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The Impact of Flocculation on In Situ and Ex Situ Particle Size Measurements by Laser Diffraction

S. I. de Lange[1], D. Sehgal[1,2], N. Martínez-Carreras[2], K. Waldschläger[1], V. Bense[1], C. Hissler[2], and A. J. F. Hoitink[1]

[1]Hydrology and Quantitative Water Management Group, Wageningen University and Research, Wageningen, The Netherlands, [2]Catchment and Eco-Hydrology Research Group, Environmental Research and Innovation Department, Luxembourg Institute of Science and Technology, Belvaux, Luxembourg

S. I. de Lange and D. Sehgal are shared first authors.

Key Points:

- The D_{50}, a generic way to parametrize particle size distributions (PSDs), is not an absolute number, but depends on the measurement method
- Differences between in situ and ex situ measured PSDs are caused by the ex situ alteration of flocculated particles
- A robust PSD measurement with laser diffraction takes longer for coarser field samples with a wider distribution

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

S. I. de Lange and D. Sehgal,
sjoukje.delange@wur.nl;
dhruvsehgal99@gmail.com

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Author Contributions:

Conceptualization: S. I. de Lange, D. Sehgal, N. Martínez-Carreras
Data curation: S. I. de Lange
Formal analysis: S. I. de Lange, D. Sehgal
Funding acquisition: A. J. F. Hoitink
Investigation: S. I. de Lange, D. Sehgal
Methodology: S. I. de Lange, D. Sehgal
Project Administration: A. J. F. Hoitink

Abstract Accurate particle size distribution (PSD) measurements of suspended particulate matter (SPM) composed of flocs and aggregates are important to improve understanding of ecological and geomorphological processes, and for environmental engineering applications. PSDs can be measured in situ (in the field) using a submersible sensor, or ex situ (in the laboratory) using samples. The methodological choice is often guided by logistical factors, and the differences in PSDs acquired by in situ and ex situ measurements is of concern. In this study, a laser-diffraction instrument (the LISST-200X) was used to compare in situ and ex situ PSD measurements. Samples measured ex situ were stored for three consecutive weeks and measured each week in a laboratory using different stirrer speeds. We observed that ex situ measurements display a higher D_{50} (median particle size) than in situ measurements of the same sample (up to 613% larger, 112% on average). Our experiments show that the difference between in situ and ex situ measurements can be explained by flocculation of the riverine sediments during the first week of storage. During the subsequent ex situ measurements, the stirring results in a significantly lower D_{50}. Ex situ measurements are therefore unsuitable for flocculated SPM. This study provides recommendations for optimizing PSD measurements by calculating the measurement times required to obtain robust PSD measurements (exceeding 3 min per sample), which are larger for field samples with coarser particles and wider PSDs.

Plain Language Summary Measurements of the size of particles suspended in a water column are important for understanding many processes related to river ecology and morphology. It is possible to measure these particles directly in the field using a submersible sensor (in situ), or by taking samples and transporting them to a laboratory (ex situ). The choice between these options often depends on logistics, with little recognition of the impact that this choice can have on the measurements. In this research, the differences between in situ and ex situ measurements are explored. We find that ex situ measured particle sizes are on average 112% larger than in situ measurements, which can be related to flocculation of the riverine particles. Flocs are a combination of mineral particles (such as silt or clay) and organic particles, forming larger aggregates. Our results show that flocs grow when a sample is taken to the laboratory and stored. During ex situ measurements, which involve stirring, they break apart. Ex situ measurements are therefore unsuitable for determining the natural particle size. We show how long a measurement should last to give a representative particle size. In situ, longer measurement periods are needed.

1. Introduction

Accurate and robust particle size distribution (PSD) measurements of suspended particulate matter (SPM) (including mineral particles, and flocs/aggregates) are important to many environmental studies. Examples include studying pollution transport by suspended particles (Davies et al., 2012), studying the effect of colmation on spawning sites of aquatic biota (Bilotta & Brazier, 2008), and tackling technological challenges such as calibration of optical sensors (Agrawal & Pottsmith, 2000; Sehgal et al., 2022a). Additionally, the local SPM PSDs, together with flow dynamics, may control the mud (clay and silt) fluxes in rivers (Lamb et al., 2020). Also, PSD represent an important physical characteristic controlling sediment transport models directly or indirectly through settling velocity and critical shear stress. An accurate measure of the PSD is thus important for the estimation of SPM fluxes. However, the accuracy and reliability of the SPM PSD measurements are affected by many factors, such as SPM composition, flocculation (Droppo, 2004), measurement methodology (in situ/ex situ), and the logistics around the measurement process.

Supervision: N. Martínez-Carreras, K. Waldschläger, V. Bense, C. Hissler, A. J. F. Hoitink
Validation: S. I. de Lange, D. Sehgal
Visualization: S. I. de Lange, D. Sehgal
Writing – original draft: S. I. de Lange, D. Sehgal
Writing – review & editing: S. I. de Lange, D. Sehgal, N. Martínez-Carreras, K. Waldschläger, V. Bense, A. J. F. Hoitink

The methodological choice of whether to measure the PSD in situ or ex situ often depends on the aim and logistics of the study. Measuring in situ provides a natural picture of the PSD, commonly referred to as the effective PSD (Gartner et al., 2001), and allows for continuous long-term monitoring (Andrews et al., 2010). The in situ PSD includes both the discrete (River & Richardson, 2019) and composite particles (flocs) (Droppo, 2001; Williams et al., 2008). Conversely, ex situ measurements are performed under controlled laboratory conditions, often to better understand the complex particle transport processes. In situ and ex situ PSD measurements are subject to different factors and will therefore yield different results. These differences, typically neither acknowledged nor studied, will be discussed below.

A measured PSD is also impacted by decisions made before, during, and after the measurements. These include the choice of instrument type (e.g., laser diffraction, image analysis, or sieving), measurement time to obtain a reliable average, and data (post-)processing. Even more uncertainty is introduced when measuring ex situ, where sample collection (e.g., grab sampling, using Niskin bottles, or automatic samplers), sample storage (including storage duration and temperature), sample treatment (e.g., pre-sieving, oxidation, or chemical dispersion) and transportation become necessary (Gartner et al., 2001). Many studies (Boss et al., 2018; Chakraborti et al., 2009; Czuba et al., 2015; Federal Interagency Sedimentation Project, 1941; Livsey et al., 2022; Phillips & Walling, 1995; Zhao et al., 2018) attempt to understand and quantify the individual uncertainties associated with each of the above-mentioned choices. The LISST series of instruments developed by Sequoia (LISST-100X/200X and LISST-SL) are commonly used for in situ measurements. These instruments use laser diffraction, and the resulting measurements are affected by (a) the instrument itself (measurement range, optical system [number and location of the detectors] and the selected PSD model [Fraunhofer, Mie]), (b) the particle properties (shape, composition and mass density) and (c) the measurement environment (turbulence and thermal fluctuations) (Bieganowski et al., 2018; Czuba et al., 2015). Hence, different laser diffraction instruments may yield different results.

Instrument-related differences become evident when comparing the PSDs of a sample measured using different measurement instruments for both in situ and ex situ. For example, Czuba et al. (2015) compared PSDs measured with an in stream LISST-SL, and physical samples using the pipette method and a Sedi-Graph (a lab based instrument). Boss et al. (2018) compared PSDs measured with a LISST-100X using an in situ flow-through chamber and physical samples using a Beckman Coulter (a lab based instrument). Both studies found comparable PSDs in situ and ex situ, but post-measurement adjustments were necessary to account for differences in the size ranges measured with each technique. Without adjustments, Czuba et al. (2015) measured lower D_{50} values in the stream than on the physical samples, whereas Boss et al. (2018) measured similar PSD shapes but a 2.5 times higher particulate volume concentration with the Beckman Coulter than with the LISST-100X. As different instruments measure at different ranges and might use different measurement principles, accurate comparison of in situ and ex situ PSD measurements is only possible using a single instrument.

An additional drawback of the laser-diffraction instruments used in the previously discussed studies is that flocculated particles can break when using a LISST-SL and a pump-controlled flow through a chamber. Breaking or deforming the flocs during measurements can result in unreliable PSD measurements (Lamb et al., 2020), as flocs get spread across multiple size classes (Chassagne et al., 2021). The (de)formation of flocs changes the PSD, density and particle settling velocity (Guo & He, 2011). For example, freshwater flocs with diameters of 150–250 μm (similar to fine sand) can have similar settling velocities as 20 μm silt because of the low densities of flocs, thus affecting the theoretical SPM flux estimations (Lamb et al., 2020), although this may necessitate a deeper analysis on SPM theory to present a holistic understanding of flocs and fluxes in rivers (Hunt, 1969; McLean, 1992). Measuring in situ PSDs is therefore essential when using SPM flux estimation models (Chassagne & Safar, 2020). The in situ use of a LISST-200X, which will be used in this research, overcomes this limitation as particles pass through an open flow chamber, minimizing local turbulence during both in situ and ex situ measurements. Additionally, water sampling for ex situ measurements might induce breakage of flocs or promote flocculation (Gibbs, 1981; Phillips & Walling, 1995), which eventually attain a new equilibrium with the ex situ measurement setup after sampling (Kranck, 1979).

Another factor to be taken into account when using laser diffraction to determine PSDs is that a measurement time must be chosen to obtain representative measurements. Very little is known about the influence of SPM characteristics (e.g., dominant size-class) on the required measurement times. They should be long enough to be statistically representative, while remaining time and resource efficient. In existing literature, different

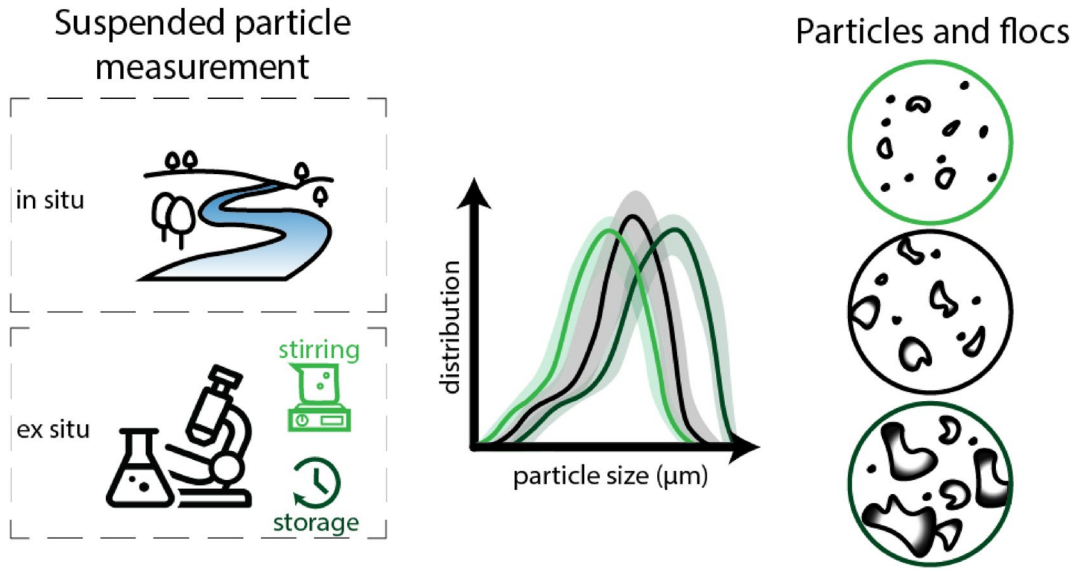

Figure 1. Graphical overview of this research.

measurement and averaging intervals are indistinctly used. For example, measurements by Czuba et al. (2015) included an average of 16 readings taken in 2 s, while Gartner et al. (2001) averaged 16 readings taken in 20 s, and subsequently averaged this over 1 min. Alternatively, Andrews et al. (2010) took 10 measurements every second, and averaged this over 100 s. Zhao et al. (2018) looked more critically at the averaging method. They used an average of 30 measurements, indicating little difference (<∼10%) between readings, and showed that both 30 or 60 readings yield approximately the same result. It should be noted that the aforementioned authors used different LISST versions, and that there is currently a lack of guidance on how to optimize measurement times.

It is crucial to acknowledge that the measured SPM PSD of a water sample collected from a river (ex situ) may not match the actual PSD in the natural environment. This is because the existing flocs or aggregates could be altered during sampling, storage and ex situ PSD measurements, changing its SPM characteristics (Federal Interagency Sedimentation Project, 1941). Similarly, optimum measurement time lengths might vary depending on SPM characteristics. We argue that the magnitude of the alteration when using ex situ methods is largely unknown, and that this lack of knowledge hampers the formulation of clear guidelines to measure PSDs in and ex situ, affecting the multitude of disciplines depending on particle size information. In this study, we hypothesize that the change in floc size is the main cause of divergence between in and ex situ PSD measurements, and that larger measurement times are needed as floc size increases. The latter is because the PSD of flocculated sediments is likely to cover a larger number of size classes. We test this by performing in situ and ex situ PSD measurements using the same instrument, storing samples for different duration of times and at different conditions (hot and light, and cold and dark), and by investigating the relationship between statistical uncertainty, number of measurements, and PSD characteristics. The objectives are (a) to examine the how the D_{50} and PSD of flocculated particles changes as a function of the ex situ measurement environment (shear stress parametrized by stirring speed), (b) to determine the impact of sample storage duration on ex situ D_{50}/PSD measurements, and (c) to establish optimal measurement times for in situ and ex situ measurements as a function of SPM characteristics. The key novelties of this study are the quantification of the effect of flocculation on grain size distributions and the presentation of an optimized measurement time for recording PSD and calculating reliable D_{50} values. The aims of this paper are conceptualized in Figure 1.

2. Methods

PSD measurements were performed using a LISST-200X (Sequoia Scientific), hereafter referred to as a LISST, for both in situ and ex situ measurements. Additionally, a Mastersizer-3000 (Malvern Panalytical), hereafter referred to as a Mastersizer, was used to test higher stirring speeds ex situ. During ex situ analysis, microscopic images were taken to visualize particles. This allows for identification and explanation of the differences between

measurement methods. Finally, requirements for the duration of the in and ex situ measurements (measurement time length) were determined.

2.1. Particle Size Distribution Measurements

2.1.1. LISST-200X

A LISST-200X is a submersible laser-diffraction based particle-size analyzer. Laser diffraction instruments are based on the scattering of collimated laser light by small particles, and the subsequent detection (Agrawal & Pottsmith, 2000). The instrument projects a laser beam through a sample of particles in suspension and measures the forward scattering divided in multiple angles (Andrews et al., 2010; Czuba et al., 2015). The detector has multiple rings with logarithmically increasing radii, which correspond to a range of scattering angles (Agrawal & Pottsmith, 2000). The largest particles are detected by the innermost ring, and vice versa. The LISST has an optical path length of 2.5 cm through which the laser passes the sample. Light is scattered in 36 angles, resulting in 36 log-spaced size classes between 1.00 and 500 µm. Additionally, the laser passes through the center of the rings, and a photo-diode behind the ring detector measures the transmission. The measured reduction in light intensity by attenuation is used to de-attenuate the measured scattered light. It is essential to correct for attenuation since the magnitude of scattering is related to the number of particles, and therefore needed to derive the PSD (Agrawal & Pottsmith, 2000). Before the light distributions are inverted to a PSD, they must be corrected for background scattering in pure water and aging of the laser and windows. Finally, the detected light is back-calculated to a PSD assuming a certain optical model. The LISST outputs PSD, total volume concentration, optical transmission, depth, and temperature on a desired measurement interval.

Limitations should be considered when using the LISST. First, too fine or too coarse particles outside of the instrument's range (1.00–500 µm) are grouped into the smaller and larger size classes, respectively, where the smallest or largest size classes are being affected the most ("rising tails") (Fettweis, 2008), which can lead to an over or underestimation of D_{50}. In this study, rising tails are not observed. Second, multiple scattering caused by high particle concentrations can affect the PSD measurements (Czuba et al., 2015; Sehgal et al., 2022b). However, in this study, the measured suspended particulate matter concentrations (SPMC) were below 150 mg/L, what lies within the recommended measuring maximum limit of the manufacturer (1,332 mg/L for 31.25 D_{50}). Third, natural particles (including flocs) are not circular, impacting light scattering (Mikkelsen & Pejrup, 2001; Pedocchi & García, 2006). We therefore used the irregular particle random shape model of the LISST, which partially takes into account the non-spherical nature of particles (Agrawal et al., 2008). The model incorporates slightly irregular particles, but might not fully represent the highly irregularly-shaped flocs.

2.1.2. In Situ Measurements

The schematic diagram (Figure 2) summarizes the steps taken to perform the measurements in situ and ex situ. In situ particle size measurements were performed in the Attert River in Useldange, Luxembourg. The Attert River enters Luxembourg from Belgium in the northwest and runs from west to east. It covers a catchment area of 247 km^2. The Attert River near Useldange is an example of a rural basin (Martínez-Carreras et al., 2012). The bedrock geology is dominated by Trias marls and dolomites, Lias sandstone, Devonian shales, and phyllites (Pfister et al., 2017). The sampling site has a stabilized river channel with large boulder blocks. The sampling period covered the rising limb of a runoff event (16 November 2022 to 18 November 2022). At the sampling location, a LISST was mounted on a stepladder submerged close to the riverbank. The sensor was constantly submerged, positioned 20 cm above the stream bed, and parallel to the stream channel. This reduced particle adherence and sedimentation in the measurement cells. For optimum data quality, the LISST was cleaned and the background calibration was updated 12 hr before deployment. It was programmed to measure every 30 s.

The in situ PSD of each measurement was calculated as the average of the in situ measurements recorded for 15 min, evenly spread around the grab sampling time. This was not the case for the first measurement (out of four) however, where it is an average of the first 7.5 min due to a technical failure.

2.1.3. Ex Situ Measurements

To perform ex situ measurements in the laboratory, four grab samples (12-L each; sample 1, sample 2, sample 3, and sample 4) were collected near the LISST using a 5 L plastic sampling container with a handler immersed upside down approximately 30 cm. A lid was secured before lifting the bucket out of the water. Each grab sample

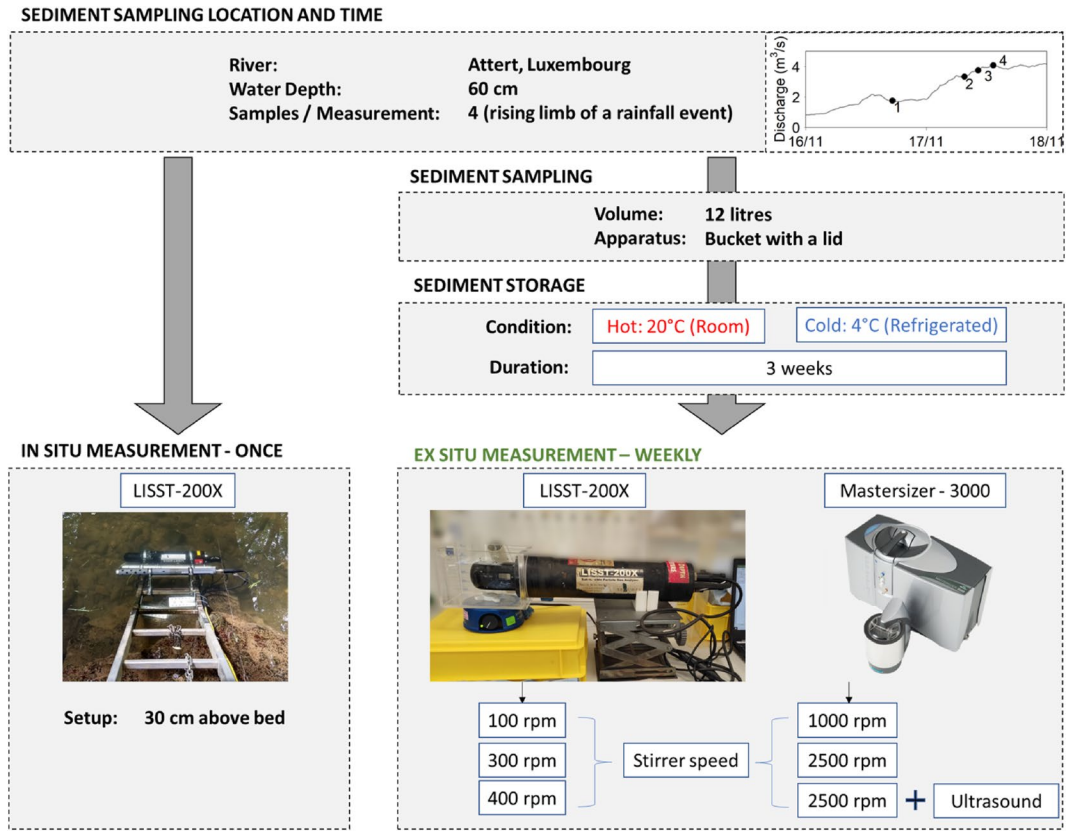

Figure 2. Summary of the sampling steps for in situ and ex situ particle size distribution measurements using a LISST-200X and a Mastersizer-3000. The picture of the Mastersizer is taken from Malvern Panalytical (www.malvernpanalytical.com). Inset: Hydrograph of the rising limb of the sampled rainfall-runoff event between 16 November 2022 to 18 November 2022, indicating the four sampling times.

was split into 12 1-L bottles (hereafter called sub-samples). Out of the 12 sub-samples, six sub-samples were stored at room temperature (18–23°C) while exposed to light, referred as hot-stored samples, and six were refrigerated inside a dark cold-storage (4°C), referred as cold-stored samples.

Ex situ particle size measurements were performed in the laboratory using a LISST and a Mastersizer. Additionally, the SPMC of the samples was measured, and the samples were inspected using a microscope. This analysis was done on various sub-samples, for three storage durations (1–3 weeks) and for two storage conditions (hot and cold).

The ex situ LISST PSD measurement procedure was as follows. Before doing the measurement, a background measurement was carried out with clear tap water. Then, after gentle agitation of the sediment bottle, the sample was poured into a test volume chamber provided by the LISST manufacturer (Figure 2). A magnetic stirrer kept particles in suspension, without air bubbles forming. Each sample was measured at three different stirrer speeds (100, 300, 400 rpm). Higher speeds were not used to avoid disalignment of the magnetic stirrer. Measurements were performed for 5 min. The LISST was set to average 10 recordings per second, resulting in 1 measurement per second. Measurements were taken consecutively with increasing stirring speeds starting at 100 rpm. We observed an exponential decrease in D_{50} in the first minute of stirring after changing the stirrer speed. After this time, the D_{50} and transmission (indication of turbidity) remained constant. We therefore excluded the data collected during the first minute. The raw data was converted to the corresponding PSD using the random-shape model (Agrawal et al., 2008). The averaged data was used to calculate the D_{50} value per sample, which was done for each individual stirrer setting (100, 300, 400 rpm), storage duration (1, 2, and 3 weeks) and storage condition (hot and cold). The calculated values were subsequently used to determine the effect of storage duration and stirring on the established PSD.

Additionally, ex situ particle size measurements were performed using a Mastersizer-3000 (Malvern Panalytical Ltd., Malvern, United Kingdom), hereafter referred to as Mastersizer (MS), to test high stirrer speed settings.

Table 1
The List of Data Sets Used to Generate Results in This Study

			Ex situ LISST				Ex situ mastersizer (MS)		
			Stirrer speed (rpm)				Stirrer speed (rpm)		
Data set	Amount of samples	In situ LISST	100	300	350	400	1,000	2,500	2,500[a]
This paper	28 (4 in situ, 24 ex situ)	X	X	X		X	X	X	X
Tank setup (no ox)[b]	32				X				
Tank setup (oxidized)	28				X				
Huncherange[b]	70					X			
Everlange[c]	26	X							
Rotterdam[c]	36	X							

Note. Data set in gray is used for the Monte Carlo analysis (Section 3.5).
[a]Additionally, ultrasonic vibrations were applied. [b]Sehgal et al. (2022d). [c]Sehgal et al. (2022c).

Three different settings were used for this purpose: 1,000, 2,500, and 2,500 rpm along with ultrasonic vibrations (US). The procedure is detailed in Text S2 in Supporting Information S1.

A standard gravimetric method was used to measure the SPMC of all water samples after filtration through 1.2 μm Whatman GF/C glass fiber filters (General guidelines: Guy, 1969). Finally, a settling column was used to visualize the SPM samples under an inverted microscope (Leica® DMR). First, the samples were transferred using a pipette into the settling column, where they were allowed to settle for 15 min. Next, a Leica-DFC 500 high-resolution digital camera (v. 3.7.0, Leica Microsystems) fitted on the microscope was used to take 2D images on a scale of 50 μm. 2D images may not reflect the spatial complexity of natural sediment and flocs, however, they provide a simple solution to infer the levels of intra-particle aggregation (Spencer et al., 2021). Here, we do not intend to quantitatively analyze the 2D images. Rather, we provide an example of the difference in the scale of primary particles (PPs) (clay, silt, and sand) and flocs.

2.1.4. Additional Data Sets

Additional in situ and ex situ data sets (Table 1, in gray) were used to calculate the required measuring time to obtain representative PSDs, with the aim of including samples with contrasting characteristics. All additional data sets were collected using the same LISST-200X.

The additional in situ data from measurements at Everlange (Luxembourg) and Rotterdam (The Netherlands) were taken from Sehgal et al. (2022c). The additional ex situ sources consist of two data sets: (a) measurements from several consecutive events sampled at Huncherange (Luxembourg), and (b) experimental data sets collected using a tank setup. Both data sets, except for a few experiments from the second data set (oxidized, tank setup), were taken from Sehgal et al. (2022d). A detailed description of the tank setup and measurement protocol is available in Sehgal et al. (2022b). The same measurement protocol and samples were used to characterize the sediment samples that were oxidized using hydrogen peroxide (H_2O_2) 60% at 1:1 solution (H_2O_2 and Mili-Q water) for 15 days, with intermittent stirring and warming at 30°C. Measurements recorded at concentrations of 100 mg/L and 1,000 mg/L were used. The oxidized data set was added to include PSD measurements of samples with nearly no organic matter or inter-particle cohesion.

2.2. Data Analysis

2.2.1. Sample Characterization

We characterized the PSDs based on (a) size percentiles, (b) distribution width, and (c) bi- or multi-modality. To account for differences in volumetric concentration when visualizing the data, the PSDs are normalized by dividing the area per bin by the total area under the PSD.

The particle size of the sample was parameterized by taking the 10th, 50th, or 90th percentile of the PSD, resulting in the D_{10}, D_{50}, and D_{90} [μm], respectively. To group the samples, the PSD of a sample was defined as small

if its D_{50} was smaller than the median D_{50} of all collected samples (51 μm). The PSD width was characterized as the span value (SV [–]):

$$SV = \frac{D_{90} - D_{10}}{D_{50}} \quad (1)$$

The PSD was defined as narrow if its SV was smaller than the median SV of all collected samples (2.38).

Finally, the bi- and multi-modality of a sample was defined by identifying local maxima (peaks) in its PSD. A local maximum is a data point in the PSD that is larger than its two neighboring maxima. If the local maximum was at least 0.5 times the height of the concentration indicated by the global maximum (highest peak), then the sample was labeled as bi- or multi-modal.

2.2.2. Measuring Time Requirements

We studied the relation between statistical uncertainty and the number of measurements, which was used to determine how many measurements are required to obtain a representative PSD. We performed a Monte Carlo bootstrap analysis to find which subset of all collected measurements of a sample reflects the characteristics of the entire population. We assume that the entire population is not changing over time. We randomly drew a subset of measurements and calculated the D_{50} of the sample. The size of the subset ranged from one measurement to all measurements in the entire set. Next, a Monte Carlo bootstrap analysis was performed 1,000 times for each subset size to determine the deviation of the subset from the data set mean D_{50}. The minimum and maximum values were taken from each run. These simulations were performed for 233 samples (Table 1) with varying values of D_{50}, SV, modality, and measurement method (in or ex situ).

The measurement frequency (which could be more than 1 measurement per second) was used to convert the number of measurements, as calculated by the Monte Carlo bootstrap analysis, to measurement time. By studying the change in maximum deviation from the data set mean when adding more measurement readings (when measurement time increases), we gave an estimate on how many readings (and hence measurement time) were needed to give a representative estimate of the D_{50} of the sample. The threshold to determine when the sample is statistically representative was defined in three different ways, and can be tailored to the researchers' needs. The first two thresholds were based on the slope of the maximum and minimum deviation from the data set mean. The slope of the deviation decreased when adding more measurements, indicating that the information gain (or decrease in uncertainty) was decreasing when including more measurements. The first threshold is reached when the slope of the maximum and minimum deviation from the data set mean is equal or less than ±0.05. A stricter formulation of this is used for the second threshold, where the slope should be equal to or less than ±0.005. Finally, a maximum deviation of 5% from the data set mean is allowed for the third threshold. Different thresholds can be chosen depending on the accuracy level required.

3. Results and Discussion

Sections 3.1 and 3.2 describe the PSD behavior in the in situ and ex situ measuring environments. Sections 3.3 and 3.4 highlight the influence of storage and stirring on D_{50} with reference to in situ D_{50}. Section 3.5 provides the minimum measurement time needed to obtain a reliable average value of D_{50} for different SPM characteristics. Section 3.6 describes the implications of the results and recommendations for PSD measurements based on this study.

3.1. In Situ Sample Characterization

Figure 3 shows the in situ and ex situ PSD of the 4 samples collected during the rising limb of a runoff event. In-situ measurement 1 (and sample 1) was taken during the onset of the event and measurements 2–4 were taken during the rising limb (Figure 2).

Discharge dynamics impact the PSDs of the samples in three different ways. First, while discharge increased with measurement number, so did the average D_{50} of the in situ samples (D_{50} = 26 ± 3, 47 ± 4, 53 ± 3, and 53 ± 2 μm for samples 1–4, respectively), and also in the SPMC of the samples (11, 47, 53, and 53 mg/L for samples 1–4, respectively; see also Figure S11 in Supporting Information S1). An absolute difference of 1.1, 3.6, 1.3, and 2.7 μm was found between the average D_{50} of the in situ samples measured over 15 min (26.2, 47.6,

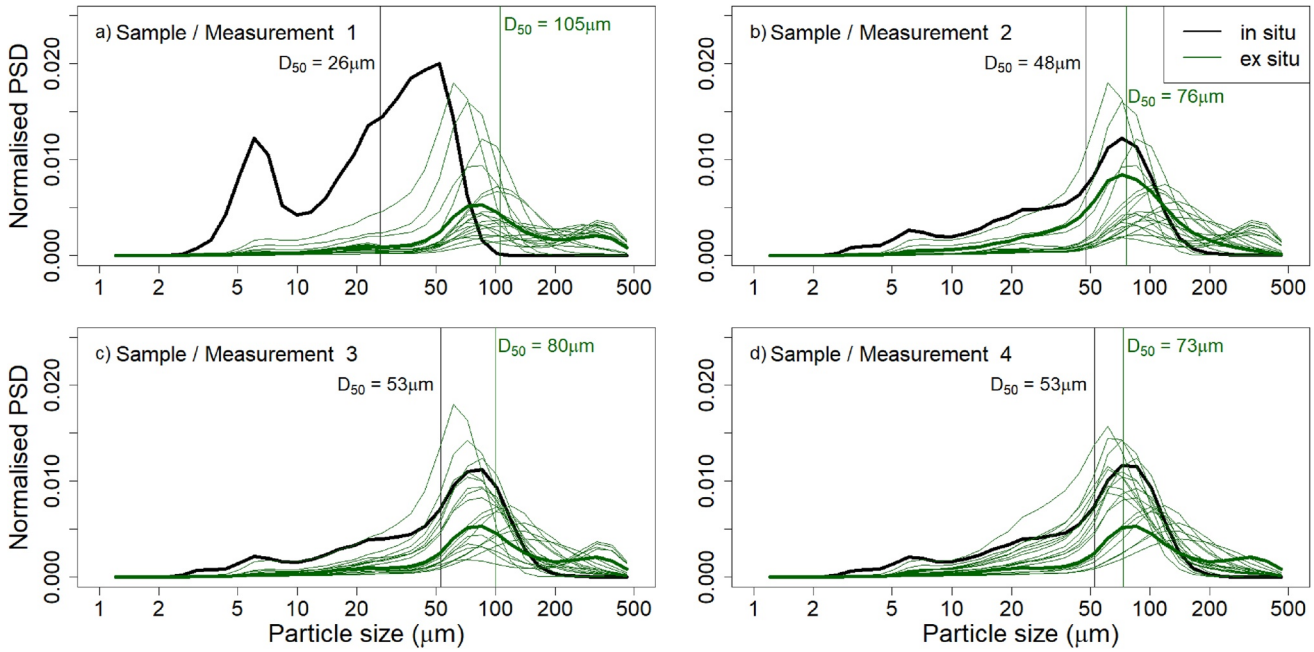

Figure 3. Average of in situ (black) and ex situ (green) normalized particle size distributions (PSDs) of four samples measured using a LISST-200X (ex situ: each thin line indicates a different storage condition, storage duration, and stirring speed). Mean in situ and ex situ D_{50} are indicated with vertical lines in the corresponding colors. See Figures S7–S10 in Supporting Information S1 for the individual PSDs.

52.9, and 52.5 µm) and the in situ measurements corresponding to the ex situ sampling at 7.5 min (27.3, 44.1, 51.6, and 49.8 µm). However, averaging of LISST data is essential (see Section 3.5), necessitating us to use the averaged value. With increasing discharge, the particle size and concentration increases, which can be related to remobilization of sediment stored on the river bed (Lee, 2019) and the role of shear stress in altering particle size (Grangeon et al., 2012).

Second, the nature of the particles that are dominating the PSD differs per measurement. During the onset of the event (sample 1), the D_{50} is smaller, and the bimodal distribution of the PSD (peaks at 6 and 22 µm) could be related to the presence of small PPs (clay) and small flocs. These peaks may represent the base flow conditions, which become less dominant as larger particles are entrained. However, these sizes are still visible as plateaus in the PSDs of samples 2–4. The peaks and plateaus in the in situ PSDs are located at 3, 6, 22, 50–85, and 385 µm (the largest plateau only in sample 2). These sizes correspond to the often made division between primary clay particles (3 µm), flocculi (15 µm), microflocs (50–200 µm) and macroflocs (200–500 µm) (Lee et al., 2012).

Finally, the discharge signature is also visible in the variability of in situ PSDs. This variability can be indicated by the coefficient of variation (standard deviation divided by mean) of the volumetric SPMC, which are 11, 9.7, 7.8, and 6.6 µL/L for measurements 1–4 respectively (see also Figure S11 in Supporting Information S1). The variability is the largest in the first sample. This could be related to the fact that flocs are often more irregularly shaped at low discharge, with a more open matrix (loosely bonded) in which macro-pores can develop (Williams et al., 2008), while they are more densely packed at high discharge (Droppo et al., 2005).

3.2. Discrepancy Between In and Ex Situ PSDs

Ex situ PSDs shown in Figure 3 include the PSDs from both storage conditions (hot and cold) measured after 1, 2, and 3 weeks of storage using different stirrer settings (100, 300, and 400 rpm; Table 1). The average D_{50} of the samples measured ex situ (105 ± 34, 76 ± 26, 80 ± 26, and 73 ± 31 µm for samples 1–4 respectively, see Table S1 in Supporting Information S1 for the D_{50} corresponding to each measurement) is larger than those measured in situ, which is primarily caused by the presence of larger particles (Figure 3)—possibly flocs that form when particles settle at the bottom of the sample bottles during storage.

The presence of flocs in the samples is confirmed from microscopic images. They show that the particulate matter found in our samples range from PPs (clay, silt, sand; Figures 4a–4c) to flocs of different sizes (Figures 4d–4f).

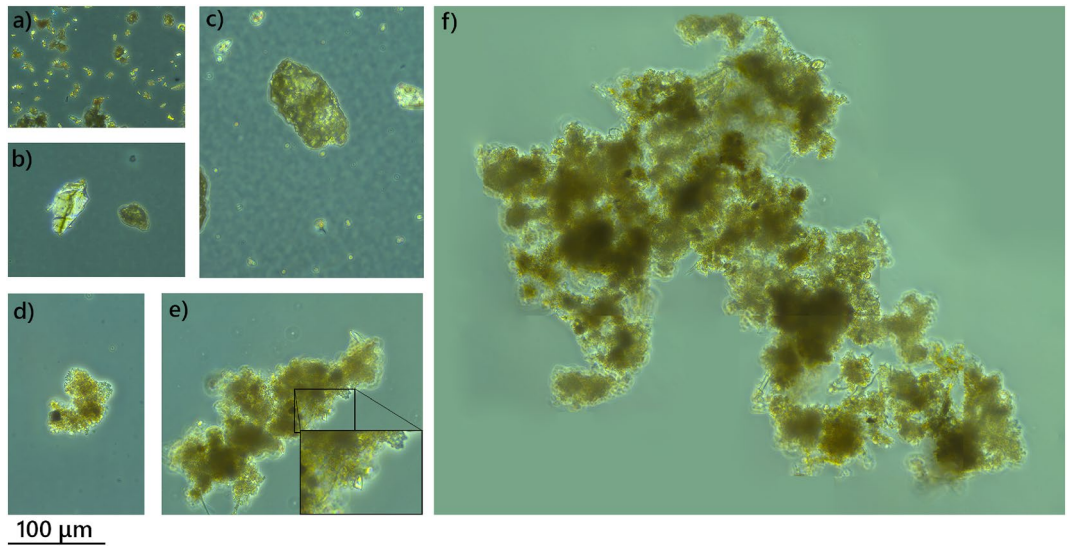

Figure 4. Examples of primary particles (PPs) and flocs as seen under a microscope. (a) clay, (b) silt, (c) sand, (d) small floc, (e) medium sized floc, insert showing the interaction between a PP and a floc, (f) composite picture of a large floc. The scale is the same for all sub-figures, except for the insert.

The flocs found in our samples are rich in organic matter (Figure 4), and range up to 0.5 mm. Under low transport conditions, flocculated particles can be found in rivers, often in the presence of organic matter (Bungartz & Wanner, 2004; Nicholas & Walling, 1996) which is known to help in binding particles together in estuaries (Dyer, 1989; Mietta et al., 2009; Winterwerp, 2002). It is important to derive the effective PSD, including the flocculated particles, since flocs impact sediment transport by changing the settling velocity: flocs the size of medium sand have a settling velocity equivalent to fine silt (Lamb et al., 2020). Excluding flocs from the PSD would result in a shift in D_{50} toward smaller sizes (Droppo, 2004). In the following sections, we explore the impact of flocs on ex situ PSD LISST measurements.

3.3. Impact of Stirring on Ex Situ Measurements

The stirrer speed has a large impact on PSD ex situ measurements (Figure 5). For all samples, a decrease in D_{50} values with an increase in stirrer speed was observed. This was on average 56% when stirrer speed changed from 100 to 300 rpm and 23% with a change from 300 to 400 rpm (Figure 5).

The stirrer speed is a measure for shear stress in the mixing jar, which is often several orders of magnitude higher than in natural rivers (Chakraborti et al., 2009). Since floc size is known to attain an equilibrium with the shear stress in the water column (Kranck, 1979), the stirrer speed will impact the floc size. The decrease in D_{50} with increasing stirrer speed, and therefore increased shear, is related to deformation (densification and coiling) (Chassagne et al., 2021), and/or breaking of flocs (Oles, 1992). Coiling is the restructuring of a floc into a more compact arrangement while maintaining its integrity, even after being subjected to external forces. This deformation often coincides with densification. Densification can also occur when flocs break and re-aggregate (Selomulya et al., 2003), but this results in flocs with weaker attachment strengths (Clark & Flora, 1991; Yeung & Pelton, 1996). It is unclear which process (deformation or breaking) leads to the decrease in D_{50} of our samples. Yeung et al. (1997) used turbidity as a proxy of the inverse of flocculation. Turbidity can be estimated by the transmission value of the LISST, and was found to be relatively constant (on average a decreased a 2% at the end of the measurement) in this study. Additionally, the total volume concentration remained constant. This implies that the number of particles remained the same, indicating that the deformation process dominated rather than the breaking process.

The D_{50} values of the in situ LISST measurements of each individual sample are considered a reference for the ex situ LISST and Mastersizer measurements (Figure 5). The largest difference between the in situ and ex situ D_{50} values using the LISST was observed at 100 rpm: the mean D_{50} measured ex situ using LISST was on average 180% greater than the in situ value. 90% and 60% greater values were observed using 300 and 400 rpm.

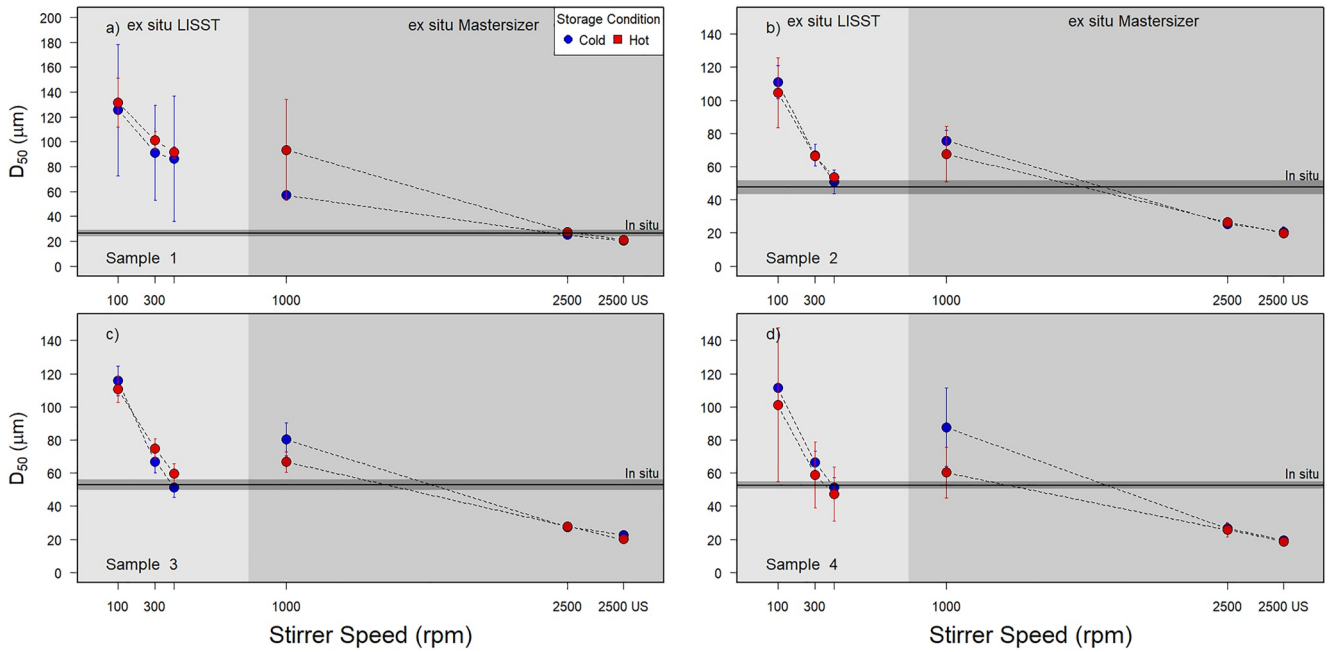

Figure 5. Impact of stirring speed on the D_{50} values of the four samples (a–d) measured ex situ using a LISST and a Mastersizer. The D_{50} values were calculated for the measurements taken for 3 consecutive weeks (week 1, 2, and 3) in both storage conditions (hot and cold) and applying different stirrer speeds using a LISST (100, 300, and 400 rpm) and a Mastersizer (1,000, 2,500, and 2,500 rpm + ultrasonic vibrations (US)). The mean D_{50} values are averaged over the storage duration; error bars indicate the standard deviation. The horizontal lines indicate the average in situ D_{50}, and the gray shading the variability within the 15-min measurement period.

The stirrer speed of the Mastersizer was larger than during the LISST measurements, resulting in smaller values of D_{50} (Figures S1 and S2 in Supporting Information S1). At the lowest stirrer speed of the Mastersizer (1,000 rpm), the ex situ D_{50} values are larger than the in situ values. At 2,500 rpm (+US), the in situ values of D_{50} are larger than the ex situ equivalents. Adding US slightly decreases the D_{50}, which could be due to breaking of the flocs, or because the vibrations caused by the high frequency sound waves lead to coiling of the flocs. The Mastersizer results suggest that there should be an intermediate stirring speed which breaks or deforms the flocs to such an extent that the conditions are equal to riverine conditions. Chakraborti et al. (2009) suggested that the choice of ex situ stirring speed can be adjusted to the in situ shear forces the researcher wants to mimic, to be able to compare in and ex situ measurements. This requires the assumption that field samples are taken in steady state, which could be true for the lake samples, but might not be the case for our riverine samples taken during the rising limb of a discharge event. As shown in this research, simulating natural conditions is very difficult, and simply measuring in situ might be the easiest and most reliable option.

Ex situ measurements are, however, valuable for determining the PSD of PPs. The difference between the effective PSD and PP PSD gives a measure of the degree of flocculation, and can also be useful to understand which size fractions in the PSD are influenced by organic matter (Lake et al., 2021). Our results suggest that the higher the stirring speed, the closer the data reflects the PSD of the PPs, which is specifically evident in the highest tested stirrer speed with the Mastersizer (Figures S3–S6 in Supporting Information S1). To fully reduce the sample to PPs, hydrogen peroxide treatment is needed, which removes all the organic matter and the corresponding cohesive bonds (Gray et al., 2010; Walling et al., 2000). Lake et al. (2021) performed ex situ PSD analysis of samples taken close to our study area after removal of the organic matter. Their data indicated that the D_{50} of PP is about 44%–52% smaller than the ex situ measurements of the non-treated samples, both measured using a Mastersizer at 2,500 rpm. This most certainly indicates that we have not reduced our samples to PPs by only increasing stirrer speed.

3.4. Impact of Storage on Ex Situ Measurements

Samples showed flocculation during the first week of storage, as shown by the large increase in D_{50} values between in situ and ex situ samples. After 1 week of storage, the ex situ mean D_{50} was 258%, 59%, 46%, and 57% larger

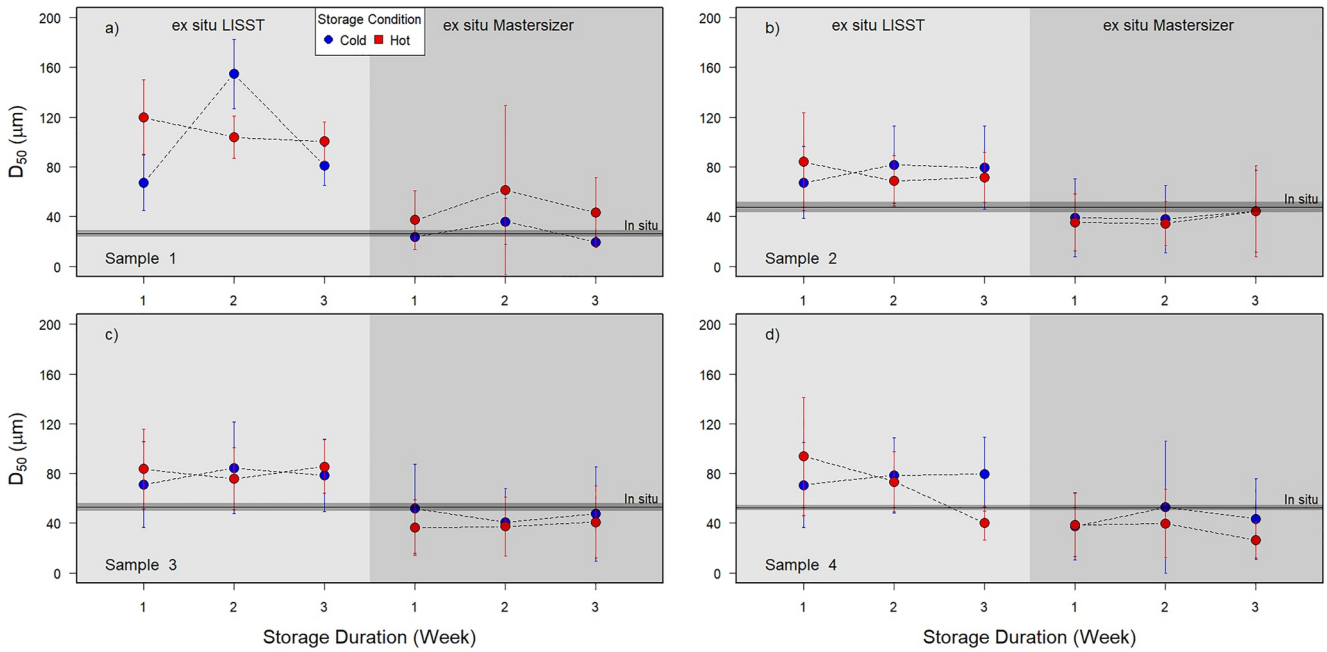

Figure 6. Impact of storage on the D_{50} values of the four samples (a–d) measured ex situ using a LISST and a Mastersizer. The D_{50} values were calculated for the measurements performed for 3 consecutive weeks (week 1, 2, and 3) in both storage conditions (hot and cold) and at different stirrer speeds using a LISST (100, 300, and 400 rpm) and a Mastersizer (1,000, 2,500, and 2,500 rpm + ultrasonic vibrations [US]). The mean D_{50} values are averaged over stirrer speeds; error bars indicate the standard deviation. The horizontal lines indicate the average in situ D_{50}, and the gray shading the variability within the 15-min measurement period.

than the in situ mean D_{50} (Figure 6). Phillips and Walling (1995) explored the effects of storage on the sample in the first days after sampling. They found an increase in D_{50} of 9%–63% compared to in situ measurements after a relaxation time of up to 3 days and using the lowest stirrer speed possible to keep particles in suspension. After storing our samples for 7 days, we found an increase in D_{50} of 207%–588% (average 293%) using the lowest stirrer speed. This is much larger than the findings of Phillips and Walling (1995), suggesting that the process of floc formation increases beyond their study time. Neither in this study, nor in the study of Phillips and Walling (1995), it was possible to resemble the in situ reference state with ex situ measurements, once the sediment had settled in storage. However, they did report a good agreement between in and ex situ measurements when storage time was short enough to avoid particle settling in the sample containers, despite the fact that flocs can also break, deform, or grow during sampling (Eisma, 1986; Gibbs, 1981). However, the storage time until settling is so short that it is practically infeasible to transport the samples to a lab for ex situ measurements. This underlines the recommendation to measure in situ to obtain robust and representative PSDs, rather than to perform ex situ measurements.

Surprisingly, the influence of storage on flocculation beyond the first week was minimal (Figure 6), and stirrer speed turned out to be far more important for D_{50} determination than storage time. The relatively constant D_{50} over time indicates that flocculation did not continue, independent of storage condition. Stabilized conditions might inhibit any further floc formation. The slight increase (13% on average, compared to week 1) in D_{50} for cold-stored samples, could potentially indicate that bonds had strengthened over time due to stabilization. In contrast, the decrease (40% on average, compared to week 1) in D_{50} for hot-stored samples could be related to the disintegration of the organic-rich flocs. Organic-rich flocs could be more susceptible to decomposition and bio-degradation in warm conditions, leading to floc breakage rather than formation. Only the cold-stored samples in week 2 showed a large increase in D_{50} compared to week 1 (201%–292%, depending on stirrer speed), which could be caused by an unusually large microbiological presence in this specific sample.

3.5. Required Measurement Time for a Representative PSD

Figure 7 shows an example of the Monte Carlo bootstrap analysis for six samples. With an increasing number of measurements, the deviation of the minimum and maximum D_{50} (and hence the possible range of outcomes) from the mean D_{50} value obtained for the total population decreased exponentially. After a certain threshold, adding

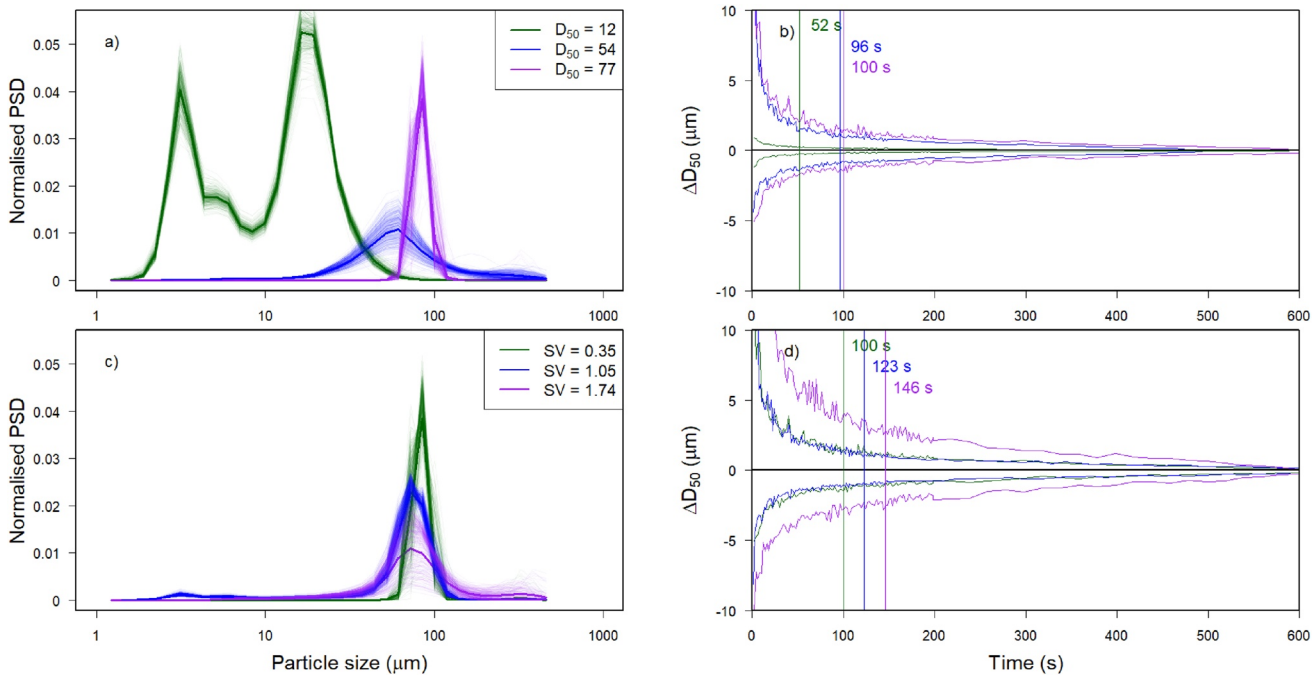

Figure 7. Example of the Monte Carlo bootstrap analysis to determine measurement time requirements. Panels (a) and (c) show examples of particle size distributions (PSDs) of individual measurements, with the average distribution indicated by the thicker line. The PSDs have different values of both D_{50} (a) span value (SV) (span values, c). Panels (b) and (d) show the corresponding measurement time requirement (in seconds) calculated from the Monte Carlo bootstrap analysis, for the threshold slope = 0.005. The threshold is reached at the vertical line in the corresponding color.

more measurements results in only a minor decrease in the statistical uncertainty (Figures 7b and 7d). This threshold defines the minimum amount of measurements (time) that are needed to obtain a statistically representative D_{50}. The threshold (threshold 1) measurement time is indicated with the vertical line, and is achieved when the smoothed slope of the minimum and maximum deviation from the actual mean reaches a slope lower than 0.005.

For all three thresholds, the required measurement time increases if the median particle size D_{50} increases, and if the SV SV increases (Figure 8). Samples which are characterized by a low D_{50} but a high SV, or the other way around, require generally less measurement time to reach the threshold. The threshold of 5% deviation from the actual mean is the strictest threshold, which is mostly sensitive to SV (Figure 8). The finding that larger grain sizes require longer measurement time, is also found by Topping et al. (2011). They compared point-measurements of SPMC to sequential SPMC measurements, and found that errors in suspended particulate sediment concentration measurements are induced by inadequate time-averaging (i.e., a too short measurement time). These errors

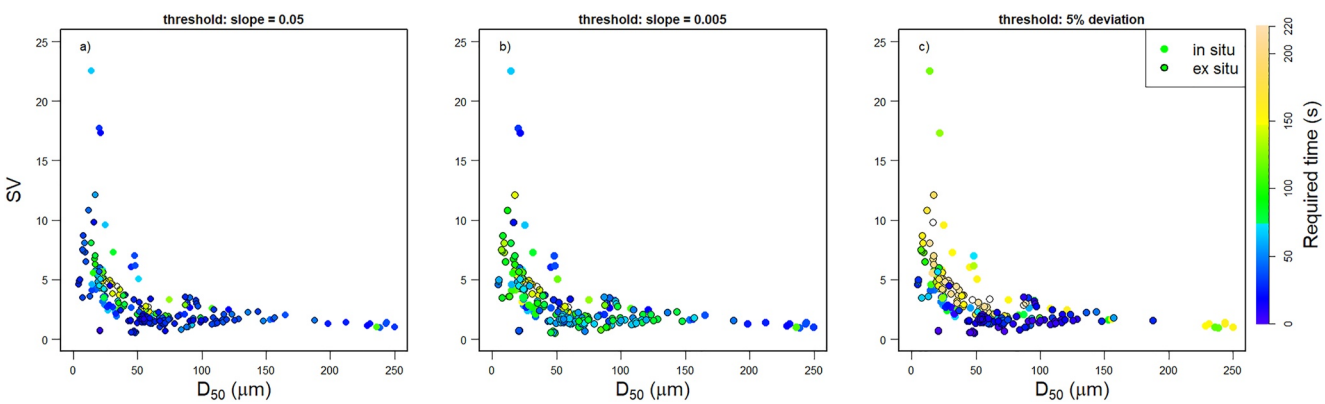

Figure 8. The relation between median particle size (D_{50}), span value (SV), and required measurement time (colors), for three different thresholds (a–c). Ex situ samples are indicated with a black circle. For the original data set source (Table 1), see Figure S15 in Supporting Information S1.

Table 2
Measurement Time Requirements (Median, Mean, and Max) for Different Types of Samples (Including Their Number) and the Three Thresholds (Slope = 0.05, Slope = 0.005, and 5% Deviation)

	Threshold (th)								
	Slope = 0.05			Slope = 0.005			5% deviation		
Sample type (#)	Median (Mean) (s)	Max (s)	# > th	Median (Mean) (s)	Max (s)	# > th	Median (Mean) (s)	Max (s)	# > th
Ex situ (83)	33 (45)	158	2	59 (67)	172	2	29 (66)	186	6
In situ (150)	57 (61)	154	3	64 (70)	179	3	121 (117)	217	6
Small (116)	32 (43)	153	1	64 (67)	179	1	30 (60)	217	6
Large (117)	47 (58)	158	4	80 (83)	172	4	108 (108)	212	6
Narrow (117)	31 (39)	153	0	65 (67)	172	0	20 (45)	217	3
Wide (116)	52 (62)	158	5	80 (83)	179	5	135 (126)	214	9
Unimodal (139)	33 (43)	153	0	66 (69)	160	0	29 (59)	214	4
Bi- and multimodal (94)	50 (63)	158	5	78 (83)	179	5	130 (123)	217	8

Note. Samples characterized as "large," are samples with a D_{50} that is larger than the population median. The opposite is true for samples characterized as "small." Samples with a "narrow" PSD are characterized by an SV that is smaller than the population median, the opposite is true for samples with a "wide" PSD. # > th indicates the number of samples for which the threshold is not reached.

were positively correlated with grain size, therefore they recommended to average over at least 60 s. To explore the robustness of the relation between sediment characteristics and required measurement time in our data, the required measurement times of all in situ and ex situ samples were calculated.

The impacts of the measurement method (in situ or ex situ), D_{50}, SV, and modality are summarized in Table 2. Regardless of the threshold, in situ, bi- or multi-modal samples with a large D_{50} and SV required longer sampling times. However, these PSD characteristics are interrelated. For example, the percentage of field samples that is classified as wide, large, and bimodal is 70%, 68%, and 60%, respectively. Similarly, only 18% of the samples are classified as wide and small, and 15% as wide and bimodal. We performed an ANOVA (analysis of variance) analysis (Text S1 in Supporting Information S1 and Figures S12 and S13 in Supporting Information S1) to determine the relative importance of PSD characteristics on the required measurement time. The required measurement time primarily depends on measurement method (in/ex situ) for thresholds 1 and 3, and the interaction between the measurement method and D_{50} for threshold 2. Other important variables were the interaction between D_{50} and bimodality (threshold 1), the interaction between SV and D_{50} (threshold 2), the interaction between SV and measurement method (in/ex situ) (threshold 2 and 3), and SV (threshold 3).

The relation between measurement method, SV, bimodality, and measurement time can be understood intuitively. In situ samples show higher temporal variability than their ex situ equivalents, thereby increasing the required sampling time. Similarly, wide and bimodal distributions are more variable, and a longer sampling time is needed to remove the effect of this variability. By approximately knowing the character of the samples, the sampling time can be tailored to a research area. The fact that similar samples have similar characteristics (i.e., most field samples have a wide, bimodal distribution; Table 2), can be used in our favor, since only one of the characteristics has to be known to make an estimation of the required sample times. Samples with flocculated particles often have a wider, coarser, and more bimodal distribution compared to the non-flocculated equivalents. This means that the presence of flocs increases the sampling time required.

The recommended sampling time can serve as a baseline for the design of in situ monitoring protocols, or as an indication for the initial design of an ex situ measurement campaign. Especially for in situ measurements, resources (time, costs, battery duration) are limited, and sampling time should be minimized as much as possible. The obtained sampling times can help optimize time and resource allocation in data collection. Minimizing sampling time means a higher spatial resolution can be obtained if time is no constraint.

When implementing this strategy in future research, one should be aware that the required measuring time is an indication, and may be system specific. Therefore, the same Monte Carlo bootstrap analysis method should be adopted in other systems independently. When a few samples with relatively long sampling times are taken, the

bootstrap analysis can determine the sampling time needed in that specific system. Furthermore, the analysis can also be used to optimize the measurement time for other statistical parameters describing the PSD, such as D_{10} or D_{90}. The procedure itself can be adjusted to the researcher's needs. The choice of threshold, which determines the time needed to obtain a representative number of measurements, is dependent on the required accuracy of the study. Additionally, if there is a need for higher spatio-temporal resolution, outlier reduction in post-processing can be considered. We tested this by excluding PSD outliers when calculating the D_{50}. An outlier is defined as the 95-percentile of the worst correlating individual samples, determined with cross-correlation. This decreased the averaged sampling time by 2 s. Care should be taken when filtering outliers, since "outliers" on the large side of the PSD spectrum could be flocculated particles.

3.6. Implications and Recommendations

The effects of storage and stirring when doing ex situ measurement of suspended (flocculated) particles should be considered carefully. The formation of flocs during storage is not neutralized by the destruction/deformation of flocs during stirring, and the PSD as measured has very little resemblance to the original in situ PSD. Ex situ measurements give reliable data only about PPs, after the right sampling treatment. When interested in the effective PSD, in situ measurements should be preferred. The drawbacks of in situ measurements are the non-controlled environment in which they are performed and the impact of bubbles and debris on the measurements. To account for this variability the sampling time needed to obtain a robust mean is longer for in situ than ex situ measurements. Additionally, the presence of the device slightly alters the water flow, the effect of which can be minimized by optimizing the positioning of the device. When in situ measurements are logistically infeasible, ex situ measurements should take place right away after sampling, without allowing the sediments to settle (Phillips & Walling, 1995), which comes with its own challenges.

This analysis reveals great variability among D_{50} estimates that are often considered equivalent. Values of D_{50} depend on the measurement instrument (LISST, Mastersizer), the measurement method (in situ and ex situ) and the sampling manipulation (storage, stirrer speed). The variability has several consequences. First, this means that "The" PSD does not exist, which can have serious consequences. For example, implementing an erroneous D_{50} of only 50 μm (300 instead of 250 μm—a realistic error as shown in this analysis) in the sediment transport predictor of Ribberink (1998), results in an underestimation of the non-dimensionalized sediment bed-load transport of 26% (Figure S14 in Supporting Information S1). Second, particle size measurements reported in one study cannot be directly compared with other studies. This stresses the need for accurate reporting of PSD measurement and analysis protocols. Unfortunately, a standard protocol to measure PSDs is lacking. The constant change and improvements of measuring instruments (e.g., from the LISST-100X to the LISST-200X, and from the Mastersizer 2000 to the 3000 edition) leads to the development of new protocols based on different assumptions. Those changes hamper the direct comparison of PSD measurements that were taken over the course of time. Especially for multimodal PSDs, such as PSDs characterizing flocculated particles (Lee et al., 2012, 2014), there is a need for a standard that allows for better comparison between measurements with alternative devices.

4. Summary and Conclusions

Experiments were performed to acquire in situ and ex situ PSD measurements with a LISST-200X. The probe was used to measure in situ during the rising limb of a runoff event, when water samples were simultaneously taken. Those samples were stored under hot and cold conditions for 1–3 weeks and subsequently measured with a LISST in the laboratory (ex situ) using a measurement chamber and magnetic stirrer. Additionally, a Mastersizer-3000 was used to study the impact of higher stirrer speeds. From these experiments, we can conclude that:

- There is a difference between the D_{50} of in situ and ex situ PSD measurements. The D_{50} of samples measured ex situ are larger, due to the formation and/or growth of flocs during the first week of storage.
- Values of D_{50} do not significantly change during the subsequent weeks of storage. The process of flocculation does not continue after the first week. Stabilization of the material on the bottom possibly prohibits further floc growth, but may strengthen the flocs. This process is more pronounced in cold-stored samples, resulting in slightly larger flocs than in hot-stored samples.
- During ex situ measurements, the magnetic stirrer causes the flocs to break and/or coil. This reduces the D_{50} value of the samples significantly, and has a larger effect than storage duration after the first week. A higher

stirrer speed results in a lower value for D_{50}. This was also visible in the measurements with the Mastersizer, where further stirrer speed increases results in even lower values of D_{50}. Adding US disperses the flocs even more, thereby decreasing the D_{50}.

- It was impossible to return ex situ samples to their original, in situ, state, despite the fact that stirring effectively decreased floc size. Therefore, we recommend in situ measurements if the effective PSD is to be acquired. Ex situ measurements are only useful for obtaining the PSD of PPs.
- The Monte Carlo bootstrap analysis shows that the PSD measurement time required to obtain a consistent and accurate value for D_{50} primarily depends on the measurement methodology (in or ex situ). Furthermore, the median grain size, the SV, and the modality are important, confirming previous research.
- The variability during in situ measurements is higher than in controlled laboratory conditions, requiring a longer measuring time for a robust estimate of the median grain size. The average measurement time was 45 s for ex situ samples, and 61 s for in situ samples, for a threshold of slope = 0.05. The other tested thresholds were stricter, resulting in measurement times of up to 217 s.

Acronyms

D_{50}	Median particle size
PSD	Particle Size Distribution
PP	Primary Particle
SPM	Suspended Particulate Matter
SPMC	Suspended Particulate Matter Concentration
SV	Span Value
US	Ultrasonic Vibrations

Data Availability Statement

The data used to generate the results in this study are made available at Sehgal et al. (2023). The script for the Monte Carlo bootstrap analysis, will be made available through the public repository of 4TU via de Lange (2023). The data for site Everlange and Rotterdam was taken from Sehgal et al. (2022c). The data for site Huncherange and tank-setup was taken from Sehgal et al. (2022d).

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