Available online at www.sciencedirect.com
ScienceDirect
Continental Shelf Research 27 (2007) 475–488
CONTINENTAL SHELF RESEARCH
www.elsevier.com/locate/csr

Flocculation, heavy metals (Cu, Pb, Zn) and the sand–mud transition on the Adriatic continental shelf, Italy

Douglas A. George[a,*], Paul S. Hill[b], Timothy G. Milligan[c]

[a]United States Geological Survey, 400 Natural Bridges Dr., Santa Cruz, CA 95060, USA
[b]Department of Oceanography, Dalhousie University, Halifax, NS, Canada
[c]Bedford Institute of Oceanography, Dartmouth, NS, Canada

Received 26 June 2004; received in revised form 24 June 2005; accepted 24 June 2005
Available online 11 January 2007

Abstract

Across a limited depth range (5–10 m) on many continental shelves, the dominant sediment size changes from sand to mud. This important boundary, called the sand–mud transition (SMT), separates distinct benthic habitats, causes a significant change in acoustic backscatter, represents a key facies change, and delimits more surface-reactive mud from less surface-reactive sand. With the goal of improving dynamical understanding of the SMT, surficial sediments were characterized across two SMTs on the Adriatic continental shelf of Italy. Geometric mean diameter, specific surface area (SSA), mud fraction (<63 μm) and heavy metal concentrations were all measured. The SMT related to the Tronto River is identified between 15 and 20 m water depth while the SMT associated with the Pescara River varies between 15 and 25 m water depth. The sediment properties correlate with a new, process-based sedimentological parameter that quantifies the fraction of the sediment in the seabed that was delivered as flocs. These correlations suggest that floc dynamics exert strong influence over sediment textural properties and metal concentrations. Relative constancy in the depth of the SMT along this portion of the margin and its lack of evolution over a period during which sediment input to the margin has dramatically decreased suggest that on the Adriatic continental shelf energy is the dominant control on the depth of the SMT.

Keywords: Sediment transport; Flocculation; Sand–mud transition; Heavy metals; Adriatic sea

1. Introduction

The sand–mud transition (SMT), or mudline (Stanley et al., 1983), is a nearshore boundary on the seafloor where the dominant sediment size changes from sand (63–2000 μm) to silts and clays (0.24–63 μm), known collectively as "mud" (McCave, 1972). Through this study, "SMT" and "mudline"are used interchangeably. SMTs associated with river inputs have been identified at various depths around the world: the Yangtze at 5 m (Wright and Nittrouer, 1995), the Mississippi at 20 m (Stanley et al., 1983), the Ebro at 30 m (Palanques and Drake, 1990), the Pescara at 30–40 m (Passega et al., 1967), the Eel at 55 m (Wheatcroft and Borgeld, 2000) and the Kunene at 60 m (Bremner and Willis, 1993). While these and other explorations of the SMT have described the occurrence and position of the mudline, surprisingly

*Corresponding author. Tel.: +1 831 427 4759; fax: +1 831 427 4748.
E-mail address: dgeorge@usgs.gov (D.A. George).

0278-4343/$ - see front matter
doi:10.1016/j.csr.2005.06.013

little research has been dedicated to understanding the dynamic controls of this unique boundary.

The significant differences in sediment character on either side of the SMT make it an important biological, physical, geological and chemical boundary in the sea. Changes in benthic community structure have been attributed to shifts in sediment substrate (Snelgrove and Butman, 1994; Grant et al., 1991), and the effects of grain size on acoustic returns are well documented (Urick, 1983; Davis et al., 1996; Goff et al., 1999). Understanding major sediment facies changes, such as the SMT, is key to interpreting recent Earth history (e.g., Harris et al., 1997; Els and Mayer, 1998). Furthermore, heavy metals, which are potentially toxic, show an affinity for mud particles and accumulate where fine-grained sediments deposit. 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 sandier 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). Single-grain settling cannot produce a significant depositional flux of muds in most environments (Kranck, 1980). Flocculation has therefore been invoked to explain observed accumulation rates of mud. Consequently, the SMT likely marks a boundary in the net depositional flux of flocs. This simple kinematic explanation for the SMT has not been tested. Flocs are fragile, so they cannot be sampled intact from the seabed. Kranck and Milligan (1985) determined the proportion of suspended sediment bound as flocs based on analysis of the disaggregated inorganic grain size (DIGS) distribution. Direct measurements of particle vertical flux in turbulent boundary layers are not yet possible either. A new parameterization was developed recently that estimates the fraction of sediment deposited as flocs from the seabed DIGS distribution (Curran et al., 2004).

The primary goal of this paper is to apply this new parameterization to interpret textural variation across two SMTs on the Adriatic continental shelf in Italy. Two factors make this an excellent location to place mechanistic constraint on the underlying causes for the transition from sand to mud on continental margins. First, it was the site of an extensive observational program in 2001–2003 that was sponsored jointly by the US Office of Naval Research and the European Union. Data from this program eventually will permit detailed assessment of the mechanisms by which environmental conditions produce observed distribution of sediment on this shelf. Second, the margin also has been the site of past sedimentological research (Passega et al., 1967) that documented a clear SMT in relatively shallow water. Comparison between the modern SMT depth and the depth 35 years previously, when undammed rivers delivered larger sediment loads to the margin, can provide insight into controls on the position of the boundary.

The secondary goal of this paper is to use the new parameterization to explore the correlation of floc deposition and metal concentrations in the seabed. The affinity metals exhibit for fine-grained sediments is well documented (Fowler and Knauer, 1986; Ongley et al., 1992; Zhang et al., 1992; Brassard et al., 1994; Puig et al., 1999; Droppo et al., 2002). The fundamental process behind these observations is the binding of negatively charged clay particles with positively charged metals. Mineralogical and chemical composition, specific surface area and the amount of organic material have been suggested as controls for cation adsorption (Horowitz and Elrick, 1988). Most metal 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. This process has been used to account for removal of metals in estuaries (Zwolsman et al., 1997), rivers (Pettine et al., 1994) and the ocean (Giani et al., 1994). The potential for accumulation of metals via floc deposition is significant, yet direct links between floc deposition and metal concentrations are rarely documented (Milligan and Loring, 1997).

This work examines the environmental controls on the SMT and on heavy metal loading in the vicinity of the SMT. Two hypotheses are investigated: (A), the SMT reflects a boundary in the net

depositional flux of flocs; and, (B), flocs are the primary transport vehicle for heavy metals. To address (A), the sediment textural properties of grain size and specific surface area are combined with a quantification of sediment deposited as flocs to describe the depositional conditions for two mudlines. For (B), measured concentrations of Cu, Pb and Zn are correlated with specific surface areas and the quantification of sediment deposited as flocs to explore the metal–floc relationship.

2. Methods

2.1. Study site and data collection

This research was conducted in the nearshore region of the Adriatic continental shelf of Italy (Fig. 1). This area of the western Adriatic Sea experiences tides of ~0.5 m and a dominant southerly current (Artegiani et al., 1997). Significant wave height occurrence frequencies, calculated from 3 years (1999–2002) of data from the Ortona buoy (42.4011°N, 14.5339°E, World Meteorological Organization Code 61217, Italian Sea Wave Network, 2002), 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.

Surficial seabed sediments were characterized near the mouth of two rivers: the Pescara and the Tronto. Milliman and Syvitski (1992) reported that these rivers discharge similar amounts of suspended sediment to the sea (0.9 and $1.1 \times 10^6\,\mathrm{t\,yr^{-1}}$, respectively). 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). Sand deposits are also 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.

In April and May 2002, sediment was collected from the Italian ships, *R/V Urania* and *M/N Ermione* at 101 stations: 75 centered on the Pescara River and 26 on the Tronto River (Fig. 1). The sampling strategy was to collect grab samples on the 6-, 10-, 15-, 20- and 25-m isobaths. Sixteen shore normal cross-shelf transects for the Pescara River and five cross-shelf transects for the Tronto River were completed. Thirteen additional samples were collected from depths greater than 25 m on 9 of the 21 transects. The percentage of samples at each depth (6, 10, 15 and 20 m) is the same for both areas. 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) on the same shelf. Stations at the Tronto were generally farther apart (~1500–2000 m) because the bathymetric gradient is less steep than off the Pescara. 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 subsampled with plastic spoons from the top 1–2 cm of the sample. The bagged sub-samples were kept frozen until analysis. 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.

2.2. Laboratory analyses

DIGS distributions of the prepared sediment were determined using a Coulter Multisizer IIe electro-resistance particle size analyzer (Milligan and Kranck, 1991). Only the inorganic fraction of the sediment was analyzed as information about depositional processes is retained regardless of post-depositional organic–geochemical transformations. Dry sediment from each sample was treated with hydrogen peroxide to remove organic material and dispersed with a sapphire-tipped ultrasonic probe in an electrolyte solution. A discrete particle size distribution was produced by combining particle sizing runs from 30-, 200- and 400- (for mud-dominated samples) or 1000-μm (for sand-dominated samples) aperture tubes. The resulting size distribution was normalized over the range of sizes analyzed and results were plotted as log equivalent weight in percent vs. log diameter in microns (Milligan and Kranck, 1991).

Geometric mean diameter (GMD), floc fraction in the sediment (f_s) and the sand, silt and clay fractions were calculated at each station from the DIGS distribution. GMD is calculated as

$$\mathrm{GMD}(\mu\mathrm{m}) = 2^{\left[-\sum_i^{n\ class} \Phi(i)p(i)\right]} \times 100, \qquad (1)$$

where $\Phi(i) = -\log d(i)/\log 2$ with $d(i)$ as the nominal diameter of Coulter size class i, which is taken as the equivalent spherical diameter of midpoint of size class i, and $P(i)$ is the proportion

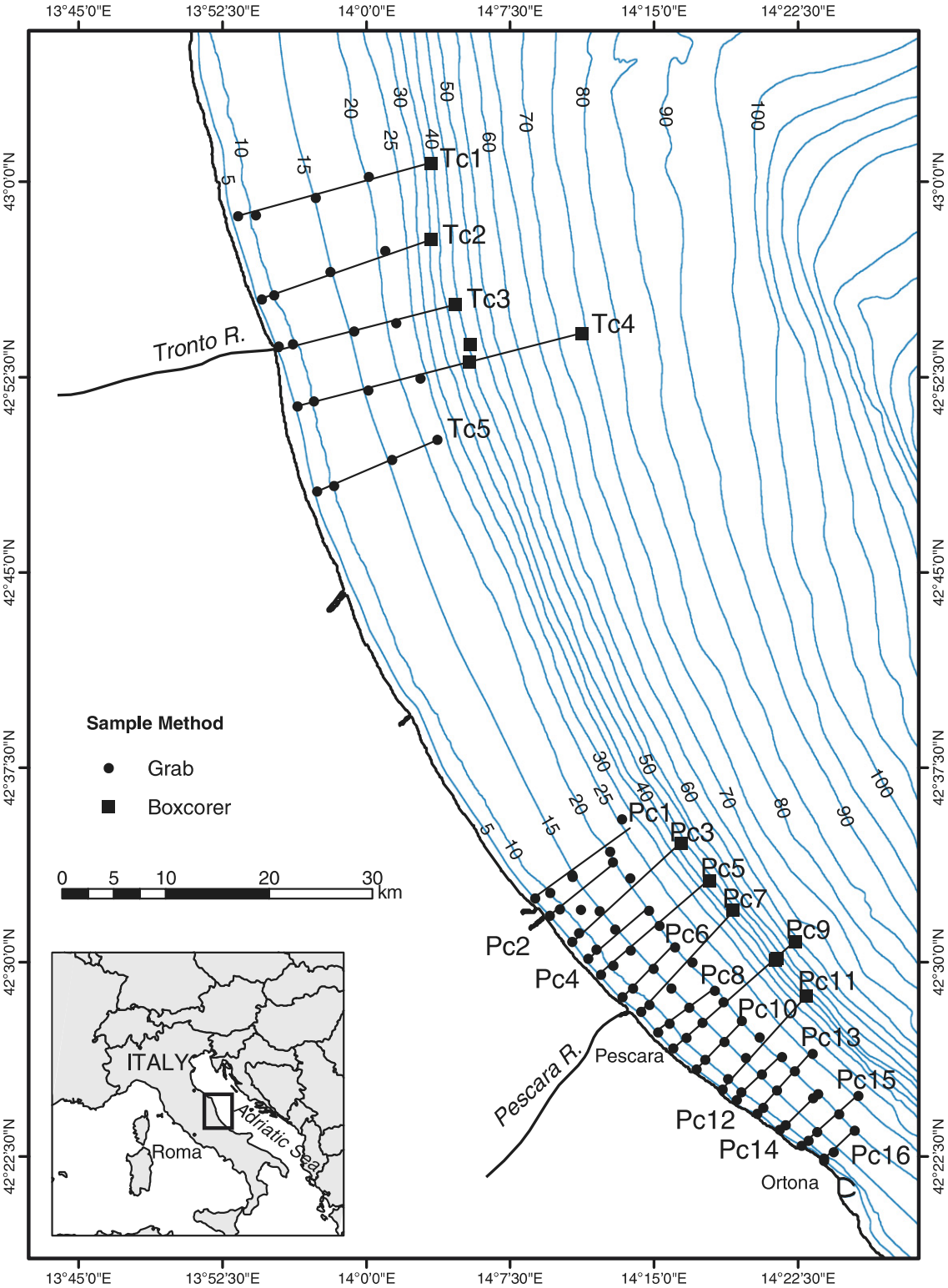

Fig. 1. Study site and sampling transects. Grab samples (●) were collected from the *M/N Ermione* and box corer samples (■) were acquired on the *R/V Urania*. A total of 101 samples were gathered from the five Tronto (Tc1–Tc5) and 16 Pescara (Pc1–Pc16) transects in April and May 2002.

of material in size class i to the total material analyzed. The three size class percent fractions (clay, silt, sand) were calculated by summing the particle concentrations across all size classes (0.75–256 μm), summing the concentrations across the range of each fraction (0.75–4 μm for clay, 4–64 μm for silt, 64–256 μm for sand) and then dividing the fractional concentration by the total. The mud fraction is the sum of the silt and clay fractions.

To estimate floc fraction in the sediments (f_s), the following equation is used (Curran et al., 2004; Fox et al., 2004):

$$f_s = \frac{\sum_{i=1}^{n\ class} C(i)}{\sum_{i=1}^{n\ class}\left(1+\left(\frac{d(i)}{d_f}\right)\right)C(i)}. \quad (2)$$

In Eq. (2), $C(i)$ is concentration of particles at size class i (kg m^{-3}), and d_f is a parameter called the "floc limit" (m). The floc limit is the particle diameter for which the fluxes of single grains and flocs are equal. Flux of particles smaller than the floc limit is dominated by floc deposition, while particles larger than the floc limit arrive at the seabed primarily as single grains. The floc limit is determined by applying an inverse model to a DIGS distribution of a seabed sediment sample (Curran et al., 2004; Fox et al., 2004). The dimensionless parameter f_s ranges from 0–1 with larger values corresponding to higher percentages of floc deposited sediment.

Specific surface area (SSA) 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 at the Darling Marine Center, University of Maine, was used to analyze specific surface area for all samples. Dry, homogenized sediment was washed and centrifuged twice, first with distilled water to remove salts and second with 10% ACS-grade acetone to remove water. Residual water was removed by freeze-drying and organic compounds combusted in a muffle furnace set at 350 °C. Monosorb runs were performed on each sample until two consecutive desorption counts were within 1% of each other.

Assuming metal concentrations were negligible in sand-dominated samples (Bremner and Willis, 1993; Emelyanov, 2001), only fine-grained samples were analyzed for heavy metals and were sent to ALS Chemex laboratories in Canada. Dried, homogenized sediment that passed through an ASTM E-11 No. 80 (180 μm) sieve was placed in plastic vials to be sent to the 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) depending on the protocols set by ALS Chemex. Mercury was quantified by cold vapor atomic absorption spectrometry (AAS).

3. Results

3.1. Parameter observations

On the Adriatic continental shelf, GMD decreases as depth and distance from the shore increase, with the smallest GMDs found at the deepest stations (Fig. 2). GMDs at depths shallower than 15 m are approximately 80 μm, and at depths larger than 20 m they are an order of magnitude smaller. The largest cross-shelf decreases in GMD occur between 15 and 20 m for the Tronto and between 15 and 25 for the Pescara. These zones of rapid change mark the SMT on this margin. The slight depth difference for the seaward flank of the SMT maybe accounted for by the Pescara shelf being marginally steeper.

The majority of the shallow stations' sediment have floc fractions in the sediment of 0.01–0.20 (Fig. 2). Floc fraction in the seabed near both rivers shows a noticeable increase at 20 m, with values reaching between 0.21 and 0.40. As a result of the abrupt change, sediment from all of the deep stations have floc fractions greater than 0.30. All of the Tronto transects show a seaward increase in f_s by 20 m, but sediment at eleven of the Pescara transects remains below 0.20 at the 20 m isobath. The similar depths of rapid change in GMD and f_s lend support to the hypothesis that the SMT marks a boundary in the depositional flux of flocs to the seafloor.

The mud fraction generally increases seaward and with depth for both river areas. Most stations shallower than 20 m show less than 50% mud. At 20 m on the Tronto and by 25 m on the Pescara the sediment is 50% or more mud. Deeper than 25 m, all stations are 76–100% mud.

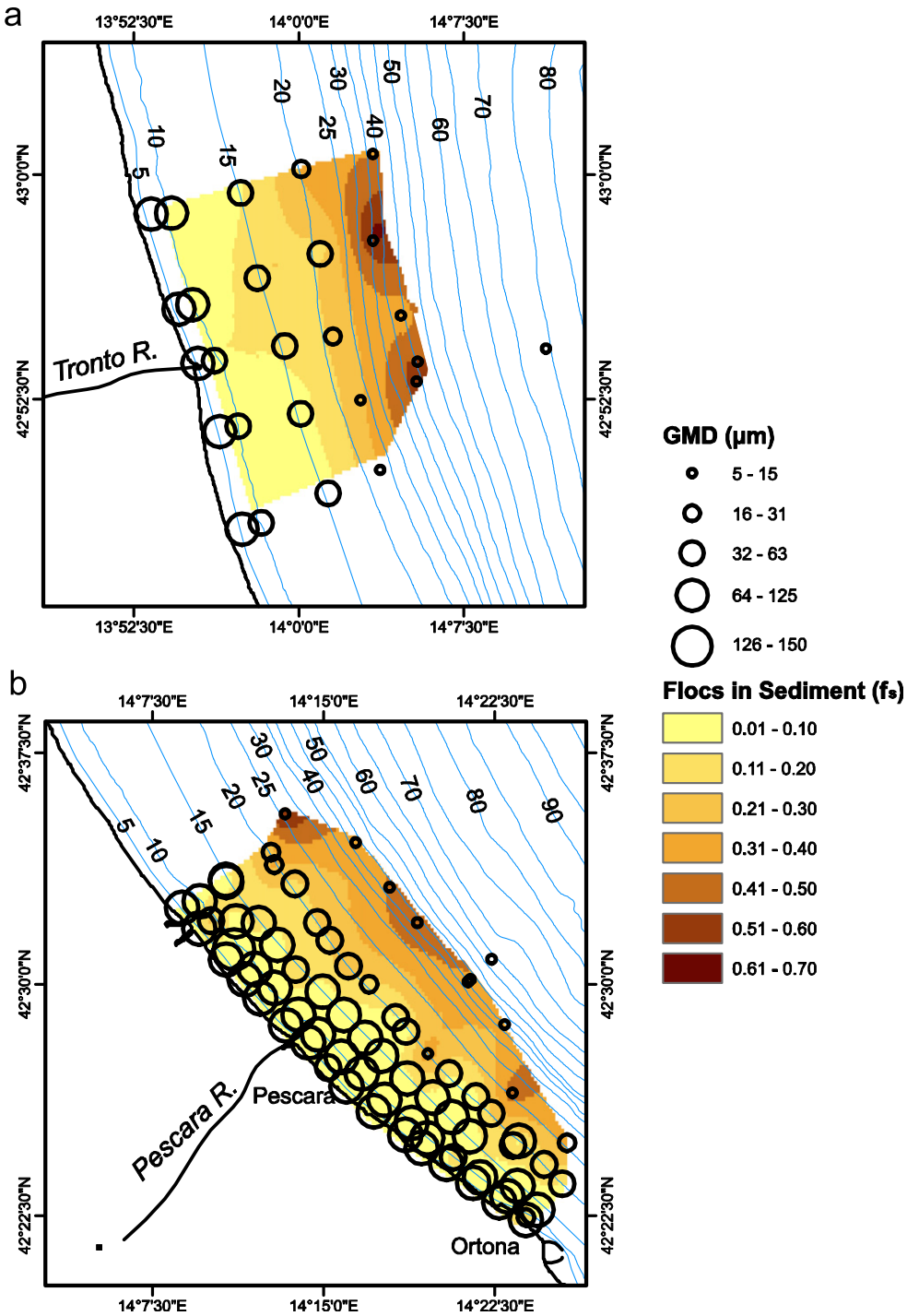

Fig. 2. Interpolated floc fraction in the sediment (f_s) and geometric mean diameter (GMD) distribution for (a) the Tronto SMT and (b) the Pescara SMT. Bathymetry is in meters. GMD shows a rapid shift to smaller sediment classifications where f_s increases rapidly.

Larger SSA corresponds to smaller grain size (Mayer and Rossi, 1982). Sediment from most of the stations in water depths of 15 m and shallower has SSAs of 2–15 $m^2 g^{-1}$ while sediment from 20 m and deeper has SSAs larger than 16 $m^2 g^{-1}$. For both rivers, the largest increase in SSA occurs between 15 and 20 m.

Among the 48 tested heavy metals, Cu, Pb and Zn are known to track with fine-grained sediment through particle scavenging (Libes, 1992) and therefore were investigated further sedimentologically. During the laboratory analysis, the minimum detectable amount was 0.2 mg-kg^{-1} for Cu, 0.5 mg-kg^{-1} for Pb and 2 mg-kg^{-1} for Zn. Metal concentrations were normalized against aluminum to identify enrichment not accounted for by sediment size. Shallower than 20 m, sediment contains Cu and Pb concentrations less than 20 mg-kg^{-1} and Zn concentration less than 40 mg-kg^{-1}. The largest change in metals concentration in the sediments off both the Tronto and Pescara rivers occurs between 15 and 20 m. Deeper than 25 m, Cu and Pb concentrations are larger than 31 mg-kg^{-1} while Zn concentration is larger than 61 mg-kg^{-1}. The connection to depth for the Tronto is more evident than for the Pescara, where the metal concentrations are less homogeneous. Copper and zinc show similar patterns of steady increase with depth along each transect. Lead, on the other hand, varies only slightly throughout the entire Pescara region and peaks along the 20-m isobath in the Tronto area.

3.2. Parameter correlations

Sediment size, surface area, floc fraction in the sediment and metals all show an abrupt change between 15 and 20 m. Pearson's correlation coefficients between the parameters were calculated to investigate links among these sediment properties (Table 1). At the 95% confidence level, GMD and f_s show a significant negative correlation of $R = -0.86$ ($p < 0.001$), indicating sediment with large GMD (coarse silts and sands) shows low values of f_s (Fig. 3a). The relationship between SSA and f_s has 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 suggests these size classes deposit more frequently as flocs, while larger size classes are more likely to deposit as single grains (Fig. 3b). A significant positive correlation ($R = 0.93$, $p < 0.001$) between floc fraction and mud percent shows that as the percentage of mud increases, the sediment is more likely to be floc deposited (Fig. 3c). 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.

Table 1
Correlation coefficients for SMT and metal parameters

	z	f_s	GMD	Mud	SSA	Cu	Pb	Zn
z	1.00							
f_s	0.76	1.00						
GMD	−0.74	−0.86	1.00					
Mud	0.78	0.93	−0.95	1.00				
SSA	0.83	0.89	−0.91	0.95	1.00			
Cu	0.57	0.76	−0.86	0.86	0.91	1.00		
Pb	0.49	0.71	−0.78	0.80	0.81	0.84	1.00	
Zn	0.72	0.84	−0.92	0.93	0.98	0.89	0.81	1.00

All have $p < 0.001$.
z = depth (m); f_s = floc fraction in sediments; GMD = geometric mean diameter (μm); Mud = mud fraction (%); SSA = specific surface area (m^2 g^{-1}); Cu = copper (mg-kg^{-1}); Pb = lead (mg-kg^{-1}); Zn = zinc (mg-kg^{-1}).

Correlation between floc fraction and other textural parameters can be explained in two ways. First, deposition of flocculated sediment may be the primary, but not exclusive, mechanism for transfer of mud from suspension to the seabed. Alternatively, floc fraction may simply be a metric of particle size, like GMD or SSA. In the former case, textural parameters and floc fraction can vary independently, whereas in the latter they cannot.

The interpretation placed on the correlation between floc fraction and other textural parameters in this study assumes that floc fraction exerts active control over GMD and SSA. This assumption is consistent with the fact that calculated floc fraction depends on the overall shape of the disaggregated size distribution, in particular on the shape of the coarse end of the distribution relative to the fine end (Kranck et al., 1996; Curran et al., 2004). Observations in another study demonstrate that particle size range in a sample can vary independently from the shape of the size distribution (Curran et al., 2004). In that study, small GMDs accompanied small floc fractions in low energy, source-distal turbidites whereas closer to the source, overall grain size was coarser and floc fraction was greater.

Exponential dependence of floc fraction on GMD and SSA describes the data better than linear dependence because of the difficulty in hydraulically sorting small sediment grains. Single small grains sink so slowly that delivery of fine sediment to the seabed in marine environments is dominated by flocs. Flocs, however, incorporate a full range of sediment sizes indistinguishable from that of the parent suspension, so they are unbiased samplers of

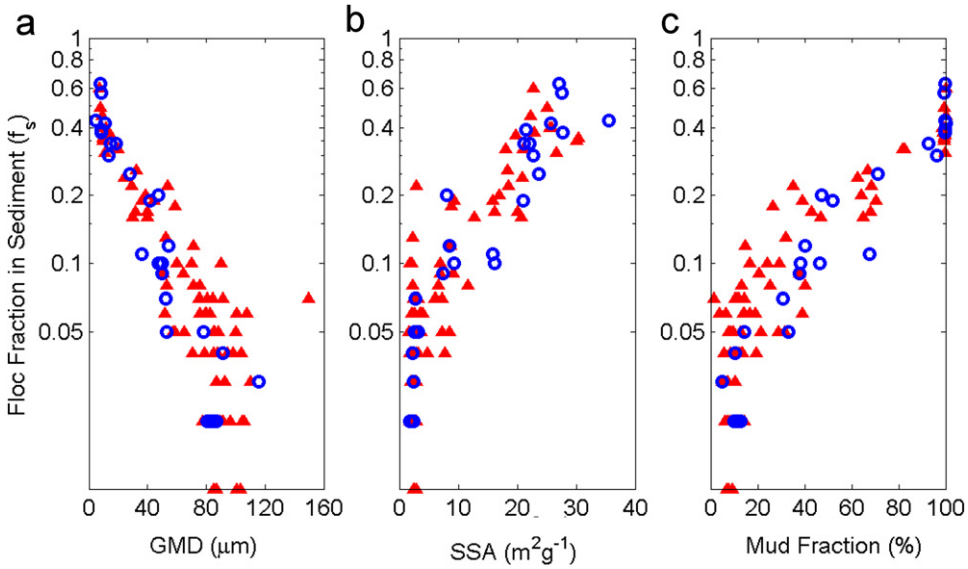

Fig. 3. Scatter plots showing variation of sediment textural parameters with floc fraction in the sediment (f_s). Tronto stations are represented by circles (○) and Pescara stations by triangles (▲). (a) Increasing geometric mean diameter (GMD) is associated with decreasing f_s, suggesting fine-grain sediment is deposited as flocs. (b) Increasing specific surface area (SSA) is associated with increasing f_s, indicating that sediment with high SSA is more likely to be floc deposited. (c) Mud fraction increases as f_s increases.

the water column (Kranck et al., 1996; Curran et al., 2004). In the absence of single grains larger than about 10 μm, flocculated suspensions tend to produce deposits with the same GMD and SSA as the overlying parent suspension, regardless of the specific amount of flocculation in suspension. Thus, at high values of f_s, changes in floc fraction beget relatively little change in values of SSA and GMD (Fig. 3). This fundamental limit to the size of sediment that can be sorted has been recognized previously and underlies the removal of particle sizes less than 10 μm from calculation of the "sortable silt" parameter (McCave et al., 1995). The "sortable silt" parameter has been used successfully in environmental interpretation of grain size in fine sediment deposits (Hall et al., 2001).

Given the link between SSA and f_s documented above, metal concentrations in the sediment should increase as f_s increases. These expected behaviors emerge from the correlation analysis. SSA and concentrations of Cu, Pb, and Zn are positively correlated ($R_{Cu} = 0.91$; $p < 0.001$; $R_{Pb} = 0.81$; $p < 0.001$; $R_{Zn} = 0.98$; $p < 0.001$) (Fig. 4). 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 relatively elevated Pb levels. Copper and zinc do not show elevated levels at these stations. With this exception,

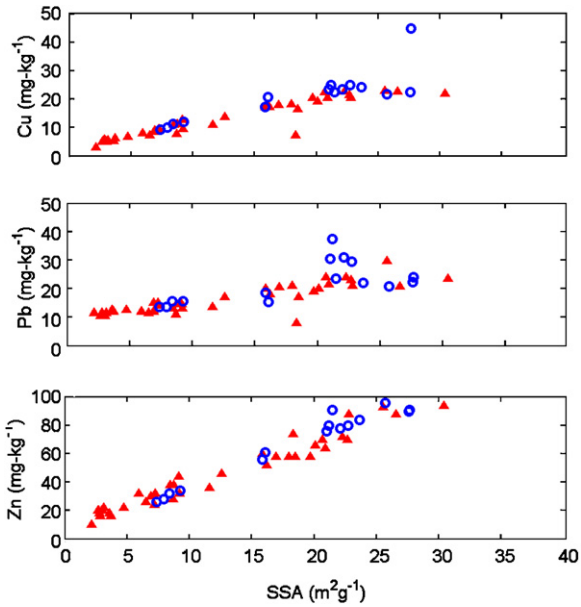

Fig. 4. Specific surface area (SSA)–metals scatter plots. Tronto stations are represented by circles (○) and Pescara stations by triangles (▲). Copper (*top panel*), lead (*middle panel*), and zinc (*bottom panel*) all show increasing concentrations with larger SSA.

both rivers show nearly identical behavior for SSA and metal concentration. Positive significant correlation also exists between f_s and the metals

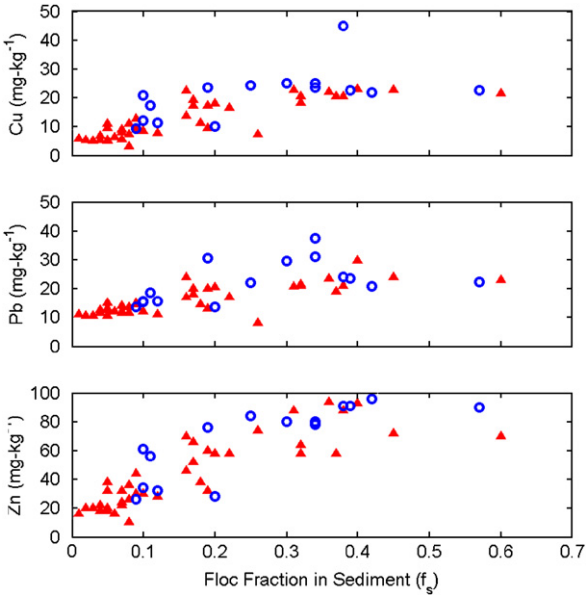

Fig. 5. Floc fraction in the sediment (f_s)–metals scatter plots. Copper (*top panel*), lead (*middle panel*), and zinc (*bottom panel*) all show an increasing trend with increasing f_s. This suggests that metals are deposited primarily by flocs.

($R_{Cu} = 0.76$; $p < 0.001$; $R_{Pb} = 0.71$; $p < 0.001$; $R_{Zn} = 0.84$; p < 0.001) (Fig. 5). As f_s increases, metal concentrations increase, although more scatter is observed compared to the SSA correlation. The slightly weaker correlations between f_s and the metals again could be due to the decreasing sensitivity of SSA to floc fraction at high values of the latter.

4. Discussion

4.1. Floc dynamics and the smt

Although the SMT is a sediment textural boundary (Chough and Kim, 1981; Stanley et al., 1983; Kachel and Smith, 1989; Demirpolat, 1991), the results here show that it can also be considered as a transition in depositional flux of flocculated sediment. The correlations between high f_s and GMD, SSA and mud fraction support this contention. Two factors that may affect the depositional flux of flocs are turbulent energy and sediment concentration. Floc deposition should increase when energy is low, because under these conditions fragile flocs can settle to the seafloor without being disrupted by turbulence (McCave, 1985; Hill et al., 2001; Curran et al., 2004). Deposition should also increase when suspended sediment concentration is high, because rapid floc formation is favored by abundant sediment (McCave, 1972; Stanley et al., 1983; Curran et al., 2004).

Turbulent energy and suspended sediment concentration were not measured in this particular study, so the relations between sediment concentration, energy and floc fraction in the sediment cannot be investigated explicitly. The links can be investigated by proxy, however. Two proxies are chosen for the proposed factors: depth as a proxy for energy and distance from river mouth (d) as a proxy for concentration. Of these two proxies, depth and f_s correlate for both rivers ($R_z = 0.77$, 0.76; $p < 0.001$, Tronto and Pescara, respectively) while distance is correlated for the Tronto area ($R_d = 0.70$; $p < 0.001$) but not the Pescara area ($R_d = 0.40$; $p < 0.001$). The relatively constant depth of the SMT, even in the vicinity of the river mouths can be explained in two ways. First, the constant depth may indicate that energy is the primary control on floc deposition for the Adriatic continental shelf. Alternatively, it may indicate that the rivers on this shelf are not the primary factor in determining suspended sediment concentration. Instead sediment advected in the Western Adriatic Coastal Current may be the dominant sediment source to the region. In either case, the rivers on this shelf apparently today play a minor role, if any, in setting the position of the SMT.

A temporal examination of the Pescara SMT was conducted as an alternative to using the sediment concentration proxy. The sediment loads of both the Tronto and Pescara rivers have been extensively altered by damming and aggregate extraction, reducing the supply of sediment to the shelf. Passega et al. (1967) described the grain size distribution of the Pescara area in the mid-1960s. Seafloor sediment was sampled from 15 cross-shelf transects at the 10-, 15-, 20-, 25-, 30-, 40- and 50-m isobaths. Passega et al., (1967) concluded that the SMT occurred at 30–40 m based on median grain size (M) from each station. By design, the present study reoccupied and sampled the same region. Depth averages were generated and cross-shelf profiles from 1967 and 2002 were compared (Fig. 6). The cross-shelf distribution of sediment texture has changed little in 35 years, despite the considerable decreases of suspended sediment input from the Pescara River (Aquater, 1982). This observation supports the contention that sediment advection from the north provides the source for SMTs and

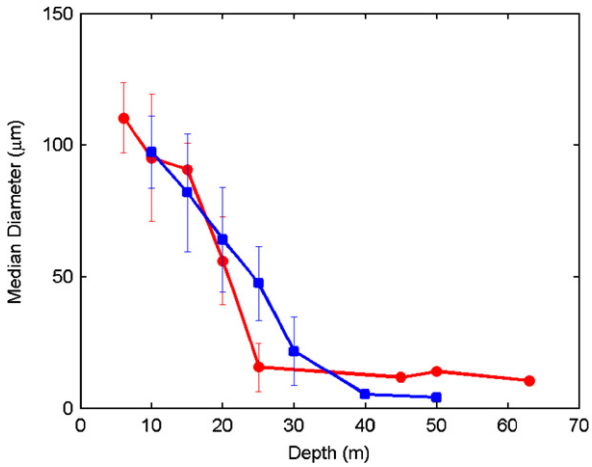

Fig. 6. Comparison of median grain size on the Pescara River shelf from this study and one from 35 years earlier (Passega et al., 1967). Cross-shelf depth-averaged median grain size from the Passega study are shown by squares (■) while data from this study are represented by circles (●). Error bars represent one standard deviation.

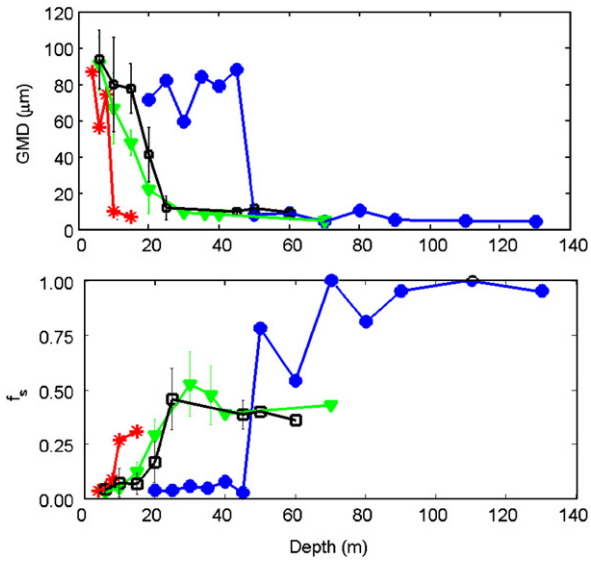

Fig. 7. Cross-shelf profiles of geometric mean diameter (GMD) and floc fraction in the sediment (f_s) for four rivers: Po (*), Tronto (▼), Pescara (□) and Eel (●). The Po (Fox et al., 2004) and Eel (Tim Milligan, unpublished data) profiles are from one transect only, while the Tronto and Pescara profiles are depth-averaged. Error bars on the Tronto and Pescara represent one standard deviation.

that energy remains the primary control for the Pescara SMT.

The association between floc deposition and the transition from sand to mud applies to other shelves, as well. 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 discharges $24.0 \times 10^6\,\mathrm{t\,yr^{-1}}$ of suspended sediment into the Pacific Ocean along the exposed Eel margin. The shelf is wave-dominated with a 30-year average significant wave height of 2.66 m (US National Buoy Data Center, Buoy # 46022). A mudline was identified at ~55 m by Wheatcroft and Borgeld (2000). The Po River discharges $17.0 \times 10^6\,\mathrm{t\,yr^{-1}}$ of suspended sediment into the semi-enclosed basin of the northwestern Adriatic Sea. Significant wave height is 0.73 m (Fain et al., 2007) and therefore similar to the Apennine section of the Adriatic continental shelf. The depth of the SMT on the Po prodelta, however, is in much shallower water at 8–10 m depth (Fox et al., 2004).

Depth-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 (Fig. 7). A drop in GMD accompanied by an increase in f_s across a small depth range defines each SMT. The Eel and Po SMTs are the most abrupt, followed by the Tronto and 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 ranges of 5–10 m water depth for all three systems. Similar behavior is observed for f_s where landward of the transitions, f_s is below 0.05 but increases rapidly at the transitions. On the Eel margin, f_s levels near unity. In contrast, Po f_s rises only to about 0.3 and on the Pescara and Tronto margins, f_s asymptotes to values just under 0.5. In summary, each of these margins is characterized by similar cross-shelf evolution in GMD and f_s. The margins differ in the extent to which sediment is floc-deposited seaward of the SMT.

Each progressively deeper SMT reflects a more wave-dominated system, which partly supports the hypothesis that wave energy controls the position of an SMT. The SMT on the prodelta of the Po River, however, is much shallower than the Apennine SMTs, despite the fact that wave regimes are similar (Fig. 7). The Po SMT is in 8–10 m of water to either side of the main mouth, but mud blankets the seabed to depths as shallow as 4 m directly off of the main mouth (Fox et al., 2004). These observations

suggest that in systems with large sediment input, SMT depth may be more strongly tied to concentration than in systems with lower supply. Observations made on the Amazon Shelf (Allison et al., 1995) suggest that in extreme cases the SMT can reach the shore. Similarly, the observation that f_s seaward of the SMTs increases with increasing depth of the SMT for the four rivers suggests that factors in addition to wave energy level determine f_s beyond the transition itself.

Understanding of the dynamic controls on the SMT will benefit from two lines of investigation in the future. First, a comparative study of the depths of the SMTs across a range of environments could be developed from a systematic survey of the literature and sedimentological databases. By comparing SMT depths to environmental variables such as wave climate, tidal flows, and river discharge, better understanding of the dominant controls on SMT depth could be generated. Second, detailed measurements of seabed stresses and in situ suspended sediment concentration and size distributions in the vicinity of SMTs will produce insight into the boundary layer conditions that lead to relatively abrupt transitions in seabed grain size.

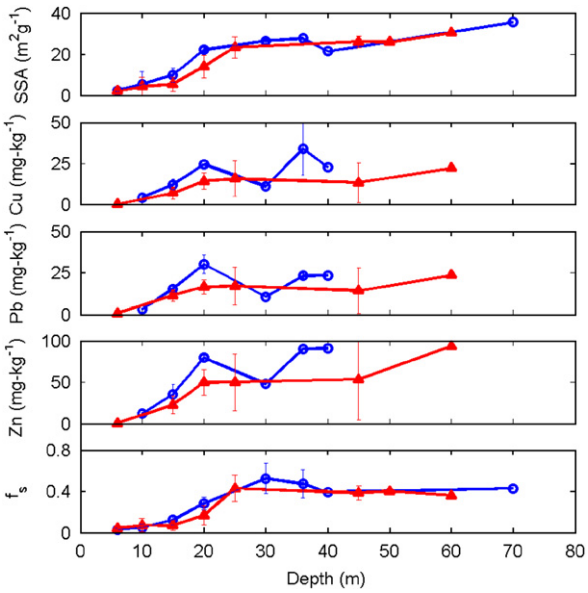

Fig. 8. Cross-shelf average profiles for specific surface area (SSA), metals and floc fraction in the sediment (f_s). Tronto stations are represented by circles (○) and Pescara stations by triangles (▲). Only stations 15 m or deeper were analyzed for metals except for a 10-m station off the Tronto and a 6-m station off the Pescara. Error bars represent one standard deviation.

4.2. Metal concentrations and floc deposition

Cross-shelf profiles of depth-averaged SSA and metal concentrations (Fig. 8) and the high correlation between SSA and the metals agree with conclusions from many studies that high metal concentrations in sediment rely on large SSA and small grain size (Mayer and Rossi, 1982; Horowitz and Elrick, 1988; Buckley and Cranston, 1991). The most abrupt increases in metal concentrations occur across 15–20 m water depth for both rivers. In addition, low f_s values and low metal concentrations are found at shallow depths, and high values of f_s and high metal concentrations are found in deeper water. The most abrupt increases in metal concentrations and f_s are at the same depth, which explains why f_s correlates so strongly with the metal concentrations.

Milligan and Loring (1997) presented a clear connection between contaminated sediment and floc deposition in Ship Harbour, Nova Scotia, Canada. While evaluating quantities of Cd and Zn, they defined bottom sediment as "floc deposited" rather than as the traditional categories of $<63\,\mu m$ or $<16\,\mu m$ and formalized the metal–floc association. Data from the Adriatic continental shelf supports the Milligan and Loring approach to parameterization of bottom sediment size distributions and associated metal concentrations.

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 for f_s has been identified as energy, a logical extrapolation can be made: particles with large SSA provide adsorption sites for metals and when these particles enter lower energy zones conducive to flocculation, net floc deposition increases and metals deposit on the seafloor. Hence, metal deposition and energy zones are implicitly connected, even in regions where advection plays a significant role in sediment distribution. Metal concentrations would be expected to be higher in lower energy regimes although a localized relatively large sediment supply could conceivably cause metals to accumulate in higher energy, shallower water settings. 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 may affect site availability for metals adsorption (Ongley et al., 1992; Pettine et al., 1994; Dyer and Manning, 1999).

5. Conclusions

The transition from sand in shallow water to mud in deeper water that occurs on many continental shelves records a change in the net depositional flux of fine-grained flocculated sediment to the seabed. This interpretation of the sand–mud transition (SMT) is based on correlations between a process-based parameter, floc fraction in sediment (f_s), with other measured properties of seabed sediments on the Adriatic continental shelf of Italy. Large floc fractions are associated with small mean sediment diameters and high specific surface areas. Floc fractions transitioned from 0.05 to 0.5 in water depths of 15–20 m off the mouth of the Tronto River and in depths of 15–25 m seaward of the mouth of the Pescara River. Across the same depth range in both areas, GMD fell from 80 to 10 μm, and SSA rose sharply. Correlation calculations are negatively significant between f_s and GMD and positively significant between f_s and SSA, which formally supports the connection between floc delivery to the seabed of fine-grained sediment and the association of f_s with the SMT.

Concentration of three heavy metals (Cu, Pb, Zn) in the collected sediment was quantified to explore how metals correlate with f_s and the SMT. All three metals increased in concentration across the SMT with Cu and Zn showing the strongest signal. The metals were significantly correlated with SSA and f_s, indicating that flocs are the primary transport vector for metals.

The similarity between the modern Pescara SMT with one characterized in the 1960s indicates that reduced sediment supply has produced minimal change in the depth of the transition, a finding that implicates energy as the dominant controlling factor on SMT depth on this margin. In contrast, on the Po margin, which receives an order of magnitude more sediment each year but is exposed to a similar wave climate, the depth of the SMT apparently responds to suspended sediment concentration as well as energy levels. By implication, seafloor metals distribution should be related to energy levels on margins that are not influenced by a major sediment source, with higher concentrations found in lower energy regimes. On margins with large sediment supply, metals may be able to accumulate in higher energy, shallower water settings. Future work should consider how floc fraction and accompanying sediment properties vary as functions of concentration and energy on a range of different continental shelves.

Acknowledgements

Many thanks to the ships' crews, laboratories and people on both sides of the Atlantic who helped make this research possible, especially Alfredo Boldrin, Fabio Trincardi, Brent Law, Paul MacPherson, Larry Mayer and Linda Schick. This work was supported by United States ONR contracts N00014-97-1-0160 and N00014-99-1-0113.

References

Allison, M.A., Nittrouer, C.A., Kineke, G.C., 1995. Seasonal sediment storage on mudflats adjacent to the Amazon River. Marine Geology 125, 303–328.

Aquater. 1982. Studio generale per la difesa delle coste: prima fase. Regione Marche. Relazione generale, 1. Rapporti generale, 176p. 2. Relazione di settore, 706p.

Artegiani, A., Bregant, D., Paschini, E., Pinardi, N., Raicich, F., Russo, A., 1997. The Adriatic Sea general circulation. Part II. Journal of Physical Oceanography 27, 1515–1532.

Boldrin, A., Juračić′, M., Menegazzo Vitturi, L., Rabitti, S., Rampazzo, G., 1989. Geochemical considerations on trace element distributions in suspended matter and sediments at the river–sea interface, Adige River mouth, northern Adriatic Sea. Applied Geochemistry 4, 409–421.

Brassard, P., Kramer, J.R., McAndrews, J., Mueller, E., 1994. Metal–sediment interaction during resuspension. Hydrobiologia 284, 101–112.

Bremner, J.M., Willis, J.P., 1993. Mineralogy and geochemistry of the clay fraction of sediments from the Namibian continental margin and adjacent hinterland. Marine Geology 115, 85–116.

Buckley, D.E., Cranston, R.E., 1991. Grain size in oceanography. In: Syvitski, J.P.M. (Ed.), Principles, Methods and Application of Particle Size Analysis. Cambridge University Press, Cambridge, pp. 311–331.

Chough, S.K., Kim, D.C., 1981. Dispersal of fine-grained sediments in the southeastern Yellow Sea: a steady-state model. Journal of Sedimentary Petrology 51 (3), 721–728.

Curran, K.J., Hill, P.S., Milligan, T.G., Cowan, E.A., Syvitski, J.P.M., Konings, S.M., 2004. Fine-grained sediment flocculation below the Hubbard Glacier meltwater plume, Disenchantment Bay, Alaska. Marine Geology 203, 83–94.

Davis, K.S., Slowey, N.C., Stender, I.H., Fiedler, H., Bryant, W.R., Fechner, G., 1996. Acoustic backscatter and sediment textual properties of inner shelf sands, northeastern Gulf of Mexico. Geo-Marine Letters 16, 273–278.

Demirpolat, S., 1991. Surface and near-surface sediments from the continental shelf off the Russian River, northern California. Marine Geology 99, 163–173.

Droppo, I.G., Irvine, K.N., Jaskot, C., 2002. Flocculation/aggregation of cohesive sediments in the urban continuum: implications for stormwater management. Environmental Technology 23, 27–41.

Dyer, K.R., Manning, A.J., 1999. Observation of the size, settling velocity and effective density of flocs, and their fractal dimensions. Journal of Sea Research 41 (1-2), 87–95.

Els, B.G., Mayer, J.J., 1998. Coarse clastic tidal and fluvial sedimentation during a large late Archean sea-level rise; the Turffontein Subgroup in the Vredefort Structure, South Africa. In: Alexander, C.R., Davis, R., Henry, J. (Eds.), Tidalites: Processes & Products. SEPM Special Publication 61, Tulsa, OK, pp. 155–165.

Emelyanov, E.M., 2001. Biogenic components and elements in sediments of the central Baltic and their redistribution. Marine Geology 172, 23–41.

Fain, A.M.V., Ogston, A.S., Sternberg, R.W., 2007. Sediment transport event analysis on the western Adriatic continental shelf. Continental Shelf Research 27, 431–451.

Farroni, A., Magaldi, D., Tallini, M., 2002. Total sediment transport by the rivers of Abruzzi (central Italy): prediction with the RAIZAL model. Bulletin of Engineering Geology and the Environment 61, 121–127.

Fowler, S.W., Knauer, G.A., 1986. Role of large particles in the transport of elements and organic compounds through the oceanic water column. Progress in Oceanography 16, 147–194.

Fox, J.M., Hill, P.S., Milligan, T.G., Boldrin, A., 2004. Flocculation and sedimentation on the Po River Delta. Marine Geology 203, 95–107.

Giani, M., Gabellini, M., Pellegrini, D., Costantini, S., Beccaloni, E., Giordano, R., 1994. Concentration and partitioning of Hg, Cr and Pb in sediments of dredge and disposal sites of the northern Adriatic Sea. Science of the Total Environment 158, 97–112.

Goff, J.A., Orange, D.L., Mayer, L.A., Hughes-Clarke, J.E., 1999. Detailed investigation of continental shelf morphology using a high-resolution swath sonar survey; the Eel margin, northern California. Marine Geology 154 (1–4), 255–269.

Grant, J., Emerson, C.W., Hargrave, B.T., Shortle, J.L., 1991. Benthic oxygen consumption on continental shelves off Eastern Canada. Continental Shelf Research 11 (8–10), 1083–1097.

Hall, I.R., McCave, I.N., Shackleton, N.J., Weedon, G.P., Harris, S.E., 2001. Intensified deep Pacific inflow and ventilation during Pleistocene glacial times. Nature 412, 809–812.

Harris, M.K., Thayer, P.A., Amidon, M.B., 1997. Sedimentology and depositional environments of middle Eocene terrigenous-carbonate strata, southeastern Atlantic Coastal Plain, USA. Sedimentary Geology 108 (1–4), 141–161.

Hill, P.S., Voulgaris, G., Trowbridge, J.H., 2001. Controls on floc size in a continental shelf bottom boundary layer. Journal of Geophysical Research 106 (C5), 9543–9549.

Horowitz, A.J., Elrick, K.A., 1988. Interpretation of bed sediment trace metal data: methods for dealing with the grain size effect. In: Lichtenberg, J.J., Winter, J.A., Weber, C.I., Fradkin, L. (Eds.), Chemical and Biological Characterization of Sludges, Sediments, Dredge Spoils and Drilling Muds, ASTM STP 976. American Society for Testing and Materials, Philadelphia, pp. 114–128.

Italian Sea Wave Network, 2002. Italian Agency for Environmental Protection and Technical Services, Tides and Waves Monitoring Department. World Wide Web page, http://www.apat.gov.it/site/en-GB/default.html.

Kachel, N.B., Smith, J.D., 1989. Sediment transport and deposition on the Washington continental shelf. In: Landry, M.R., Hickey, B.M. (Eds.), Coastal Oceanography of Washington and Oregon. Elsevier, Amsterdam, pp. 287–348.

Kranck, K., 1980. Experiments on the significance of flocculation in the settling of fine-grained sediment in still water. Canadian Journal of Earth Sciences 17, 1517–1526.

Kranck, K., Milligan, T.G., 1985. Origin of grain size spectra of suspension deposited sediment. Geo-Marine Letters 5, 61–66.

Kranck, K., Smith, P.C., Milligan, T.G., 1996. Grain-size characteristics of fine-grained unflocculated sediments. 1. 'One-round' distributions. Sedimentology 43, 589–596.

Libes, S.M., 1992. An Introduction to Marine Biogeochemistry. Wiley, New York.

Mayer, L., 1994. Surface area control of organic carbon accumulation in continental shelf sediments. Geochimica et Cosmochimica Acta 58 (4), 1271–1284.

Mayer, L., Rossi, P.M., 1982. Specific surface areas in coastal sediments: relationships with other textural factors. Marine Geology 45, 241–252.

McCave, I.N., 1972. Transport and escape of fine-grained sediment from shelf areas. In: Swift, D.J.P., Duane, D.B., Pilkey, O.H. (Eds.), Shelf Sediment Transport: Process and Pattern. Dowden, Hutchinson and Ross, pp. 225–247.

McCave, I.N., 1985. Mechanics of deposition of fine-grained sediments from nepheloid layers. Geo-Marine Letters 4, 243–245.

McCave, I.N., Manighetti, B., Robinson, S.G., 1995. Sortable silt and fine sediment size/composition: parameters for palaeocurrent speed and palaeoceanography. Paleoceanography 10, 593–610.

Milligan, T.G., Kranck, K., 1991. Electroresistance particle size analyzers. In: Syvitski, J.P.M. (Ed.), Principles, Methods and Application of Particle Size Analysis. Cambridge University Press, Cambridge, pp. 109–118.

Milligan, T.G., Loring, D.H., 1997. The effect of flocculation on the size distributions of bottom sediment in coastal inlets: implications for metal transport. Water, Air and Soil Pollution 99, 33–42.

Milliman, J.D., Syvitski, J.P.M., 1992. Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers. Journal of Geology 100, 525–544.

Ongley, E.D., Krishnappan, B.G., Droppo, I.G., Rao, S.S., Maguire, R.J., 1992. Cohesive sediment transport: emerging issues for toxic chemical management. Hydrobiologia 235–236, 177–187.

Palanques, A., Drake, D.E., 1990. Distribution and dispersal of suspended particulate matter on the Ebro continental shelf, northwestern Mediterranean Sea. Marine Geology 95, 193–206.

Passega, R., Rizzini, A., Borghetti, G., 1967. Transport of sediment by waves, Adriatic Coastal Shelf, Italy. AAPG Bulletin 51 (7), 1304–1319.

Pettine, M., Camusso, M., Martinotti, W., Marchetti, R., Passino, R., Queirazza, G., 1994. Soluble and particulate metals in the Po River: factors affecting concentrations and partitioning. Science of the Total Environment 145, 243–265.

Puig, P., Palanques, A., Sanchez-Cabeza, J.A., Masqué, P., 1999. Heavy metals in particulate matter and sediments in the southern Barcelona sedimentation system (northwestern Mediterranean). Marine Chemistry 63, 311–329.

Schiff, K.C., 2000. Sediment chemistry on the mainland shelf of the Southern California Bight. Marine Pollution Bulletin 40 (3), 268–276.

Snelgrove, P.V.R., Butman, C.A., 1994. Animal sediment relationships revisited—cause versus effect. Oceanography and Marine Biology 32, 111–177.

Stanley, D.J., Addy, S.K., Behrens, E.W., 1983. The mudline: variability of its position relative to shelfbreak. In: Stanley, D.J., Moore, G.T. (Eds.), The Shelfbreak: Critical Interface on Continental Margins. SEPM Special Publication 33, Tulsa, OK, pp. 279–298.

Sternberg, R.W., Berhane, I., Ogston, A.S., 1999. Measurement of size and settling velocity of suspended aggregates on the northern California continental shelf. Marine Geology 154 (1–4), 43–53.

Urick, R.J., 1983. Principles of Underwater Sound. McGraw-Hill, New York.

Wheatcroft, R.A., Borgeld, J.C., 2000. Oceanic flood deposits on the northern California shelf: large-scale distribution and small-scale properties. Continental Shelf Research 20 (16), 2163–2190.

Wright, L.D., Nittrouer, C.A., 1995. Dispersal of river sediments in coastal seas: six contrasting cases. Estuaries 18 (3), 494–508.

Zhang, J., Huang, W.W., Liu, S.M., Liu, M.G., Yu, Q., Wang, J.H., 1992. Transport of particulate heavy metals towards the China Sea: a preliminary study and comparison. Marine Chemistry 40, 161–178.

Zwolsman, J.J.G., VanEck, B.T.M., VanderWeijden, C.H., 1997. Geochemistry of dissolved trace metals (Cd, Cu, Zn) in the Scheldt estuary, southwestern Netherlands: impact of seasonal variability. Geochimica et Cosmochimica Acta 61 (8), 1635–1652.