Fractionation of surface sediment fines based on a coupled sieve–SPLITT (split flow thin cell) method

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Abstract

In traditional sediment grain-size separation using sieve technique, the bulk of the organic matter passes through the smallest mesh size (generally 38$\mu$m) and is not further fractionated. In this study, a common sieve separation has therefore been coupled with an extra high capacity split flow thin cell fractionation (EHC-SPLITT) instrument to separate the bulk surface sediment not only into size-based sieve fractions (>100, 63–100, 38–63 and <38$\mu$m) but particularly to further fractionate hydrodynamically the fine fraction (<38$\mu$m) using the EHC-SPLITT. Compared to the few previous studies using a smaller high capacity (HC) SPLITT cell, the EHC-SPLITT evaluated in detail here has several advantages (e.g., 23 times higher throughput and allowance for large particle diameters). First, the EHC-SPLITT was calibrated with particle standards. Then, its ability to fractionate fine surface sediments hydrodynamically was demonstrated with material from biogeochemically distinct regimes using two cutoff velocities (1 and 6 m d\textsuperscript{-1}). The results from particle standards indicated a good agreement between theory and experiment and a satisfactory mass recovery for the sieve–SPLITT method (80–97\%) was observed for sediment samples. The mass distributions revealed that particles <38$\mu$m were predominant (70–90\%), indicating the large need for a technique such as the EHC-SPLITT to further fractionate the fine particles. There were clearly different compositions in the EHC-SPLITT-mediated subfractions of the sediment fines as indicated by analyses of organic and inorganic parameters (POC, Si, Fe and Al). The EHC-SPLITT technique has the potential to provide information of great utility to studies of benthic boundary layer transport and off-shelf export and how such processes fractionate geochemical signals.

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1. Introduction

Studying composition of coastal surface sediment allows us to understand the fate of the terrestrial organic matter exported to the continental shelf as well as the factors controlling the content and preservation of organic matter in marine sediments (Keil et al., 1994; Hedges and Keil, 1995; Bianchi et al., 2002). Suspended particles and aggregates in the river and estuarine waters are hydrodynamically sorted during transport across the continental shelf. When the particles/aggregates reach the ocean and the horizontal transport rate decreases, the gravitational forces increase in importance, forcing the particulate matter to settle and sediment. This suggests that different particles/aggregates sediment at different distances from the river mouth to the open ocean (Gibbs et al., 1989). Settling velocity is governed by shape, size and density of the particles/aggregates under gravitational force. The properties that control the settling velocity also control hydrodynamic sorting and resuspension/resedimentation processes.

It is suggested that there is a strong relationship between sediment grain size and total organic matter due to the greater sorption capacity of fine sediments with large surface areas (Mayer, 1994a). This indicates that the size distribution of sediment is important for the study of the carbon content in sediments. Especially, it is important to examine the fine particles (<38 μm) because most of organic and inorganic compounds are concentrated in this fraction (Mayer, 1994a; Bergamaschi et al., 1997; Keil et al., 1997).

In previous studies, most techniques used to separate particles depend on size only, which is unlikely to satisfactorily simulate the natural fractionation occurring at the outlet of most rivers. Other methods have been used but they included lack of precise particle separation in size classes <20 μm, low throughput, contamination, loss of material to the separation medium and reliance on density or size alone to isolate the discrete classes (Keil et al., 1994).

In this paper, we evaluated and tested in detail a little-used method called SPLITT (split flow thin cell fractionation) for further separation of sieve-passing fine (<38 μm) particles. The SPLITT method is based on hydrodynamic fractionation of the particles based on the size, density, shape and settling velocity. It seeks to imitate the natural settling of particulate matter and large volumes can be processed rapidly.

The SPLITT technique was first introduced by Giddings (1985) and Springston et al. (1987). SPLITT fractionation has been applied to some natural aquatic systems such as hydrodynamic sorting of bottom sediments (Keil et al., 1994), river particles (Contado et al., 1997) and surface ocean particles (Gustafsson et al., 2000), as well as characterization of dust and ground water particulates (Lee et al., 2001) and more recently to separate quantitatively diatom frustules from lake sediments (Rings et al., 2004).

However, previous studies in water research used only a so-called high capacity (HC) SPLITT cell (Keil et al., 1994). It is the objective of this present study to thoroughly test and demonstrate the feasibility of the extra high capacity (EHC) SPLITT to aquatic particles. The EHC-SPLITT cell enables processing 20 times more sample in a given amount of time compared to the previously applied HC-SPLITT cell and, further, pre-concentration of particles before the EHC-SPLITT fractionation is not required for geochemical measurements. In this study, the method was first tested with silica beads to calibrate the EHC-SPLITT cell. Then, its applicability to real aquatic sediments was demonstrated by analysis of organic and inorganic components (POC, Al, Si and Fe) in separated fractions of surface sediment samples from five biogeochemically distinct regimes.

2. Materials and methods

2.1. The SPLITT principle

The SPLITT is a separation method where particles are gently sorted during laminar fluid flow in a thin channel based on a combination of their size, wet density and diffusion coefficient. The SPLITT has an
easily adjusted “cutoff” separation based on particle settling velocity (Giddings, 1985; Fuh et al., 1992).

The SPLITT cell is composed of laminated plastic and glass boards with a metal sheet in the middle in order to create a thin cell within the system. There is a pair of inlets on one side of the cell and a pair of outlets on the other side (Fig. 1). The sample suspension, which is referred to as the feed, is introduced at the upper inlet (called a) and a carrier solution free of particles (here: deionized water) at the lower inlet (called b). These liquid media are continuously introduced by pumps, which can be set to different flow rates and cutoffs. It is important that the particles are disaggregated and the concentration of suspended solids is low. Keil et al. (1994) estimated that the optimum concentration of particles in the feed sample is \( \sim 1.4 \) weight percent suspended solids. This means that up to 14 g suspended solids per liter is allowed to not change the viscosity of the solution.

Inside the SPLITT, the inlet splitting plane separates the sample and carrier solutions as the particles are advected laterally in the cell with the laminar flow; they are affected by the gravitational pull (Fig. 1). Depending on the horizontal velocity of the suspension in the cell and the particle properties, particles above a certain settling velocity cutoff will sink before reaching the outlet splitting plane. Particles passing above the outlet splitting plane are termed large colloids and exit through the upper outlet (a; Fig. 1). Those that sink beneath are termed gravitoids and exit through the lower outlet (b). The gravitoids and the large colloids are then collected after centrifugation of both fractions was determined after centrifugation and drying in the oven at 60 \(^\circ\)C. The large size of the EHC-SPLITT cell is advantageous for the separation of particles in sediment samples. For example, the high capacity of the EHC-SPLITT cell and the appropriate particle concentration in the feed solution (10 g/l) allow to fractionate rapidly a large volume of sample (4 l in 160 min). In the present study, the feed concentration was around 0.4 g l\(^{-1}\).

2.3. The EHC-SPLITT calibration

In contrast to most previous applications, in this work, the EHC-SPLITT was explicitly calibrated by using spherical monodisperse particle standards (silica beads of 7.8 \( \pm \) 1.0 \( \mu m \), 2.52 g cm\(^{-3}\); Sigma Chemicals). These dense inorganic particles have settling velocity (4.89 m d\(^{-1}\)) similar to detrital particles predominant in surface sediments. The silica beads were mixed in deionized water and fractionated by the EHC-SPLITT cell operated at varying cutoff velocity. To verify the EHC-SPLITT cutoff, quantification of two SPLITT fractions were evaluated and compared with theoretical predictions by Stoke’s Law.

2.4. Demonstration of sieving/EHC-SPLITT to surface sediment samples

To evaluate the sieving–SPLITT method, a variety of different surface sediment samples were tested. The samples were collected from the surface layer of
sediments (0–2 cm) underlying different biogeochemical regimes (Fig. 2): Alaska region (Yukon River and Prudhoe Bay), Peru Margin and Swedish coast (Koster Fjord and Örserum Bay).

2.5. Chemical analysis

Subsamples of sieving–SPLITT fractions were analyzed for the concentration of particulate organic carbon (POC) by Europa IRMS (Isotope Ratio monitoring gas Mass Spectrometer in cooperation with UC Davis Laboratory, USA). The preparation of sieving–SPLITT fractions for IRMS analysis was identical to that of Gustafsson et al. (1997). Subsamples of sieving–SPLITT fractions (10–20 mg dry weight) were also subjected to inorganic element analysis (Al, Si, Fe) using inductively coupled plasma-atomic emission spectrometry (ICP-AES) in cooperation with SGAB Analytica AB (Luleå, Sweden). For the SPLITT fractions, the subsamples were obtained after filtration onto nitrocellulose filters (0.45 μm). All samples were acidified with ultra-pure acid before analyses for a complete digestion of particles and filter. Measurements were done on each fraction without pre-concentration following previously described method by Ingri et al. (2000).

3. Results and discussion

3.1. Calibration result

The EHC-SPLITT fractionation of standard monodisperse silica beads is in agreement with theoretical predictions by Stoke’s Law (Fig. 3). The calibration lines are theoretical fractograms predicted by Stoke’s Law taking into account the non-Gaussian mass distribution. This experiment confirms that a laminar flow regime was
established in the EHC-SPLITT cell. The cutoff velocities generated by the fractions in the exit of the EHC-SPLITT (gravitoids and large colloids) were in the same range as predicted by the theoretical model (from 1 to 6 m d$^{-1}$). The cutoff velocity data was estimated graphically from the intersection of the correlation lines plotted for the gravitoids and colloids mass data, respectively, and compared to the value predicted by the intersection of the Stoke’s Law curves. The experimental value was 5.0–5.5 and 4.4 m d$^{-1}$ from the Stoke’s Law model for 7.8 μm silica beads. Similar SPLITT calibration results have previously been reported for this and other standard particles for the HC-SPLITT instrument (Gustafsson et al., 2000).

3.2. Distribution of the sieve–SPLITT fractions

To be able to estimate the recovery of the sieve fractionation, each of the sieve fractions were dried and weighed. The sum of these masses was compared to the mass of the bulk sediment introduced to the sieve system. Before sieving, the dry/wet ratio of the bulk sediment was determined. The recovery was calculated according to Eq (2), where $m_i$ represents the dry mass of the sieve fraction $i$:

$$\text{Recovery} = \frac{m_{500} + m_{250} + m_{100} + m_{63} + m_{38} + m_{<38}}{m_{\text{tot}}} \times 100\%.$$  

The results of the sieve fractions indicated a good mass recovery for all five sediments ranging from 75% to 99% (Fig. 4). The mass distributions suggest that there is a significant variation between these different types of sediment (Fig. 4). The fine fraction ($<38 \mu m$) represents more than 70% of the total mass for Peru, Koster and Örserum samples. For Yukon and Prudhoe samples, the fraction 63–100 and 38–63 μm are higher even if the fine fraction stays the predominant fraction in the mass sieve distribution. On average for all sediment samples, the fine fraction represents 64% of the bulk sediment, which indicates that sieve fractionation alone...
The gravitoid fraction with velocity higher than Eq (1) and from the flow rates at the upper outlet and fractions to that in the feed fraction (bulk particles found in the sum of the large colloid and the gravitoid particles. This aspect is clearly evident for Yukon, Peru and Scandinavian (Koster and Örserum) samples, more influenced by the marine environment, have only 7% of the fine particles settling faster than 6 m d$^{-1}$. Between 40% and 50% of the fine particles have a sinking rate between 1 and 6 m d$^{-1}$ and an equal fraction is found in the $<1$ m d$^{-1}$ settling pool.

3.3. Carbon data

The weight percent of organic carbon (% POC) was measured in the sieve and SPLITT fractions and the carbon recovery was calculated for both fractionation methods (Fig. 6). The total recovery for the organic carbon ranged from 71% to 107%. This demonstrates the efficiency of both fractionation methods for the organic carbon in all sediment fractions.

One main characteristic of the POC distribution is the large difference between the sieve and SPLITT fractions. This aspect is clearly evident for Yukon, Peru and Koster sediments where the ultra-fine fractions have a very high organic carbon content (from 1.5% to 8%). For the marine sediments (Peru and Koster), the ultra-fine fractions ($<38 \mu m$) had % POC 10 times higher than the $38-63 \mu m$ and the $<38 \mu m - >6 m d^{-1}$ fractions. For Örserum sample, the large particles ($>100 \mu m$) have the highest POC content. These results are in overall agreement with the origin of sediments. For example, a high carbon value was also observed by Bergamaschi et al. (1997; 1.5–21.6%) in the Peru Margin confirming the validity of the sieve–SPLITT method.

This also indicates the importance of the fine particles, where the major carbon content is located and thus the motivation to focus biogeochemical studies on this fraction of particles. An ambition that is now attainable with the EHC-SPLITT technique is to study the influence of grain size on organic carbon preservation in marine sediments (Canfield, 1994; Bergamaschi et al., 1997) and the relationships between mineral surfaces and organic carbon concentrations in sediments (Mayer, 1994b).

3.4. Elemental ratios in the particulate SPLITT pools

In order to investigate the possible variation in composition of the three SPLITT pools (feed $<38 \mu m$, gravitoid and large colloids) as a function of the cutoff velocities (1 and 6 m d$^{-1}$), the distribution of the
inorganic elements iron (Fe) and silicon (Si) were normalized to that of aluminium (Al). Al is not very bioactive and can be used as a measure of detrital material and Si/Al and Fe/Al ratios can be compared to the average content of the continental crust. Crustal sources are likely for the detrital material and element/Al ratios higher than the average crust indicating a non-detrital enrichment of the element in the analyzed

Table 1
EHC-SPLITT flow rates and settling velocity cutoff used in this study

<table>
<thead>
<tr>
<th>$U_{cutoff}$ (m d$^{-1}$)</th>
<th>$V_a'$ (ml min$^{-1}$)</th>
<th>$V_a$ (ml min$^{-1}$)</th>
<th>$V_b'$ (ml min$^{-1}$)</th>
<th>$V_b$ (ml min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>30–46</td>
<td>115–120</td>
<td>95–108</td>
<td>21–23</td>
</tr>
<tr>
<td>6.0</td>
<td>110–120</td>
<td>630–650</td>
<td>650–660</td>
<td>125–130</td>
</tr>
</tbody>
</table>

Fig. 4. Mass distribution of sieve-SPLITT fractions of sediment samples. The dashed line delimits the sieve and the SPLITT fractionation methods. The cutoff velocities used for the SPLITT fractionation were 1 and 6 m d$^{-1}$. Values listed above the bars are the mass recovery for sieve and SPLITT fractionations. The value in comma represents the total mass recovery.
The relatively high Si/Al ratio for the particles \(<38\ \mu m\) indicates a specific particle phase with high Si content (e.g. diatoms or sand) in the fast sinking fraction (Fig. 7a). The Si/Al ratios in the other SPLITT fractions are similar or lower than in the feed \(<38\ \mu m\), which indicates that detrital material is likely to dominate.

The Fe/Al ratio in all fractions of the Alaska sediments is close to the average crust value (0.6) demonstrating that the particulate Fe predominantly existed in detrital particles (Fig. 7b). For the marine and brackish sediments, the SPLITT runs reveal that the highest value of the Fe/Al ratio is contained in the ultra-fine particles \(<38\ \mu m\) and \(<6\ \text{m} \cdot \text{d}^{-1}\).

**4. Conclusion**

The EHC-SPLITT is a non-destructive and simple instrument used to fractionate particles/aggregates in natural water into different settling velocities. The large capacity of the EHC cell compared to HC increases the throughput (23 times higher), the maximum particle size and the volume of sample that it is practically possible to fractionate.

In the present study, the perspective to test the validity of the sieve-SPLITT method was afforded by the fractionation of surface sediments from five different regimes. Calibration using standard particles, never done before, clearly demonstrates that the EHC-SPLITT is well fitted to fractionate particle samples from 1 to 6\ m\cdot\text{d}^{-1} providing information about the ultra-fine particles distribution. The fractionation of sediment samples demonstrated the preponderance of fine particles \(<38\ \mu m\) in most sediment samples. Thus, the sieve separation combined with EHC-SPLITT can further separate the fines, which are important to elucidate biogeochemical processes. The carbon and inorganic elements confirmed this feature for all sediments and revealed differences could exist in between subcomponents of the SPLITT fractions. Finally, this paper suggests that many processes could be elucidated with the EHC-SPLITT.
fractionation of the fine particle, such as geochemical fractionation within the fine particle pool during off-shelf transport in the benthic boundary layer (Keil and Cowie, 1999). The hydrodynamic particles sorting in ocean margins is a topic that could benefit from the EHC-SPLITT emphasis as, for example, the lateral transport of terrestrial organic matter (Goni et al., 1997; Goni et al., 2000; Bianchi et al., 2002) and the dispersion of trace contaminants in the continental margins (Santschi et al., 1997).

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References


Fig. 7. Elemental mass ratios of the different fine particle SPLITT fractions. The dashed lines represent the continental crust average for Si/Al and Fe/Al mass ratios (3.4 and 0.6, respectively). Error bars represent the standard deviation of the propagated analytical uncertainty derived from triplicate analyses.


