

## Aggregation dynamics along a salinity gradient in the Bach Dang estuary, North Vietnam

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### ABSTRACT

Variations of the sticking properties of transparent exopolymeric particles (TEP) were investigated by studying the interactions between latex beads and TEP precursors collected along a salinity gradient in the Bach Dang estuary, North Vietnam. For each sampling station, a suspension of TEP and beads was prepared and the formation of mixed aggregates was monitored in the laboratory under controlled turbulence intensity. The number of beads attached to TEP per volume of TEP increased from  $0.22 \times 10^{-3} \pm 0.15 \times 10^{-3} \mu\text{m}^{-3}$  to  $5.33 \times 10^{-3} \pm 1.61 \times 10^{-3} \mu\text{m}^{-3}$ , from low (<1) to high (>28) salinities, respectively. The sudden increase in TEP sticking properties from salinity 10 to 15 suggests the occurrence of an “aggregation web” resulting from the stimulation of aggregation processes. For a given turbulence level, the formation of large aggregates should be enhanced seaward. The presence of a higher fraction of large aggregates seaward is supported by the increase of the slope of the particle size spectra measured *in situ*. The observed increase in TEP sticking properties toward high salinities may affect the vertical export pump in estuaries. This study suggests that the transition from a low to a high physico-chemical reactivity of TEP along estuaries may result in a succession from recycling for salinity <10 to enhanced aggregation/sedimentation processes and export dominated systems for salinity >10.

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### 1. Introduction

The magnitude of vertical flux in aquatic systems, and thus their ability to export organic matter, is determined by the abundance and sinking characteristics of large organic aggregates (Shanks and Trend, 1980; Smetacek, 1985; Fowler and Knauer, 1986; Alldredge and Silver, 1988; Asper et al., 1992; Jackson and Burd, 1998). The abundance of large aggregates mostly depends on the balance between the rate at which particles collide, on the probability of adhesion upon collision (i.e., sticking coefficient; Kiørboe and Hansen, 1993; Passow and Alldredge, 1995), and on the turbulence-induced rupture of aggregates (Fugate and Friedrichs, 2003; Bache, 2004). The influence of turbulence intensity on particles has been largely documented (e.g. van Leussen, 1994;

Uncles et al., 2006; Winterwerp, 2006). In the aggregation process, while particle concentration, size, and fluid dynamics control collision rate, adhesion depends upon the physico-chemical properties of the particles (Jackson, 1990).

The class of highly abundant transparent exopolymeric particles (TEP) (Alldredge et al., 1993) proved to play a critical role in mechanisms regulating aggregation and sedimentation in marine (Logan et al., 1995; Dam and Drapeau, 1995; Engel, 2000; Passow et al., 2001; Fabricius et al., 2003; Wolanski et al., 2003; Engel et al., 2004; Mari and Robert, 2008; Mari, 2008), fresh water (Grossart et al., 1997), and estuarine systems (Wolanski and Spagnol, 2003; Wurl and Holmes, 2008; Wetz et al., 2009). TEP are formed by coagulation of polysaccharidic fibrils, which represent the dominant part of the exopolymeric substances released by phytoplankton and other microorganisms (Bhaskar et al., 2005). Due to the stickiness properties of TEP, they present enhanced coagulation efficiency (Kiørboe and Hansen, 1993; Jackson, 1995) which tends to promote the appearance of larger aggregates. This latter, along with the altered density of the biologic/mineral blend, influence their sinking velocity (Azetsu-Scott and Passow, 2004).

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The sticky nature and the structural integrity of TEP are linked to the presence of a high fraction of polysaccharides with sulfate ester groups (Zhou et al., 1998), which give them the ability to form cation bridges (Kloareg and Quatrano, 1988) and hydrogen bonds (Mopper et al., 1995; Chin et al., 1998).

In order to determine the role played by TEP in aggregation/sedimentation processes, one needs to examine their abundance and assess their sticking properties under different conditions. While most studies on TEP addressed their concentrations in various aquatic environments, only a few focused on their sticking properties and their potential variations. All the studies conducted so far concluded that TEP stickiness was much higher than that of other particles, but also quite variable (Kiørboe and Hansen, 1993; Kiørboe et al., 1994; Dam and Drapeau, 1995; Logan et al., 1995; Engel, 2000; Mari and Robert, 2008). Since TEP sticking properties depend upon their physico-chemical characteristics, they may vary according to environmental conditions. Estuaries are transition zones where physico-chemical processes of transformation of dissolved and particulate matter are particularly dynamic due to the presence of strong gradients (e.g., salinity, pH, metals, cations, turbulence) that alter the structure of exopolysaccharides (Baalousha et al., 2006). Therefore, TEP may exhibit wide temporal and spatial variations of their sticking properties within an estuarine domain, which in turn could affect the biogeochemical functioning of the system. TEP-induced aggregation process is one of the key factors to investigate in estuaries as it affects the fate of suspended aggregates (Wetz et al., 2009). Several studies focused on the influence of the concentration of suspended particles, turbulence (e.g. Uncles et al., 2006), and salinity (e.g. Thill et al., 2001) on aggregation processes. Although studies on the influence of the physico-chemical characteristics of the suspended organic matter are scarce, they have showed that organic matter characteristics modified aggregation processes (Ayukai and Wolanski, 1997; van der Lee, 2000; Mikes et al., 2004).

The aim of the present study was to describe changes in TEP sticking properties along salinity gradients, and to discuss the implications of such variations for the cycling of elements in the tropical estuary of the Bach Dang River via control over the balance between retention and export.

## 2. Materials and methods

### 2.1. Study area

Located at the North-eastern part of the Red River delta, Haiphong is the third largest city and second largest harbor of Vietnam. The Haiphong Bay receives water from the Cam and Bach Dang Rivers whose confluence is located in the estuary, 10 km from the mouth, and from the Lach Tray River (Fig. 1). The Bach Dang River flows in northern Vietnam through the Yen Hung district of the Quang Ninh province and the Thuy Nguyen district of Haiphong. The Cam and Lach Tray Rivers are tributaries of the Van Uc River, the further Eastern main tributary of the Red River.

Haiphong Bay is characterized by a funnel-shaped estuary and an intricate tidal flat and creek system. The tide is a dominant dynamic factor and regulates its morphology and sedimentology (Tran et al., 2000). The tide is diurnal and its range in Haiphong is about 4 m in spring tide.

The hydrological regime strongly depends on the monsoon regime, with the northeast monsoon from November to May in the dry season and the southwest monsoon from May to November in the wet season. The rainfall is  $\sim 1500 \text{ mm yr}^{-1}$ . The average wind speed is  $3\text{--}4 \text{ m s}^{-1}$ , and reaches up to  $45 \text{ m s}^{-1}$  during typhoons. The average wave height is  $0.5\text{--}1.0 \text{ m}$  and the prevalent directions (East, Southeast and South) follow the wind climate which depends on the monsoon regime. The average yearly temperature is  $23.5 \text{ }^\circ\text{C}$ .

The average yearly river discharge into the Haiphong Bay lies in the range  $350\text{--}440 \text{ m}^3 \text{ s}^{-1}$  and the average suspended sediment concentration between  $290$  and  $360 \text{ mg L}^{-1}$  (Tran, 1993). For comparison, the average discharge of the Red River at the Son Tay gauging station (upstream of the bifurcation into a number of distributaries creating the Red River delta) is  $4300 \text{ m}^3 \text{ s}^{-1}$  ( $1200 \text{ m}^3 \text{ s}^{-1}$  in the dry season and  $14\,000 \text{ m}^3 \text{ s}^{-1}$  in the flood season, values based on the years 1956–1998) and the average suspended sediment concentration is close to  $1000 \text{ mg L}^{-1}$ , varying between  $200$  and  $1400 \text{ mg L}^{-1}$  in the dry and wet seasons, respectively (van Maren and Hoekstra, 2004; van Maren, 2007). The interface between saline and fresh water depends on the river flow, the tidal cycle and the river morphology. The saline intrusion

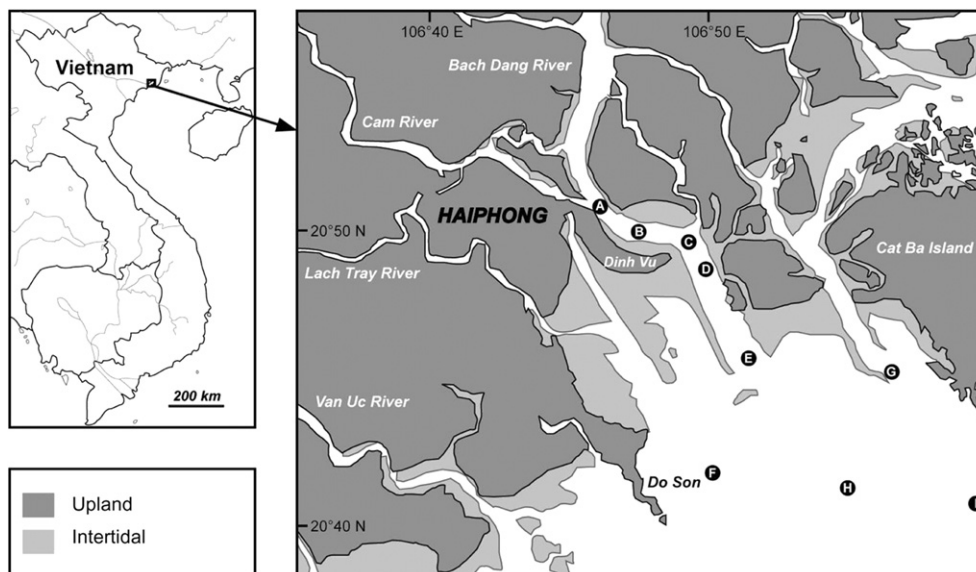


Fig. 1. Map of the study area with position of the sampling stations.

into the Bach Dang estuary is significant only during the dry season, especially from February to April.

## 2.2. Sampling

Sampling was performed using a 12-m coastal vessel during neap tides, in the rainy (July 2009) and dry (March 2010) seasons. Water samples were collected at 9 stations (Fig. 1) and 12 sampling occasions (station G has been sampled twice, and station H has been sampled 3 times) along the salinity gradient. For the determination of TEP sticking properties at each station, 5 L of water were sampled at 1 m under the surface using a 5-L Niskin bottle; 2 L were brought back to the laboratory within 2 h for aggregation experiments and 500-mL were fixed onboard with formaldehyde (1%) in order to determine the *in situ* TEP volume concentration. The vertical stratification was described at each station using a Seabird SBE 19 + CTD probe equipped with an OBS sensor.

## 2.3. Turbulent dissipation rate *in situ*

The range for the turbulent dissipation rate was evaluated by assessing instantaneous cross-sectional velocity profiles at stations A and C over one full spring tidal cycle, during the wet and dry seasons (5 or 6 days before or after sampling, during neap tides), using a 600 kHz acoustic Doppler current profiler (ADCP RDI Workhorse in bottom tracking mode) configured for a 0.5 m bin size. The turbulent kinetic energy dissipation rate integrated over the water column was calculated as a function of wind and mean current magnitude averaged over the water column (van der Lee et al., 2009):

$$\varepsilon = k_b \frac{u_{av}^3}{h_w} + k_s \frac{w^3}{\psi h_w} \quad (1)$$

where  $u_{av}$  is the depth-averaged water velocity,  $w$  is the wind velocity, and  $\psi$  the ratio between water and air density,  $h_w$  is the height of the water column and  $k_b$  (0.0025 for muddy bed) and  $k_s$  (0.0012) are the bottom and surface drag coefficients, respectively. The contribution of wind-induced turbulent kinetic energy dissipation rate was estimated from wind data collected in Haiphong City during the two sampling campaigns. Although the contribution of wind to the production of turbulence was higher during wet season than dry season (Table 1), its contribution was only significant during the wet season at station A (i.e. about 20% of the turbulence). In terms of seasonal variation of  $\varepsilon$ , a diminution was observed between the wet and dry seasons by 34 and 73% at the station A and C respectively.

## 2.4. Particle size spectra

The distribution of natural aggregates (including TEP and other particles) in the water column was determined using a submersible laser particle size analyzer (LISST-100X Type-C; Sequoia Scientific,

Inc.). The LISST-100X provides the concentration of particles per size class. Counts were automatically classified according to their equivalent spherical diameter (ESD;  $\mu\text{m}$ ) into 32 logarithmic size classes between 2.5 and 500  $\mu\text{m}$ . The acquisition frequency was set to 1 Hz. The particle size spectra were described by a power relation of the type  $N(d) = kd^{-\delta}$ , where  $N$  is the number of particles per unit volume per size class ( $\#\text{mL}^{-1} \mu\text{m}^{-1}$ ), and  $d$  is the equivalent spherical diameter of particles in  $\mu\text{m}$ . The constant  $k$  depends on the concentration of particles and  $\delta$  describes the size distribution; the smaller  $\delta$  is, the larger the fraction of large particles (Gonzalez and Hill, 1998; Jouon et al., 2008). The constant  $\delta$  was estimated from regressions of  $\log [N]$  vs.  $\log [d]$ . Additional CTD and LISST profiles, achieved in between stations sampled for investigating the sticking properties of TEP, were used to describe variations of the particle spectral slopes along the salinity gradient.

## 2.5. Experimental set-up for the determination of TEP sticking properties

Variations of the sticking properties of TEP along the salinity gradient were examined following the method detailed in Mari and Robert (2008). Briefly, seawater was filtered through GF/C Whatman filters (nominal pore size = 1.2  $\mu\text{m}$ ) of 47 mm diameter at low and constant vacuum pressure (<15 kPa) in order to remove particulate matter, including large TEP. Since the TEP pool takes root in the submicrometer size fraction, removing the >1.2  $\mu\text{m}$  fraction allows concentrating on the original material playing the role of biological glue, i.e. the TEP precursors. Polybead Carboxylate microspheres of 6  $\mu\text{m}$  diameter (Polysciences, Inc., initial concentration = 0.025  $\text{g mL}^{-1}$  for 2.5% solid volume, density = 1.05  $\text{g cm}^{-3}$ ) were added to the filtrate containing TEP precursors, to yield a final concentration of ca. 10,000  $\text{mL}^{-1}$ . The filtrate was put inside 2-L containers of a mixing device generating small-scale turbulence. This device is composed of two grids oscillating vertically inside the two 2-L Plexiglas cylindrical containers. The oscillation frequency of a rotor controls small-scale turbulent shear stress. The interactions between TEP and beads were monitored at room temperature (ca. 22 °C) under controlled turbulence intensity. The frequency of oscillations was set to reach turbulence kinetic energy dissipation rates,  $\varepsilon$ , of 0.1  $\text{cm}^2 \text{s}^{-3}$  during 1 h. Samples were collected every 15 min over the course of 1 h.

As this work focused on the influence of TEP on aggregation processes (i.e. not on the effect of turbulence), a representative value for  $\varepsilon$  was selected for the description of TEP sticking properties during all the laboratory experiments. Since water sampling was performed in neap tides and the range for  $\varepsilon$  was measured during spring tides, the selected value ( $\varepsilon = 0.1 \text{ cm}^2 \text{ s}^{-3}$ ) was chosen as of the same order of magnitude but less than the mean value obtained for spring tide (Table 1).

## 2.6. TEP and beads determination

During the laboratory experiments described above, the TEP size spectra, the abundance of beads in suspension and the relationship between TEP and beads were determined from 2 mL sub-samples filtered through 0.2- $\mu\text{m}$  polycarbonate filters and stained with Alcian Blue (Alldredge et al., 1993). The retained particles were transferred onto a microscope slide (Passow and Alldredge, 1994). The size of individual TEP and the total abundance of beads were determined for each slide by counting and sizing TEP and by counting beads at 250 $\times$  magnification using a compound light microscope. The ESD of individual TEP was estimated by measuring its cross-sectional area with an image-analysis system (ImagePro Plus, MediaCybernetics) and counts were combined and classified into 20 logarithmic size classes (Mari and Burd, 1998). The number

**Table 1**  
Seasonal variation of  $\varepsilon$  (in  $\text{cm}^2 \text{ s}^{-3}$ ) and ratio of wind-produced turbulence during one spring tidal cycle in dry and wet seasons.

	Station A				Station C			
	Wet season		Dry season		Wet season		Dry season	
	Wind	Flow	Wind	Flow	Wind	Flow	Wind	Flow
$\varepsilon$ min	0.008	0.081	0.000	0.022	0.002	0.103	0.000	0.032
$\varepsilon$ max	0.241	0.911	0.007	0.752	0.172	9.583	0.003	2.083
$\varepsilon$ mean	0.078	0.316	0.003	0.257	0.065	3.012	0.001	0.821
$\varepsilon$ total	0.395		0.260		3.078		0.822	
% $\varepsilon$ wind	19.9		1.0		2.1		0.2	

of beads attached per TEP volume during the laboratory experiments was determined for each sample by sizing individual TEP and enumerating its associated beads at 400 $\times$  magnification. A minimum of 20 mixed aggregates of TEP-beads were studied for each slide, i.e., more than 100 mixed aggregates were studied for each station.

*In situ* TEP volume concentrations were determined from TEP size spectra as described above. *In situ* TEP size spectra are not reported because they were determined under microscope at only one magnification ( $\times 250$ ). While this approach allows determining the TEP volume concentration, it does not allow describing the TEP size spectra accurately since small TEP, which are the most abundant, but represent the smallest contribution to the total TEP volume, cannot be observed at this magnification (Mari and Kjørboe, 1996).

### 3. Results and discussion

#### 3.1. Particle size spectra along the estuary

As indicated by the decrease of the spectral slope  $\delta$ , the fraction of large particles in the upper water column (i.e., from 0 to 2 m) tended to increase towards the sea (Figs. 2 and 3). This trend was particularly well established during wet season with values for  $\delta$  decreasing by half from low to high salinity (Fig. 3). This result supports the often-formulated hypothesis of a salinity-induced aggregation phenomenon (Thill et al., 2001). However, the observed strong seasonal variations of the particle spectral slope, and the low modification of the spectral slope during the dry season suggest that factors other than changes in salinity-induced aggregation of particles play a key role in shaping the bulk particle size spectra. The turbulence level (Winterwerp, 2006; Maggi et al., 2007; Verney et al., 2009) and the characteristics of exopolymeric substances (Wetz et al., 2009) have often been invoked as key forcing parameters for shaping the particle size distribution via control over the collision and the sticking rates and over shear stresses applied on larger and less resistant aggregates.

Another factor, independent from aggregation, which may shape the particle size spectra and account for the difference in the relationship between bulk particle spectral slope and salinity observed between seasons (Fig. 3), is the occurrence of large

organisms, or colonies of organisms. For instance, during the wet and highly productive season, phytoplankton colonies were observed in the high salinity and low turbidity stations (Rochelle-Newall et al., 2011). The occurrence of such large particles generated outside the constraints of aggregation, hence independent from TEP sticking properties, would result in an increase of the particle spectral slope in the high salinity stations. Hence, potential variations of TEP sticking properties may constitute one mechanism among others responsible for the shape of the particle size spectra.

#### 3.2. TEP volume concentrations in the Bach Dang estuary

TEP were found in significant concentrations (from 4 to 191 ppm) in the Bach Dang estuary on all sampling occasions (Fig. 4) and were on the same range than those observed in the coastal eutrophied system of the Baltic Sea (Mari and Burd, 1998). TEP volume concentrations were significantly higher (Student's *t*-test,  $P < 0.005$ ) at low salinities ( $53 \pm 24$  ppm at salinity  $< 10$ ) than at high salinities ( $24 \pm 17$  ppm at salinity  $> 20$ ). The location and the steepness of the salinity gradient varied between seasons. Interestingly, during the dry season, TEP volume concentrations peaked to  $160 \pm 23$  ppm at intermediary salinities (i.e., between 10 and 20). During the wet season the salinity shift between 10 and 20 occurred between two consecutive sampling stations (see Fig. 4). Therefore, during the wet season we did not observed a peak in TEP volume concentration in this salinity range, which does not mean that it did not occur.

Different mechanisms can explain the diminution of TEP volume concentration toward higher salinity. It has been shown that TEP were more compacted with increasing salinity or pH and, on the contrary, presented swollen structures with decreasing salinity or pH (Baalousha et al., 2006). If those particles get more compact when salinity increases, their respective individual volume, and thus their total volume concentration, should decrease. Alternatively, a modification of TEP sticking properties may also change the naturally occurring TEP volume concentration. Assuming that TEP sticking properties are positively correlated to salinity-linked parameters, at high salinity aggregation and sedimentation processes would be more efficient, hence leading to the removal of TEP via the sinking of marine snow aggregates. This latter

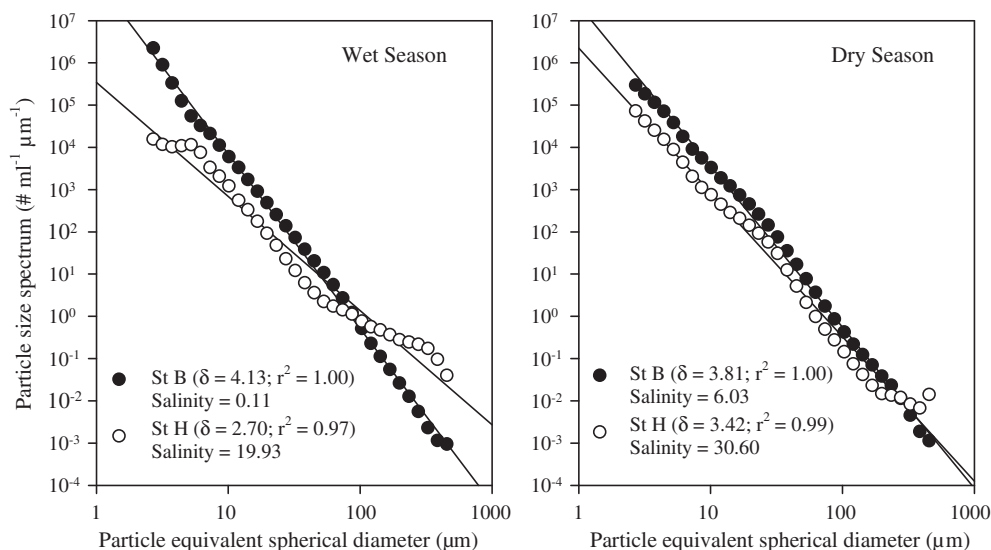
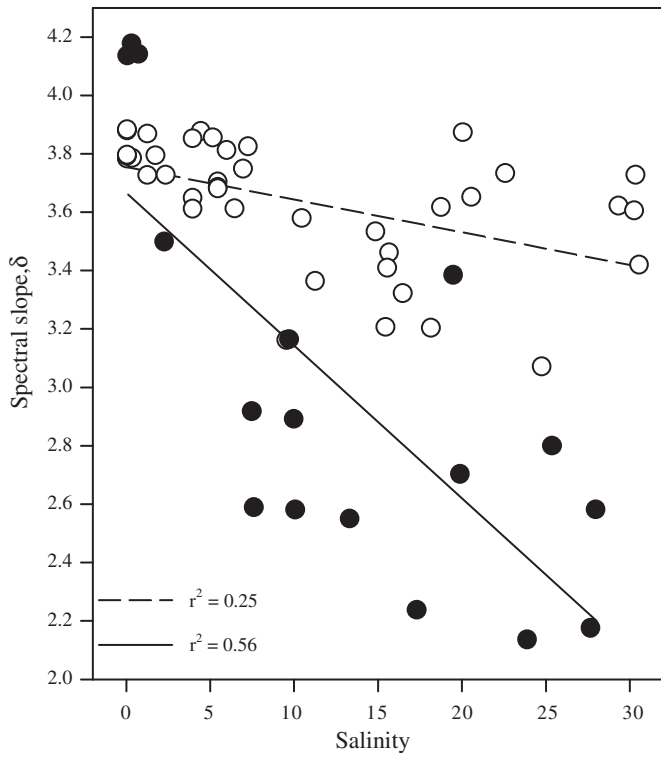
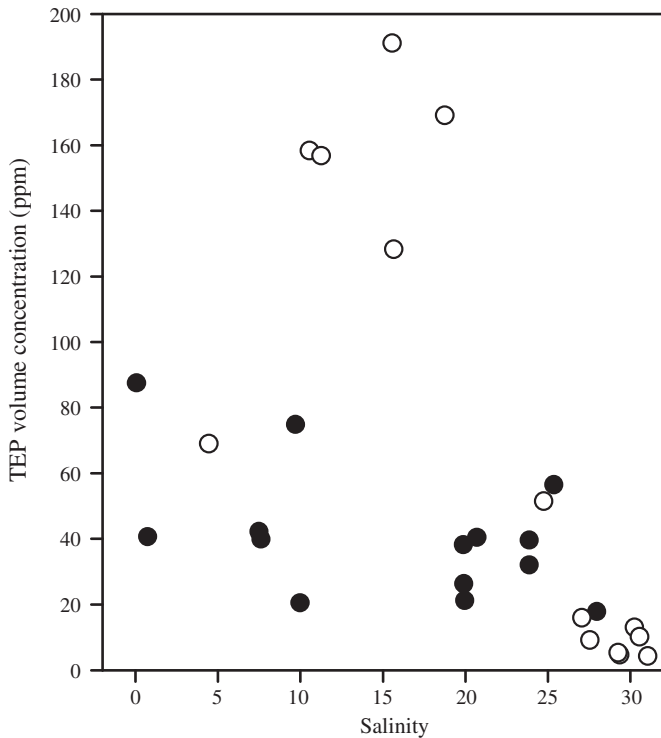


Fig. 2. Examples of particle size spectra at low (Station B) and high (Station H) salinity during the wet and the dry seasons. Regression lines ( $N(d) = kd^{-\delta}$ ) have been fitted to the data.



**Fig. 3.** Spectral slope,  $\delta$ , of the particle size distribution as measured by the LISST along the salinity gradient during the wet (closed symbols) and the dry (open symbols) seasons. Regression lines ( $N(d) = kd^{-\delta}$ ) have been fitted to the data.

mechanism would explain the lower TEP volume concentration in the water column at high salinity. The observed peak of TEP volume concentration occurring at intermediate salinities during the dry season is explained in the next paragraph.



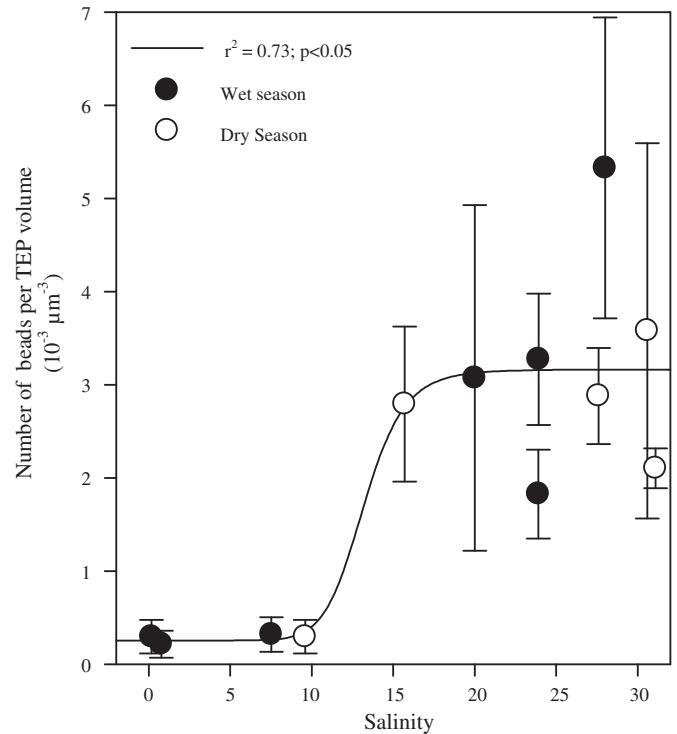
**Fig. 4.** Variation of TEP volume concentration along the salinity gradient during the wet (closed symbols) and the dry (open symbols) seasons.

### 3.3. TEP sticking properties

Sticking properties, described as a function of the number of non-sticky artificial beads associated with TEP, varied and increased seaward with positive correlation with salinity (Fig. 5). The TEP volume concentration was relatively constant after filtration (just before adding the microspheres) for all experiments and averaged  $2.42 \pm 1.68$  ppm. During the course of the twelve aggregation experiments, the TEP concentration increased to  $6.19 \pm 2.04$  ppm on average. The number of beads attached per TEP volume ( $\mu\text{m}^{-3}$ ) increased by one order of magnitude, i.e., from ca.  $0.3 \times 10^{-3}$  to  $3 \times 10^{-3}$  beads per  $\mu\text{m}^3$  of TEP, from low (<10) to high (>15) salinities. The increase of TEP sticking properties along the salinity gradient could be linked to a modification of the sticking properties of existing TEP via modification of salinity-linked parameters and/or to the production of new TEP with high sticking properties. This pattern strongly supports the idea that aggregation/sedimentation processes may vary significantly as a function of salinity-linked parameters as already suggested by the observed variation of *in situ* TEP volume concentrations (Fig. 4). Interestingly, the salinity range in which TEP sticking properties increased by one order of magnitude coincides with the salinity range in which TEP volume concentration peaked at  $160 \pm 23$  ppm, at least in dry season. Indeed, the sudden increase of TEP sticking properties in this salinity range may have promoted the rapid formation of large TEP due to an increase of TEP–TEP coagulation processes, and their temporary accumulation in the water column (Fig. 4).

### 3.4. Fate of TEP along the salinity gradient

It is now acknowledged that the settling characteristics of suspended particulate matter are closely linked to the sticking properties of TEP (Azetsu-Scott and Passow, 2004; Mari, 2008). In fact,



**Fig. 5.** Relationship between TEP sticking properties ( $\pm$ S.D.) and salinity. A sigmoidal regression line has been fitted to the data. Closed symbols refer to the wet season, open symbols to the dry season.

TEP are sticky particles with a density lower than that of seawater (Azetsu-Scott and Passow, 2004). As a result, they settle down only if they stick and aggregate a critical amount of particles denser than seawater in order to form large and dense sinking marine snow aggregates. According to this scheme, if TEP stickiness is low, they will glue a too small amount of dense particles, hence leading to the formation of neutrally or positively buoyant marine snow aggregates remaining suspended in the water column or ascending to the air–water interface. Therefore, in low-stickiness areas of the estuary (low salinity waters), suspended particles could be lifted up via the TEP-elevator pathway and fuel the surface microlayer (SML) and, hence, sedimentation should be low. In their study of the surface microlayer in the Singapore estuary, Wurl and Holmes (2008) observed the occurrence of a TEP-enriched and thicker surface microlayer at the estuary station than at the oceanic station. This observation supports the above hypothesis.

A deficit of dense particles in the 10–20 salinity range may have permitted the observed temporary accumulation of large sticky, yet neutrally buoyant, TEP. The intermediary salinity area of the estuary may be characterized by a deficit of dense particles, in comparison to TEP. During the dry season, the volume occupied by TEP was on average 6 times lower than that of LISST-detected particles, against an average of 75 times lower during the wet season (Table 2). This suggests that the contribution of TEP to the bulk particulate pool is much lower during the wet season than during the dry season. This makes sense since during the wet season the higher water flow increases the inorganic particle discharge and, thus, their contribution to the particulate pool. The contribution of the TEP pool decreased during both wet and dry seasons when the salinity increased above 20. This general trend (i.e. low contribution of TEP to the bulk particulate pool at high salinity) supports the idea that TEP sticking properties are higher at salinity >20, which likely promotes the formation of large aggregates detectable by the LISST, and increases the removal of TEP from the water column.

While the variation of TEP sticking properties linked to salinity (and co-varying parameters) is likely to enhance the formation of large mixed aggregates at higher salinities (as supported by the changes in the relative fraction of TEP volume vs. particle volume described above), its consequence on the size distribution of suspended particles depends on the balance between the input rate of TEP (via production of TEP precursors) and their output rate (via sedimentation once associated with dense particles). Two scenarios may explain the occurrence of large, but slow-sinking TEP aggregates, simultaneously with the increase of sticking properties.

First, it could happen if the production rate of TEP precursors is higher than their output rate via sedimentation. Such an imbalance between input and output rates of TEP precursors may occur at the end of the river plume as the result of the increase of primary production linked to the diminution of turbidity on the one side, and of the input of nutrients from the river on the other side (Cloern, 1987). During their study in the Bach Dang estuary, Rochelle-Newall et al. (2011) measured dissolved (DPP) and particulate primary production (PPP). Both DPP and PPP were very low at salinity <10 (on average < 0.5 mmol C m<sup>2</sup> h<sup>-1</sup>). At intermediary salinities (i.e., between 10 and 20), during the wet season,

PPP and DPP reached on average 2.2 mmol C m<sup>2</sup> h<sup>-1</sup> and 0.6 mmol C m<sup>2</sup> h<sup>-1</sup>, respectively. During the dry season, PPP and DPP averaged 1.3 mmol C m<sup>2</sup> h<sup>-1</sup> and 3.9 mmol C m<sup>2</sup> h<sup>-1</sup>, respectively. In other words, the production of dissolved organic carbon by phytoplankton at intermediary salinities represented 33% and 75% of primary production during wet and dry seasons, respectively. Such an increase of the fraction of DPP strongly suggests that the observed peak in TEP volume concentration in this salinity range may be partly attributed to the increased production of TEP precursors. At salinity >20, DPP accounted for 46% of total primary production during both the dry and wet seasons.

Second, in order to sink, aggregates should have a high excess density. This is the case when the relative proportion of dense particles-to-TEP is high within mixed aggregates. To obtain such a high proportion of dense particles-to-TEP within mixed aggregates, two conditions are required: high TEP sticking properties and high concentrations of dense particles. The latter may be missing since a large fraction of the dense inorganic particles brought by the river discharge settles down before reaching high salinity seawater. This trend is supported by the study of the turbidity at 1-m depth (Fig. 6). Turbidity was negatively correlated with salinity (exponential decay regression;  $r^2 = 0.73$ ;  $P < 0.001$ ), i.e. decreased by about 2 orders of magnitude from low to high salinities, with the most dramatic decrease from 0 to 10 salinity. Such a rapid decrease of turbidity at the mouth of the estuary suggests that it is mainly due to dilution of the river plume in seawater. Additionally, in this intermediary zone, primary production linked to the diminution of turbidity and to the input of nutrients from the river may have not yet induced the production of large quantities of particles denser than TEP, while already stimulating the production of new TEP precursors by phytoplankton cells.

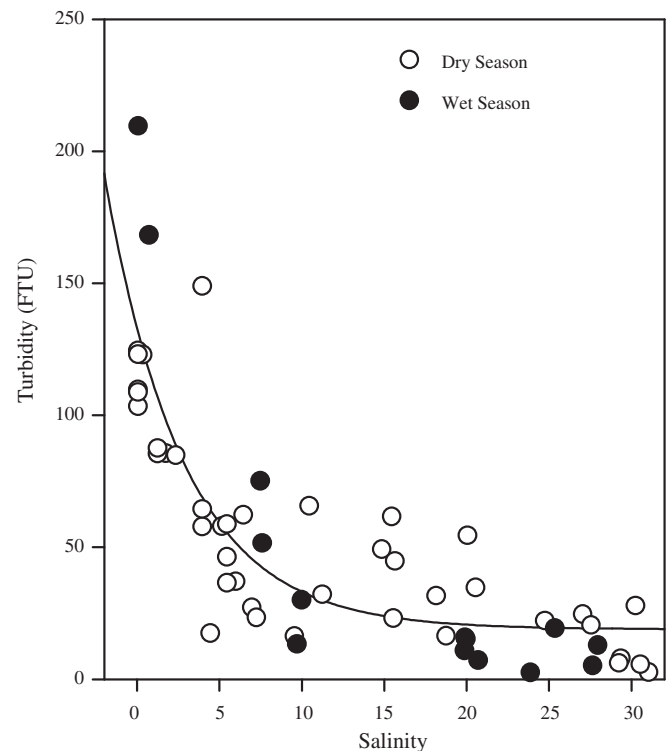


Fig. 6. Relationship between turbidity and salinity along the salinity gradient during the wet (closed symbols) and the dry (open symbols) seasons. An exponential decay regression line has been fitted to the data.

**Table 2**  
Variations of the ratio Vol<sub>Part</sub>/Vol<sub>TEP</sub> ( $\pm$ S.D.) between dry and wet seasons and as a function of salinity.

	Salinity range			
	0–10	10–20	20–30	0–30
Dry season	1 $\pm$ 0	2 $\pm$ 1	14 $\pm$ 8	6 $\pm$ 8
Wet season	36 $\pm$ 37	No observation	104 $\pm$ 165	75 $\pm$ 128

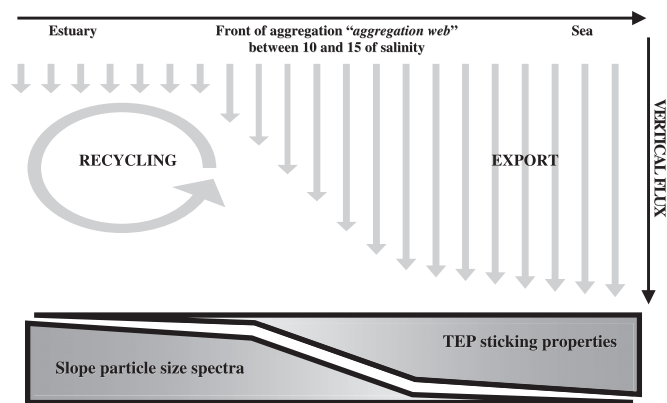


Fig. 7. Conceptual representation of the processes of aggregation/sedimentation along the salinity gradient in the Bach Dang estuary.

### 3.5. Aggregation dynamics

This coupled study of *in situ* variations of particle size spectra and laboratory investigation of TEP sticking properties under controlled turbulence intensity confirms that aggregation dynamics vary strongly along salinity gradient in the estuary. Furthermore, it demonstrates that variations of turbulence cannot be assumed to be the only factor shaping the particle size spectra; organic matter characteristics proving to be a key parameter. The observed variations of the sticking properties of TEP along the salinity gradient could be linked to several mechanisms such as: prolonged bacterial degradation linked to the high residence time of the water mass (Mari et al., 2007; Rochelle-Newall et al., 2010), direct effect of high metal concentrations (Mari and Robert, 2008), modification of pH along the salinity gradient that may lead to a modification of aggregation processes (Riebesell et al., 2007; Mari, 2008), and to microbial processes that may alter the structure of the matrix of the aggregates (Piontek et al., 2010). Other parameters co-varying with salinity in the estuary, such as the concentration of cations (Wetz et al., 2009), phytoplankton composition (e.g. Muylaert et al., 2000) or the rate of dissolved primary production (Rochelle-Newall et al., 2011) could also alter TEP sticking properties. The front of aggregation, which could be defined as an “aggregation web”, seems to occur for salinities between 10 and 15. Aggregation processes should be enhanced while particles transit via this zone, thus promoting the formation of dense aggregates likely to be exported to the bottom. According to this scheme, in the low salinity area of the estuary, particles may remain suspended in the water column (or even rise to the surface, thus fueling the SML) leading to a system dominated by recycling. On the contrary, in the area of the estuary showing high salinity (toward the sea) the sticking properties will be high, which may promote the formation of fast sinking aggregates, leading to a system dominated by export (Fig. 7).

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