing how energy controls the SMT remain for future endeavors.

5.4 – Assessment of Environmental Controls Summary
Mudlines in three different marine environments show similar evolution of GMD across the SMT. Floc fraction in sediment behaves in the same way, encouraging future use of this recently redefined parameter. Dimensional analysis on hypothesized environmental controls for the SMT revealed that $H_{1/3}$ is the dominant factor over $Q_s$. An investigation into the analogous depth of closure suggests that similar physics control both benthic features. Future work should detail flocculation in muds seaward of the SMT and explore the effects from additional factors, such as slope, tides and currents, on $h_{SMT}$. 
CHAPTER 6

Conclusion

The two goals of this thesis were to determine the environmental controls on the sand-mud transition (SMT) through a non-traditional parameter, floc fraction in sediment (fs), and to link fs to contaminant loading in the vicinity of the SMT. The SMT, or mudline, is an abrupt change in the dominant seafloor sediment from sand to mud. Floc fraction in the sediment is the portion of floc-deposited sediment within the total deposited sediment. Transport of fine grain sediment by flocs is well documented, and this knowledge was exploited to investigate the SMT. Sediment concentration and energy were suggested as the controls on fs and the depth of the SMT (hSMT). Two small mountainous rivers and their associated SMTs were selected to evaluate the proposed controls: the Tronto and Pescara rivers on the Apennine Margin of Italy. Several laboratory analyses were performed on sediment collected from cross-shelf transects including geometric mean diameter (GMD), fs, specific surface area (SSA), carbonate content (CaCO₃) and clay mineralogy. Sand and mud fractions were also calculated.
GMD, $f_s$, SSA and mud fraction indicated abrupt fining of the sediment at 15 – 20 m for the Tronto and 15 – 25 m for the Pescara, whereas CaCO$_3$ and clay mineralogy did not indicate a SMT. The Tronto SMT parallels the coastline and follows the isobaths while the Pescara SMT varies between 20 and 25 m. High correlations ($R = \pm 0.75$) were observed between GMD, $f_s$, SSA and mud fraction. Proxies were chosen to examine the suggested controls on $f_s$ and $h_{SMT}$. While the energy proxy, water depth, functioned well, a different parameter than distance from the river mouth should be used for sediment concentration proxy, such as directly measuring suspended sediment concentration above the SMT. A temporal analysis of the Pescara SMT during 35 years of reduced sediment supply showed only slight changes to $h_{SMT}$. That observation implies energy is the dominant controlling factor and this is supported by dimensional analysis on 10 observed mudlines from around the world. This analysis suggests that significant wave height explains much of the observed variability in depth of the sand-mud transition. A similar scaling is used by coastal engineers to predict the depth of closure on the shoreface. This similarity may mean that the physics that define the depth of closure also control $h_{SMT}$. The role of significant wave height ($H_{1/3}$) in determining $h_{SMT}$ should be pursued in the future.

Concentration of three heavy metals (Cu, Pb, Zn) in the collected sediment was quantified to explore how contaminants correlate with $f_s$ and the SMT. All three metals increased in concentration across the SMT with Cu and Zn showing the strongest signal. No anthropogenic enrichment was observed by Li-normalization. The metals were significantly correlated with SSA and $f_s$, indicating that flocs are the primary transport vector for metals. The distribution of Pb was the least correlated with $f_s$, which may be
due to steady aeolian input of atmospheric Pb from combustion of leaded gasoline.

Extending the findings that energy is the dominant factor for $f_s$ and $h_{SMT}$, seafloor metals distribution is related to energy levels with higher concentrations found in lower energy regimes. Future work should consider metal concentrations of suspended flocs and the chemical composition of both deposited and suspended.

The results encompassed in this thesis connect several branches of coastal oceanography and can be interpreted for use by sedimentologists, geochemists and dynamic modelers, to list a few. The contributions to mudline research are the identification of energy as the dominant control on $h_{SMT}$, successful application of $f_s$ as a functional tool for process-based parameterization of sediment size distributions and advancement of understanding of the dynamic controls on metals transport and deposition.
Appendix A

List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>Floc flux of the reference diameter</td>
<td>kg s$^{-1}$ m$^{-2}$</td>
</tr>
<tr>
<td>$C(d)$</td>
<td>Concentration of particles at diameter $d$</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$C(i)$</td>
<td>Concentration of size class $i$</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$C(i;0)$</td>
<td>Concentration of size class $i$ at time 0</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$C_e$</td>
<td>Erosion rate coefficient</td>
<td>kg s$^{-1}$ m$^{-2}$</td>
</tr>
<tr>
<td>$C_o$</td>
<td>Concentration of suspended sediment</td>
<td>kg m$^{-3}$</td>
</tr>
<tr>
<td>$CaCO_3$</td>
<td>Calcium carbonate content</td>
<td>%</td>
</tr>
<tr>
<td>$[Cu]$</td>
<td>Copper concentration</td>
<td>ppm</td>
</tr>
<tr>
<td>$D_c$</td>
<td>Depth of closure</td>
<td>m</td>
</tr>
<tr>
<td>$d$</td>
<td>Distance from river mouth</td>
<td>m</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Grain size diameter whose concentration has fallen to e$^{-1}$ of its value</td>
<td>m</td>
</tr>
<tr>
<td>$d_f$</td>
<td>Floc limit</td>
<td>m</td>
</tr>
<tr>
<td>$d_i$</td>
<td>Size class of interest</td>
<td>m</td>
</tr>
<tr>
<td>$d_o$</td>
<td>Reference diameter</td>
<td>m</td>
</tr>
<tr>
<td>$f$</td>
<td>Floc fraction</td>
<td>none</td>
</tr>
<tr>
<td>$f_s$</td>
<td>Floc fraction in the sediments</td>
<td>none</td>
</tr>
<tr>
<td>$GMD$</td>
<td>Geometric mean diameter</td>
<td>µm</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational acceleration</td>
<td>m s$^{-2}$</td>
</tr>
<tr>
<td>$H_{1/3}$</td>
<td>Significant wave height</td>
<td>m</td>
</tr>
<tr>
<td>$h$</td>
<td>Flow depth</td>
<td>m</td>
</tr>
<tr>
<td>$h_{SMT}$</td>
<td>Depth of sand-mud transition</td>
<td>m</td>
</tr>
</tbody>
</table>
### Mathematical Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J(i)$</td>
<td>Flux of all particles in size class $i$ kg s(^{-1}) m(^{-2})</td>
</tr>
<tr>
<td>$J_f$</td>
<td>Total floc flux kg s(^{-1}) m(^{-2})</td>
</tr>
<tr>
<td>$J_{f(i)}$</td>
<td>Flux of flocs with particles in size class $i$ kg s(^{-1}) m(^{-2})</td>
</tr>
<tr>
<td>$J_s(i)$</td>
<td>Flux of single grain particles in size class $i$ kg s(^{-1}) m(^{-2})</td>
</tr>
<tr>
<td>$j_d$</td>
<td>Deposition flux kg s(^{-1}) m(^{-2})</td>
</tr>
<tr>
<td>$j_e$</td>
<td>Erosion flux kg s(^{-1}) m(^{-2})</td>
</tr>
<tr>
<td>$k_a(i)$</td>
<td>Aggregation rate coefficient between flocs and particles in size class $i$ m(^3) s(^{-1})</td>
</tr>
<tr>
<td>$k_b$</td>
<td>Breakup rate for flocs s(^{-1})</td>
</tr>
<tr>
<td>$m$</td>
<td>“Source slope” of parent distribution none</td>
</tr>
<tr>
<td>$M$</td>
<td>Median grain size µm</td>
</tr>
<tr>
<td>$N_f(i)$</td>
<td>Number concentration of size $i$ particles within flocs m(^{-3})</td>
</tr>
<tr>
<td>$N_s(i)$</td>
<td>Number concentration of single grains in size class $i$ m(^{-3})</td>
</tr>
<tr>
<td>$[\text{Pb}]$</td>
<td>Lead concentration ppm</td>
</tr>
<tr>
<td>$\Pi_x$</td>
<td>Buckingham Pi Theorem variable $x$ none</td>
</tr>
<tr>
<td>$p$</td>
<td>Probability coefficient none</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density of seawater g m(^{-3})</td>
</tr>
<tr>
<td>$Q$</td>
<td>Concentration of a reference size class kg m(^{-3})</td>
</tr>
<tr>
<td>$Q_s$</td>
<td>River suspended sediment discharge t yr(^{-1})</td>
</tr>
<tr>
<td>$R$</td>
<td>Correlation coefficient none</td>
</tr>
<tr>
<td>$r^2$</td>
<td>Regression coefficient none</td>
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<tr>
<td>$S$</td>
<td>Excess shear stress none</td>
</tr>
<tr>
<td>$SMT$</td>
<td>Sand-mud transition none</td>
</tr>
<tr>
<td>$SSA$</td>
<td>Specific surface area m(^2) g(^{-1})</td>
</tr>
<tr>
<td>$T_{1/3}$</td>
<td>Dominant wave period s</td>
</tr>
<tr>
<td>$\tau_b$</td>
<td>Bottom shear stress N m(^{-2})</td>
</tr>
<tr>
<td>$\tau_c$</td>
<td>Critical erosion shear stress N m(^{-2})</td>
</tr>
<tr>
<td>$w_f$</td>
<td>Floc settling velocity m s(^{-1})</td>
</tr>
<tr>
<td>$w_s(i)$</td>
<td>Settling velocity for single grains of size class $i$ m s(^{-1})</td>
</tr>
<tr>
<td>$\omega_{1/3}$</td>
<td>Dominant wave frequency s(^{-1})</td>
</tr>
<tr>
<td>$[\text{Zn}]$</td>
<td>Zinc concentration ppm</td>
</tr>
<tr>
<td>$z$</td>
<td>Water depth m</td>
</tr>
<tr>
<td>$\zeta$</td>
<td>Wave steepness none</td>
</tr>
</tbody>
</table>


York.


