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Optimization and quality control of suspended particulate matter concentration measurement using turbidity measurements

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Abstract

The dry weight concentration of suspended particulate material, [SPM] (units: mg L⁻¹), is measured by passing a known volume of seawater through a preweighed filter and reweighing the filter after drying. This is apparently a simple procedure, but accuracy and precision of [SPM] measurements vary widely depending on the measurement protocol and experience and skills of the person filtering. We show that measurements of turbidity, T (units: FNU), which are low cost, simple, and fast, can be used to optimally set the filtration volume, to detect problems with the mixing of the sample during subsampling, and to quality control [SPM]. A relationship between T and 'optimal filtration volume', V_{opt} is established where V_{opt} is the volume at which enough matter is retained by the filter for precise measurement, but not so much that the filter clogs. This relationship is based on an assessment of procedural uncertainties in the [SPM] measurement protocol, including salt retention, filter preparation, weighing, and handling, and on a value for minimum relative precision for replicates. The effect of filtration volume on the precision of [SPM] measurement is investigated by filtering volumes of seawater ranging between one fifth and twice V_{opt} . It is shown that filtrations at V_{opt} maximize precision and cost effectiveness of [SPM]. Finally, the 90% prediction bounds of the T versus [SPM] regression allow the quality control of [SPM] determinations. In conclusion it is recommended that existing [SPM] gravimetric measurements be refined to include measurement of turbidity to improve their precision and quality control.

Suspended particulate matter (SPM) is operationally defined via filtration of seawater as the material retained on a certain type of filter with certain pore size, while the matter that passes through a small pore size filter is defined as dissolved matter

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(DM). For DM, typically a polycarbonate membrane filter with a 0.2 μm pore size is used, whereas for SPM, GF/F glass fiber filters with a nominal pore size of 0.7 μm are commonly used (ISO 1997; van der Linde 1998; Tilstone et al. 2002), although 0.4 μm pore size polycarbonate filters may also be used (Strickland and Parsons 1968; Mueller et al. 2003). We note that glass fiber filters work by adsorption of particles onto the fibers at the surface and throughout the depth of the filter (Feely et al. 1991) and have no well-defined pore size. The nominal pore size of 0.7 μm is obtained from performance tests by the manufacturer under controlled conditions and indicates a 98% retention efficiency for particles larger than 0.7 μm (<http://www.whatman.com>). Particles smaller than the nominal pore size may be retained, however, as pointed out theoretically (Logan 1993) and experimentally (Sheldon 1972; Sheldon and Sutcliffe 1969; Chavez et al. 1995).

SPM may also be referred to as total suspended solids (TSS), total suspended matter (TSM), or total particulate matter (TPM) and includes both organic (autotrophic and heterotrophic plankton, bacteria, viruses, and detritus) and min-

eral particles (Stramski et al. 2004). The term ‘total’ may be misleading, however, since very small particles pass through the filter and their dry weight is not included. We therefore adopted the symbol SPM.

The dry weight concentration of SPM, [SPM] in units of mg L^{-1} or g m^{-3} , is determined gravimetrically by passing a known volume of seawater through a preweighed filter. The filter is then reweighed after drying and [SPM] is calculated from the ratio of the difference in filter weight by the volume of the filtrate. Protocols for [SPM] measurement vary widely in procedures for filter preparation and treatment, including washing, drying, and ashing, and washing of sea salt after filtration. Also, while the measurement of [SPM] is apparently a simple procedure, accuracy and precision of the measurements vary widely depending on the measurement protocol (materials used, filter preparation and treatment, laboratory conditions, etc.) and the experience and skills of the person filtering.

Because [SPM] is defined operationally, many measurement protocol specifications have been evaluated previously. The retention of salts by glass fiber filters leading to overestimation of [SPM] has gained considerable attention, and washing of filters and filter edges with deionized water (or MilliQ water) after filtration have been proposed to remove sea salt (Strickland and Parsons 1968; van der Linde 1998). Different wash volumes have been recommended, varying between 30 mL (Pearlman et al. 1995) and 250 mL (Sheldon 1972). Despite a MilliQ wash of 300 mL, Stavn et al. (2009) found salt retention by 47 mm diameter GF/F filters to vary between 0.6 mg and 1.1 mg with increasing salinity from 15 to 34 PSU (Practical Salinity Units, see their Fig. 1) and irrespective of filtration volume. Organic material may be lost from living cells through cell-wall rupture by osmotic gradient after rinsing with MilliQ (Goldman and Dennett 1985) and/or by air suction (Goldman and Dennett 1985; Kiene and Linn 1999). Such material losses are dependent on species (Booth 1987; Kirst 1990) and filter type (Kiene and Linn 1999) and are considered to be less important on GF/F filters (van der Linde 1998), which work by adsorption. Some protocols state that the rinsing should be done with 10-20 mL of isotonic ammonium formate solution to minimize osmotic shock (ICES 2004; PML and ICES 2004). Drying time and temperature affect final dry weight (Lovegrove 1966). The vacuum pressure under which filtration takes place was not found to affect the mass retention by the filters (Sheldon 1972), even though delicate particles might break when the pressure is too high. A pressure of 300-400 mmHg is recommended (Stavn et al. 2009). The effective pore diameter of glass fiber or polycarbonate filters is known to decrease from the nominal value with increasing filtration volume until the filter is clogged (Sheldon 1972; Sheldon and Sutcliffe 1969).

The filtration volume should be such that the mass retained by the filter is sufficient to be precisely measured, but not so much that the filter clogs. Despite its importance, the estimation of filtration volume is somewhat arbitrary and depends on

the experience of the person carrying out the filtration. Typically, the person carrying out the filtration determines the filtration volume from visual inspection of the seawater sample. In this study, we investigate how low cost, simple, and fast measurements of turbidity, which is a good proxy for [SPM] (Boss et al. 2009; Neukermans et al. 2012), can be used to estimate filtration volume objectively and hence improve reproducibility of measurements. We further investigate [SPM] measurement uncertainties associated with filter preparation and treatment, salt retention, and filtration volume.

Whereas the approach described in this paper is specific to the measurement of mass concentration of SPM, the concept of pre- and post-filtration turbidity measurements may be applicable to the improvement of the quality and the quality control of the measurement of many other physical or chemical properties of SPM (e.g., Groundwater et al. 2012).

Materials and methods

Measurement of [SPM]

Measurement protocol

[SPM] is determined gravimetrically following the protocol of Tilstone et al. (2002), based on van der Linde (1998), by filtration of a known volume of sea water onto 47 mm Whatman GFF glass fiber filters with a nominal pore size of 0.7 μm . The filters were pre-ashed at 450°C for 1 h (see step 1 in the flowchart in Fig. 1), gently washed in 0.5 L of MilliQ water (2) to remove friable fractions that can be dislodged during filtration, dried at 75°C for 1 h (3), pre-weighed on a Sartorius LE 2445 analytical balance with an accuracy of 0.1 mg, denoted w_b (4), stored in a desiccator for use within 2 weeks (5), and transferred to clean 50 mm diameter Petri plates for transport.

Seawater samples were filtered immediately after collection on triplicate ashed and preweighed filters using a 250 mL Millipore apparatus with an applied vacuum of 300-400 mmHg. Filter supports were washed before filtration with MilliQ to remove any particles that had adhered to the glass. After placement on the fritted glass filter supports (6), filters

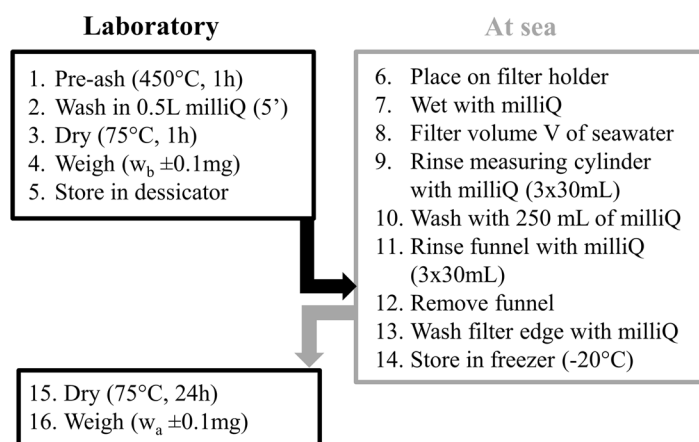


Fig. 1. Procedural flow for the measurement of [SPM] of seawater.

Table 1. Overview of types of [SPM] procedural control filters and treatments.

Filter	Filter operations (nrs as in Fig. 1)	Volume filtered	<i>n</i>	Sampled
Dry blank	1-5, 14, 15-16	0 mL	87	2008-2010
MilliQ blank	1-16, replacing samples with MilliQ water in step 8	250 mL	96	2008-2010
SSW blank	1-16, replacing samples with SSW water in step 8	500 mL	126	2007-2010
Sample	1-16	variable	366	2007-2010

were wetted with MilliQ (7), and a known volume of seawater, V , was passed through the filter (8). The measuring cylinder was rinsed with 3×30 mL aliquots of MilliQ water to flush any remaining particles (9). To remove salt, filters were washed with 250 mL of MilliQ water after filtration (10). The filter funnel was also rinsed with 3×30 mL aliquots of MilliQ water (11). After removal of the funnel, the filter edge was carefully washed with MilliQ to flush possible diffused salt (13, Strickland and Parsons 1968). The total MilliQ wash volume per filter is thus 400-450 mL, much larger than recommended by Sheldon 1972, 300 mL; Trees 1978, 50 mL; and Pearlman et al. 1995, 30 mL. The samples were stored at -20°C until further analysis in MUMM's Marine Chemistry Laboratory (14), usually within a few months after sampling. Filters were dried for 24 h at 75°C (15) and reweighed on the same balance (16), giving weight w_a , from which [SPM] is obtained as $(w_a - w_b): V$.

Filter blanks

At the start and the end of each sampling campaign, a series of filter blanks, also termed procedural control filters, were included, to assess uncertainties associated with filter operations in the laboratory and during filtrations. Three different types of blank measurements have been made with filtration of a) no water ("dry blank"), b) synthetic seawater (SSW), prepared by dissolving 34 g of NaCl in 10 L of MilliQ water, and c) MilliQ water. An overview of these filter blanks and their operations is given in Table 1.

The MilliQ and SSW filter blanks were treated exactly as the sample filters (steps 1-16 in Fig. 1) except that 250 mL of MilliQ or 500 mL of SSW was passed through the filter instead of a volume V of sampled seawater (step 8). No liquid was passed through the dry filter blanks, which were subjected only to freezing (step 14) before further analysis in the lab. A one-way analysis of variance (ANOVA) was carried out to test for differences between blanks (details of statistical tests are described further in the text).

Salt retention tests

A laboratory experiment was carried out to test whether salts diffused to the rim of the filter were properly flushed by the rim rinsing procedure (step 13 in Fig. 1). First, all steps of the procedure as described in Fig. 1 were carried out filtering a volume of 250 mL SSW onto 10 replicate filters. Next, all steps except the rim-rinsing (step 13) were carried out filtering a volume of 250 mL SSW onto another set of 10 filters. Differences between groups were then tested using an ANOVA test.

To test the dependence of salt retention on sampling volume, different volumes of SSW ranging between 150 and 2000 mL were filtered according to the procedure in Fig. 1. Differences in $w_a - w_b$ between SSW volume groups were tested with an ANOVA.

To check whether salts were properly flushed with the MilliQ wash of 400-450 mL, one unrinsed and one rinsed filter through which 500 mL of SSW was passed were analyzed using scanning electron microscopy (SEM, LEO 438VP tungsten filament SEM) with electron dispersive spectral analysis (EDS). Samples were sputter-coated with Au/Pd (Polaron SC7620).

Turbidity measurements

Turbidity, T , defined by ISO 1999 as 'the reduction of transparency of a liquid caused by the presence of undissolved matter', can be quantified in various ways (e.g., Secchi disk, light attenuation, side scatter). The Hach 2100P portable turbidity instrument measures the ratio of Light Emitting Diode (LED) light scattered at an angle of $90^{\circ} \pm 2.5^{\circ}$ at a wavelength of 860 nm \pm 60 nm to forward transmitted light, as compared with the same ratio for a standard suspension of Formazine. This optical technique for measurement of T from the side-scattering coefficient is in accordance with ISO 1999 and has significant advantages over alternative measurements of turbidity: Secchi depth measurements are obviously highly subjective and the use of instruments with a broadband light source such as the tungsten lamp suggested by EPA 1993 may be much more sensitive to spectral variations of lamp output and particle absorption properties than for the monochromatic near infrared source used here. T is expressed in Formazine Nephelometric Units (FNU) and instruments are calibrated using a set of Formazine Turbidity Standards. At the start of each sea campaign, instrument stability is ensured by recording turbidity of Hach STABLCAL Formazine standards of 0.1, 20, 100, and 800 FNU and an instrument recalibration is made if necessary. Side scattering signals are averaged over 10 measurements at 1.2 s intervals. Glass sample cells of 10 mL are used to record seawater T . The glass cell is rinsed with sampled seawater before filling. The exterior of the sample cell is rinsed with MilliQ water, dried with paper tissue, swiped with a soft microfiber lint-free cloth treated with silicon oil, and swiped again with a dry cloth. Prior to turbidity measurement, the sample cell is visually inspected for dust particles, condensation droplets, or air bubbles. T was recorded in triplicate, gently tumbling the sample cell between each measurement.

T is recorded before and after [SPM] filtrations to check adequate mixing of the water sample during subsampling for filtration. T measurement typically takes about 4 minutes to complete and portable turbidity meters can be purchased for less than 1500 US dollars. The 2100P model is no longer manufactured and has been superseded by the Hach 2100Q portable turbidimeter with improved measurements for rapidly settling samples. Calibration standards are available in sealed containers and are stable for at least 1 year, facilitating use of the method for scientists worldwide with minimal resources and/or in remote areas.

Optimal filtration volume

T as proxy for [SPM]

T and [SPM] measurements were carried out in surface waters in coastal and offshore waters around Europe and French Guyana between 2007 and 2010. Sampling sites are described and mapped in Neukermans et al. 2012. A 'least squares cubic' type II regression (York 1966) is applied to the log transformed T and [SPM] data. The least squares cubic regression, which takes into account measurement uncertainties, is applied after removal of outliers identified by the MATLAB robustfit.m routine. Correlation coefficients are given with their 95% confidence intervals, obtained from bootstrapping. Details of these statistical procedures are described in the web appendix of Neukermans et al. 2012.

Based on the [SPM]- T regression, an estimate of [SPM] can be derived from measurements of T prior to filtration. From this estimate of [SPM], the volume of seawater to be filtered can then be estimated so that an optimal mass is retained by the filter as described below.

Determining optimal filtration volume

The filtration volume, V , should be high enough so that the dry mass of the particles retained by the filter, $w_a - w_b$, is sufficient to be precisely measured, but not so much that the filter clogs. Its estimation requires a quantification of minimum measurement uncertainty on $w_a - w_b$, assessed from procedural control filters, and a maximum value for the relative uncertainty on [SPM].

For measurements of weight, the detection limit (DL) of the balance gives the minimum measurement uncertainty. The

minimum uncertainty on the difference between filter weights before and after filtration, $w_a - w_b$, is then given by (ISO 1995):

$$\Delta w_{bal} = \sqrt{2}DL \quad (1)$$

In this study, $DL = 0.1$ mg so that $\Delta w_{bal} = 0.14$ mg. Let Δw_p denote the combined uncertainties on the dry mass of retained particles resulting from filter preparation and handling (including weighing) in the laboratory and at sea, then $\Delta w_p \geq \Delta w_{bal}$. This estimate of combined uncertainties, Δw_p , is protocol dependent and can be assessed from procedural control filters. It follows that the uncertainty on [SPM] from replicate measurements, $\Delta[\text{SPM}]$, is at best equal to $\Delta w_p : V$ (in mg L⁻¹). Further uncertainties on [SPM] include uncertainties due to sample mixing and uncertainties in measurement of sample volume. For the relative uncertainty on [SPM], $\Delta[\text{SPM}] : [\text{SPM}]$, we can write:

$$\frac{\Delta w_p}{V[\text{SPM}]} \leq \frac{\Delta[\text{SPM}]}{[\text{SPM}]} \quad (2)$$

Let u_s be the maximum allowable relative uncertainty on [SPM] from replicate measurements. Then

$$V \geq \frac{\Delta w_p}{u_s [\text{SPM}]} \quad (3)$$

The optimal filtration volume, V_{opt} , is the smallest volume that satisfies Eq. 3 with a certain level of confidence, where [SPM] is estimated from T before filtration:

$$V_{opt} = \frac{\Delta w_p}{u_s [\text{SPM}]} \quad (4)$$

Effect of filtration volume on precision of [SPM] measurements

To investigate the effect of filtration volume on the precision of [SPM] measurements, six experiments were carried out in the southern North Sea in Sep 2009 and 2011 for clear ($T < 5$ FNU), moderately turbid ($5 \text{ FNU} < T < 20$ FNU), and turbid waters ($T > 20$ FNU). For each water sample listed in Table 2, [SPM] measurements were performed with filtration

Table 2. Overview of water samples collected in the southern North Sea for filtration experiments with salinity, temperature, Chl a concentration, and turbidity, T , with standard deviation ΔT .

Sample	Date	Time (h UTC)	Latitude	Longitude	Salinity (PSU)	Temp (°C)	Depth (m)	Chl a (mg m ⁻³)	T (FNU)	ΔT (FNU)
Cl	14-Sep-11	12:12	51° 29.259' N	2° 50.490' E	34.67	17.15	28.81	*	2.98	0.32
WGAB	17-Sep-09	19:48	51° 57.630' N	2° 05.510' E	34.89	17.63	*	0.9	6.83	0.14
O924A	16-Sep-09	13:59	51° 26.012' N	3° 28.474' E	32.70	17.39	16.12	4.5	10.93	0.18
Mod	15-Sep-11	11:25	51° 20.781' N	2° 57.254' E	34.63	16.86	12.64	*	12.18	0.42
T	14-Sep-11	7:05	51° 22.663' N	3° 02.194' E	34.69	16.95	10.77	*	25.53	0.31
MH5	17-Sep-09	14:16	51° 50.954' N	1° 38.965' E	34.73	17.30	22.65	< 0.06	53.30	1.59

*Not available

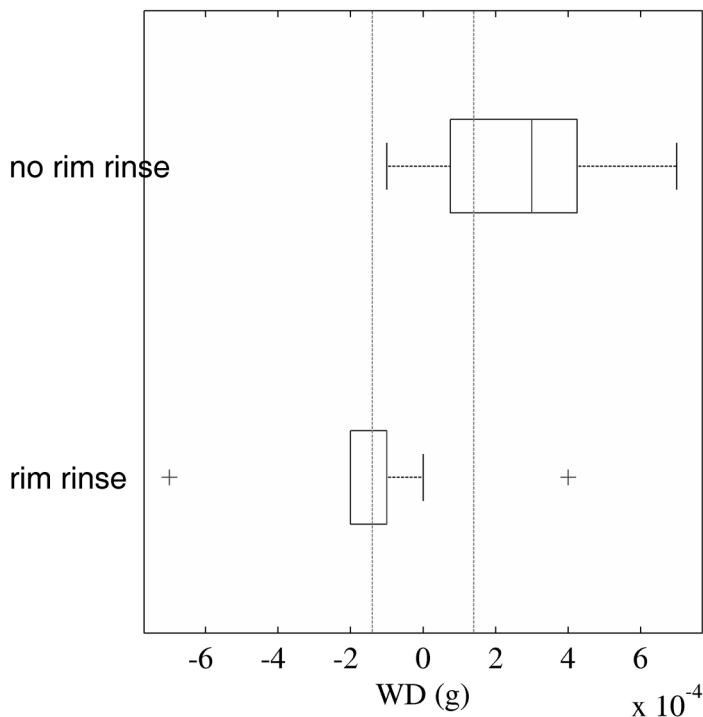


Fig. 2. Difference in filter weight before and after filtration of 250 mL of SSW of 34 PSU, with and without rinsing of the filter rim (step 13 in protocol in Fig. 1). Gray dashed lines represent uncertainty on $WD = w_a - w_b$ due to the detection limit of the balance, $\Delta w_{bal} = 0.14$ mg.

volumes of 0.2, 0.5, 1, and 2 times V_{opt} and every filtration was done on five replicate filters. T was continuously monitored during the course of each filtration experiment, to ensure good mixing of the sampled seawater. Table 2 lists the sampling time and location, salinity, temperature, depth, [Chlorophyll a], and the mean and standard deviation of T for each sample.

Statistical analysis

Between group differences are investigated by one-way analysis of variance (ANOVA), comparing the means of several groups to test the hypothesis that they are all the same, against the alternative that they are not all the same. To test which pairs of means are significantly different, paired-sample t tests were done at the 5% significance level. Analyses were carried out using the statistics toolbox of MATLAB, v. R2011b.

The distribution of observations is illustrated graphically with boxplots. The edges of the box indicate the 25th and 75th percentiles, whereas the middle line represents the sample median. The length of the box is called the interquartile range (IQR). Observations further than 1.5 IQR from the 25th and 75th percentiles are marked as outliers and indicated by crosses. This range corresponds to ± 2.7 standard deviations and 99.3% data coverage if normally distributed. The whiskers extend to minimum and maximum observations that are not marked as outliers.

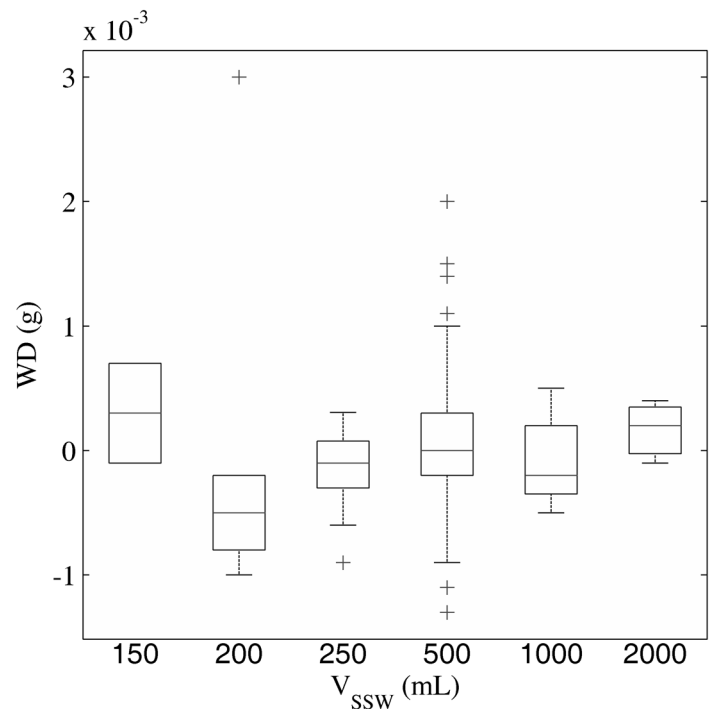


Fig. 3. Difference in filter weight before and after filtration versus filtered volume of SSW of 34 PSU. Number of observations for each volume are 2, 6, 15, 95, 5, and 3, respectively.

Results and discussion

Uncertainties in [SPM] measurement

Salt retention tests

Results from lab experiments with SSW show significantly higher residual weight ($P = 0.003$, $F = 11.76$, d.f. = 17, ANOVA) when the rim is not rinsed (see Fig. 2), compared with when the filter rim is rinsed. This is in accordance with previous works that stressed the importance of rinsing of the filter rim to flush out diffused salts (Strickland and Parsons 1968; van der Linde 1998).

The volume of SSW filtered was not found to affect SSW blank residual weights ($P = 0.72$, $F = 0.57$, ANOVA, see Fig. 3), which were not significantly different from zero. This suggests that salts are washed out using a wash volume of 400-450 mL of MilliQ, independent of the volume of SSW filtered. The independence of residual weight to SSW volume is in accordance with Stavn et al. 2009 who found salt retention of 1.1 mg, independent of volume of seawater filtered for a salinity of 34 PSU and a wash volume of 300 mL (see their Table 1).

The rinsed and unrinsed filter for SEM/EDS analysis had a WD of 0 and 1.8 mg, respectively. SEM photographs of a rectangular area of 1.72×2.29 mm² near the center of the rinsed and unrinsed filters are shown in Fig. 4a,d. Patches with high concentrations of sea salt are clearly visible in the unrinsed filter (Fig. 4a) and absent in the rinsed filter (Fig. 4d). An

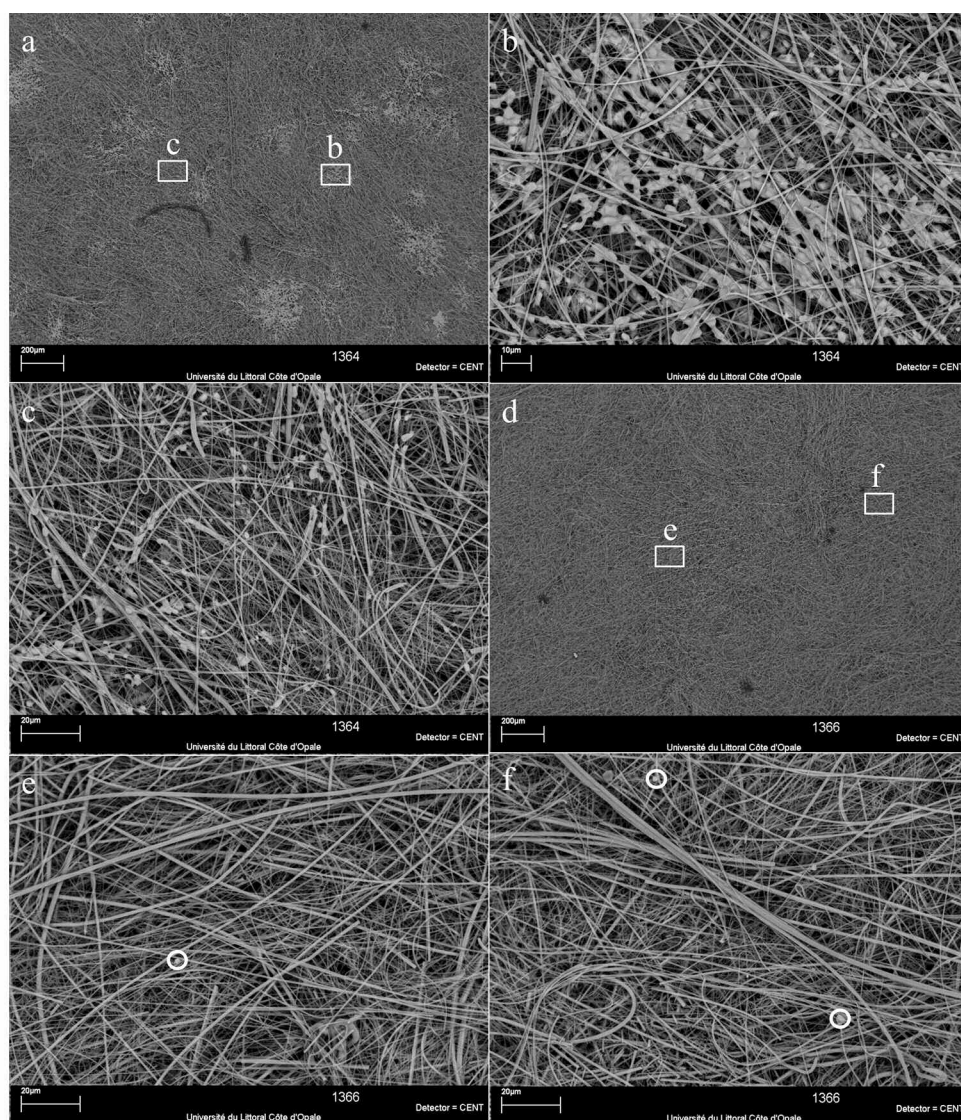


Fig. 4. SEM images of dried GFF filters after filtration of 500 mL of SSW without MilliQ wash (a, b, c) and with a MilliQ wash of 450 mL (d, e, f). Grayscale levels depict atomic weight. Patches with high concentrations of sea salt (example shown in image b) are clearly visible in image a and absent in image d. A few sea salt particles (white circles) were identified in randomly selected zones (e, f).

example of such a sea salt patch ($123 \times 164 \mu\text{m}^2$) is shown in Fig. 4b. A random zone of the same size ($123 \times 164 \mu\text{m}^2$) is shown in Fig. 4c. Fig. 4e, f show random $123 \times 164 \mu\text{m}^2$ zones on the rinsed filter, on which 1 and 2 microcrystals of sea salt were identified, respectively. This analysis shows that a MilliQ wash volume of 400-450 mL properly flushed diffused salts (Fig. 4).

Filter blanks

Fig. 5 shows the differences in filter weight before and after filtration, $WD = w_a - w_b$ for dry, MilliQ, and SSW blanks. About 46% of the blank weight differences were found within the uncertainty on WD due to the detection limit of the balance, $\Delta w_{bal} = 0.14 \text{ mg}$ (see Fig. 3). The median absolute value of WDs for all blanks is 0.2 mg, with 90% of the values below 0.6 mg.

WDs were not significantly different between blank types ($P = 0.21$, $F = 1.55$, d.f. = 2, ANOVA), indicating that salt is properly washed out.

Even though not statistically significant, negative WD are found more frequently for MilliQ and SSW blanks than for dry blanks, suggesting that friable fractions of glass fiber filters may have dislodged during filtration, while these should have been washed out before filtration (step 2 in Fig. 1). This process may be mitigated by repeating the pre-ashing, washing, and drying of the filters in the preparation phase (steps 1-4 in Fig. 1) several times until a constant weight is achieved. Stavns et al. (2009) recommend 3-4 repeat cycles to better control loss of filter mass, but this may not entirely eliminate this problem (Feely et al. 1991).

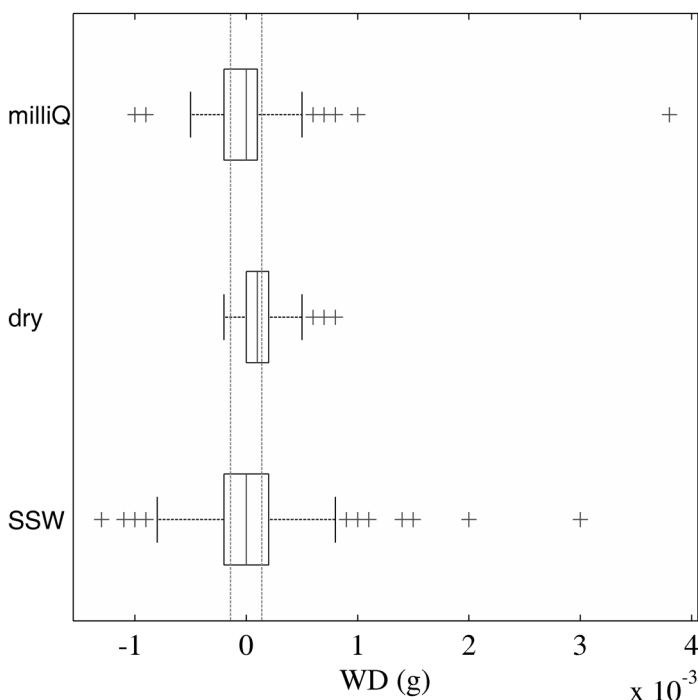


Fig. 5. Difference in filter weight before and after filtration, $WD = w_a - w_b$, for different blanks collected at the start and the end of each campaign between 2007 and 2010. Gray dashed lines represent uncertainties on WD due to the detection limit of the balance ($w_{bal} = 0.14$ mg).

No significant differences in WDs of SSW blanks were found between campaigns in 2007-2010 ($P = 0.11$, $F = 1.41$, d.f. = 27, ANOVA), indicating stability of humidity and temperature conditions in the laboratory and of sample treatment.

SSW blank WDs are thought to best reflect procedural uncertainties associated with filtration of saline waters. Therefore, estimates of Δw_p at the 50% and 90% confidence level are obtained from the 50th and 90th percentiles of absolute WDs for SSW, equal to 0.2 mg and 0.9 mg, respectively. These are further used in the calculation of the optimal filtration volume from Eq. 4.

Sample mixing

Fig. 6a shows the comparison between T recorded before and after filtration. These measurements may be separated by about 30 min and may be affected by numerous subsampling operations by different personnel taking water for measurement of SPM, chlorophyll and/or other parameters. The mean bias ($= (T_a - T_b) : T_b$) is close to zero (-2%) and symmetrically distributed with 90% of the values between -28% and 23%. Prediction error, $PE = |T_a - T_b| : T_b$, is generally between 1% and 39% with a median of 6%. In clear waters ($T_b < 5$ FNU) both bias and prediction error, denoted with 'c' subscript, show higher variability, due to higher measurement uncertainties. Also shown in Fig. 6a are observations recorded before June 2008 when seawater samples were stirred up with a measuring cylinder and then subsampled using a 1-L con-

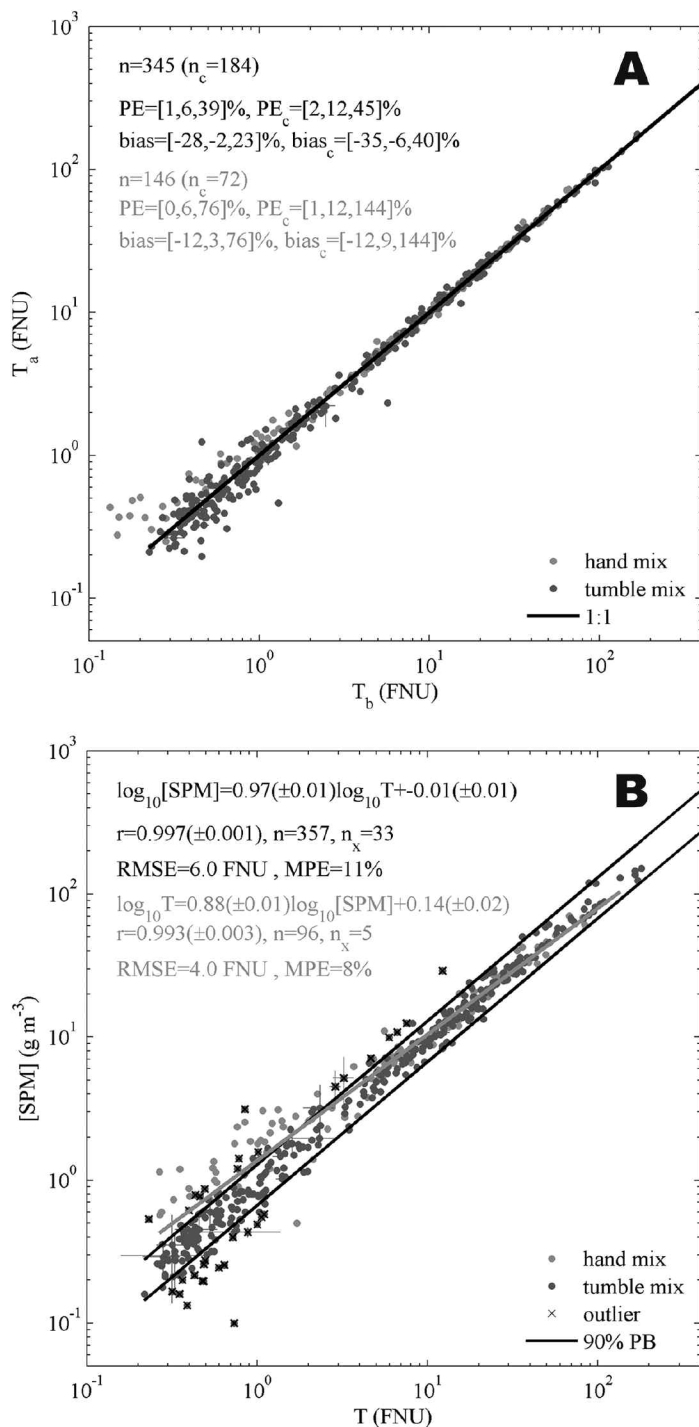


Fig. 6. (a) Comparison of T before and after filtration, with statistics given using hand mixing and tumble mixing for all observations and in clear waters ($T_b < 5$ FNU) and (b) relationship between T and [SPM] with type II regression and statistics using hand mixing and tumble mixing. The 90% prediction bounds of the regression are also shown. Error bars in (a) and (b) are shown for 5% of the observations and represent the standard deviation from replicate measurements of T and [SPM].

tainer, termed ‘hand mixing’. Comparison of T_a and T_b for this dataset is especially poor in clear water ($T_b < 5$ FNU) where the distribution of the bias is strongly positive (90% of the observations between -12% and 144% with a median of 9%). This suggests contamination of the water sample during the mixing procedure, possibly by contact with the glove worn by the person filtering. From June 2008 onwards, seawater samples were mixed by gently tumbling a closed 10 L container around several times before subsampling, termed ‘tumble mixing’. This illustrates the use of T measurements to detect problems with sample mixing.

Uncertainties in [SPM] measurement from filtration volume

Determining optimal filtration volume

A total of 366 measurements of T (= mean of T measurements before and after filtration) and [SPM] were done. Observations where only one [SPM] replicate remained were rejected ($n = 9$). Least squares cubic regression gives:

$$\log_{10}[\text{SPM}] = 0.97(\pm 0.01)\log_{10} T - 0.01(\pm 0.01) \quad (5)$$

The regression statistics and its 90% prediction bounds are shown in Fig. 6b. The offset of the regression line is not significantly different from zero for the tumble mixing dataset, whereas a significantly positive offset (0.14 ± 0.02) was found for the hand-mixing dataset, suggesting sample contamination by hand mixing. The model for [SPM] in Eq. 5 performs well with a median prediction error (MPE) of 11% and with prediction errors below 40% in 95% of the cases. The 90% prediction bounds of the regression line, shown Fig. 6b, can be used to quality control [SPM] by flagging data outside these boundaries as suspect.

For our purposes, a maximum uncertainty of $u_s = 15\%$ on [SPM] is desired. The filtration volume is optimally set by measuring T before filtration and using the regression model in Eq. 5 to predict [SPM]. From Eq. 4, it follows that $\Delta[\text{SPM}]$ is expected to be below 15% in 50% (90%) of the cases for a filtration volume V_{50} (V_{90}) of

$$V_{50} = \frac{\Delta w_{p,50}}{0.15[\text{SPM}]} \quad \text{and} \quad V_{90} = \frac{\Delta w_{p,90}}{0.15[\text{SPM}]} \quad (6)$$

where $\Delta w_{p,50}$ and $\Delta w_{p,90}$ are the 50th and 90th percentiles of weight differences for SSW blanks, i.e., 0.2 mg and 0.9 mg, respectively. Table 3 lists V_{50} and V_{90} for T between 0.5 FNU and 140 FNU. For practical use, volumes are rounded to give $R(V_{50})$ and $R(V_{90})$, respectively.

Measurements of beam attenuation have been used recently in a similar way to estimate filtration volume so that particle mass retained by polycarbonate filters was optimal for scanning electron microscopy image analysis (Groundwater et al. 2012). We note, however, that side scatter largely outperforms beam attenuation as a proxy for [SPM] (Neukermans et al. 2012) because of lower sensitivity to particle apparent density. As a consequence, [SPM] and hence optimal V can be estimated with higher precision from side scatter.

Effect of filtration volume on precision of [SPM] measurement

The filtration volume was optimally set based on T measurements before each filtration experiment using $R(V_{90})$ in Table 3. An overview of experimental results is given in Table 4, which also shows the time required to pass a given volume of sample through five replicate filters. No significant changes in T were found before and after each filtration experiment ($P > 0.05$, ANOVA), indicating good sample mixing throughout the experiments.

The coefficient of variation, c.v. (= standard deviation: mean from five [SPM] replicates), is plotted as function of filtration volume normalized by V_{opt} in Fig. 7. Results suggest that filtering more or less than the optimal volume gives a lower precision in the [SPM] measurement, except for the most turbid water sample, MH5, where c.v. is lowest at twice V_{opt} . It can be seen from filtration times in Table 4 that passing twice V_{opt} was not problematic for the most turbid samples, MH5 and T, whereas for other samples, filtration time at least tripled, to exceeding 1 h. It is thought that filter clogging may be more likely in the presence of organic particles.

Differences between c.v.’s for different filtration volumes were tested for significance by computing c.v.’s for a random selection of three out of five replicates without replacement and repeating this procedure 100 times. The median, 10th, and 90th percentiles of each c.v. dataset are also shown in Fig. 7. ANOVA tests show that the c.v. is significantly higher, and often higher than the desired precision of 15%, when one fifth of the optimal volume is filtered than when larger volumes are filtered. C.v. decreases significantly when filtration volume is increased to half V_{opt} except for sample CL. Further decrease of c.v. when filtration volume is increased to V_{opt} is significant at stations CL, WGAB, 0924A, and T. A significant increase in c.v. is observed when filtering more than V_{opt} for samples WGAB, 0924A, MOD, and T. These slight increases in inter-replicate variability may be caused by the higher likelihood of spraying off particles during rim rinsing (step 13 in Fig. 1) when filters are saturated with particles (see Figure 2.8 in Neukermans 2012).

[SPM] means were independent of filtration volume, as shown in Fig. 8, with the exception of significantly lower [SPM] for the smallest filtration volume for samples 0924A and MH5. This could be an effect of the reduction of the effective pore size with increasing volume. This phenomenon is known to be somewhat unpredictable and to depend on the particle size distribution and the shape of the particles in suspension (Sheldon and Sutcliffe 1969; Sheldon 1972) as well as potentially particle composition (“stickiness”).

Least-squares regressions of WD versus filtered volume of seawater are shown in Fig. 9. The offsets of the regression lines for all samples are not significantly different from zero, again indicating that salts are properly washed from the filters. It has been noted by Trees 1978 that the relationship between filtration volume and retained mass is linear only when salts are

Table 3. Example of a lookup table for recommended filtration volume as function of turbidity so that relative uncertainty on [SPM] replicates is within 15% in 50% of the cases $[R(V_{50})]$ and in 90% of the cases $[R(V_{90})]$.

T (FNU)	[SPM] ₅₀ (mg/L)	V ₅₀ (mL)	V ₉₀ (mL)	R(V ₅₀) (mL)	R(V ₉₀) (mL)
0.5	0.50	2673	12027	3000	12000
1	0.98	1364	6140	1000	6000
2	1.91	697	3134	500	3000
3	2.84	470	2115	500	2000
4	3.75	356	1600	350	1500
5	4.66	286	1289	250	1250
6	5.56	240	1080	250	1000
7	6.45	207	930	200	1000
8	7.35	182	817	200	800
9	8.23	162	729	150	750
10	9.12	146	658	150	600
11	10.00	133	600	150	600
13	11.76	113	510	100	500
14	12.64	105	475	100	500
15	13.51	99	444	100	400
16	14.39	93	417	100	400
18	16.13	83	372	100	400
19	17.00	78	353	75	375
21	18.73	71	320	75	300
22	19.60	68	306	75	300
26	23.04	58	260	50	250
27	23.90	56	251	50	250
32	28.18	47	213	50	200
33	29.04	46	207	50	200
37	32.45	41	185	50	200
38	33.30	40	180	50	200
40	34.99	38	171	50	175
45	39.23	34	153	25	150
50	43.45	31	138	25	150
55	47.66	28	126	25	125
65	56.04	24	107	20	110
70	60.22	22	100	20	100
75	64.39	21	93	20	90
80	68.55	19	88	20	90
85	72.70	18	83	20	80
95	80.98	16	74	20	70
100	85.11	16	70	20	70
110	93.36	14	64	10	60
115	97.47	14	62	10	60
140	117.96	11	51	10	50

Table 4. Overview of turbidity, T , with standard deviation ΔT , optimal filtration volume obtained from $R(V_{90})$ in Table 3, and time required to pass seawater through five replicate filters.

sample	T (FNU)	ΔT (FNU)	V _{opt} (mL)	Filtration time (min)			
				0.2 V _{opt}	0.5 V _{opt}	V _{opt}	2 V _{opt}
Cl	2.98	0.32	1500	17	20	29	94
WGAB	6.83	0.14	1000	13	10	24	64
O924A	10.93	0.18	500	19	12	15	78
Mod	12.18	0.42	500	10	11	16	48
T	25.53	0.31	250	20	12	30	25
MH5	53.30	1.59	150	6	8	21	18

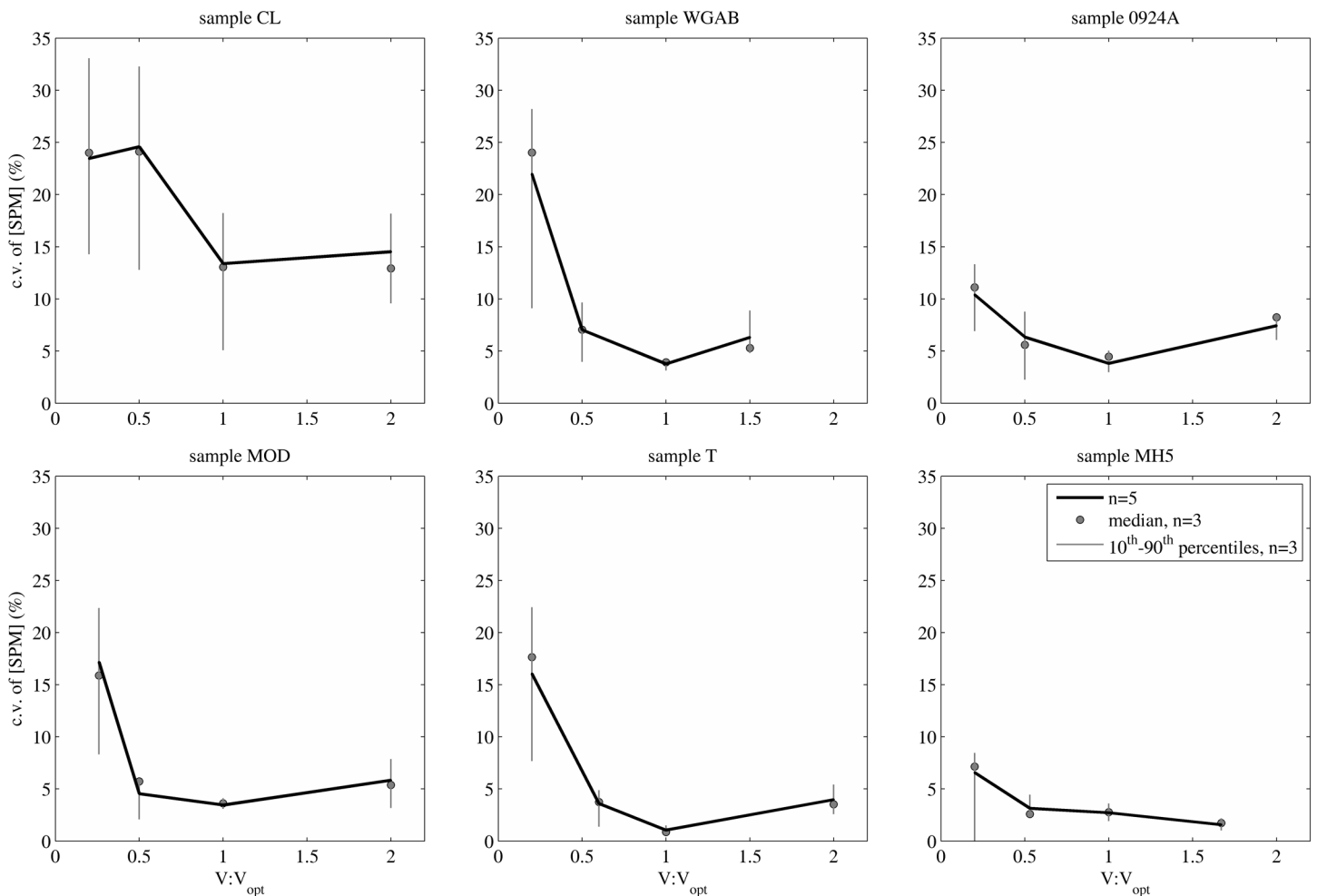


Fig. 7. Coefficient of variation, c.v. (in %) of [SPM], obtained from five replicates versus filtration volume, normalized to the optimal filtration volume, V_{opt} . Shown in gray are the median, 10th, and 90th percentiles of c.v. obtained from 100 resamplings without replacement of 3 [SPM] replicates out of 5.

washed out.

Conclusion

This study shows that simple, fast, and low-cost measurements of turbidity, T , can be used to optimize [SPM] measurements. More specifically, turbidity measurements can be used to optimally set the filtration volume, to detect problems with the mixing of the sample during subsampling for filtration, and for the quality control of [SPM]. The relationship between T and optimal filtration volume is set up using estimates of [SPM] measurement procedural uncertainties from blank measurements and a value for maximum allowable uncertainty on [SPM]. Procedural uncertainties were assessed from filter blanks where synthetic seawater of a typical salinity is passed through, representing uncertainties due to filter preparation, handling, and rinsing of sea salt. The use of various types of filter blanks subjected to different steps in the measurement procedure may help reveal sources of uncertainty. In this study, for example, differences in weights of dry

and wet filter blanks suggest that friable fractions of glass fiber filters may have dislodged during filtration. This fiber loss may be mitigated in the future by repeating the pre-ashing, washing, and drying steps of filters in the preparation phase until constant weight is achieved. Blank filters and regressions of residual weight versus filtration volume suggest that salts are properly flushed using a wash volume of 400-450 mL of MilliQ for water samples with salinities of 33-35 PSU, while a wash volume of 300 mL has been shown to be insufficient (Stavn et al. 2009).

We further investigated the role of filtration volume on the precision of [SPM] measurement by filtering volumes of seawater ranging between one-fifth and twice the optimal filtration volume. It is shown that if the optimal volume is filtered, [SPM] measurements are most precise and cost effective. In most cases filtering twice the optimal volume caused clogging and tripled filtration times to over 1 h, which is impractical and problematic in limited ship time.

It is recommended that each research group establishes

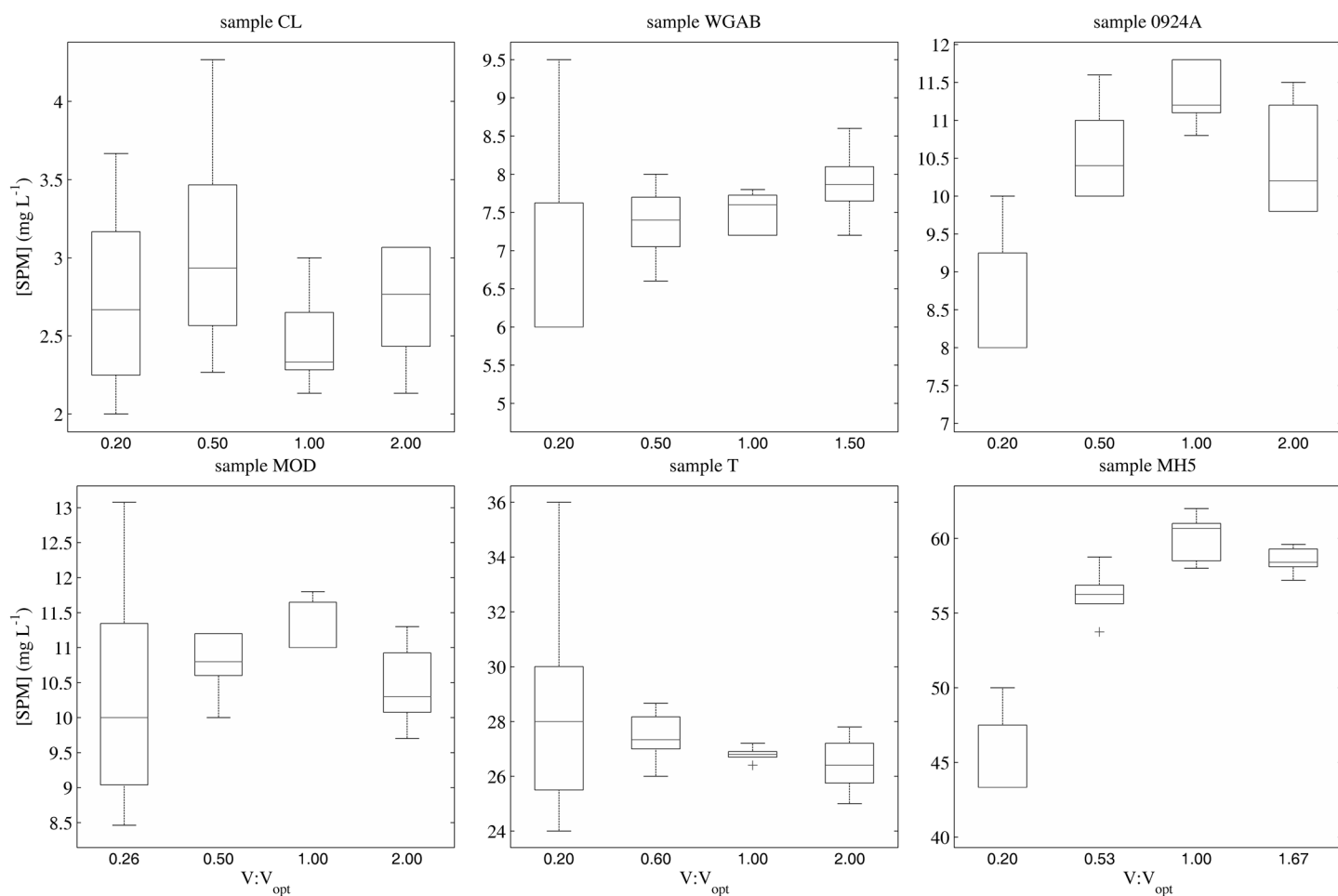


Fig. 8. Boxplot of [SPM] obtained through filtration of different volumes of sampled seawater at six different stations.

their own relationship between turbidity and optimal filtration volume, which is specific to the type of turbidity instrument (wavelength and angular response), the uncertainties of the [SPM] measurement procedure, which can be assessed from procedural control filters, the desired maximum relative variability between replicates, and the composition of the particles (organic, inorganic).

The idea of estimating optimal filtration volume from turbidity (or another suitably chosen optical proxy) and of checking turbidity before and after all filtration operations has been illustrated specifically for the mass concentration of [SPM] in this article. However, this idea could have more general application to improving the quality and the quality control for other physical or chemical properties of [SPM] (e.g., Groundwater et al. 2012).

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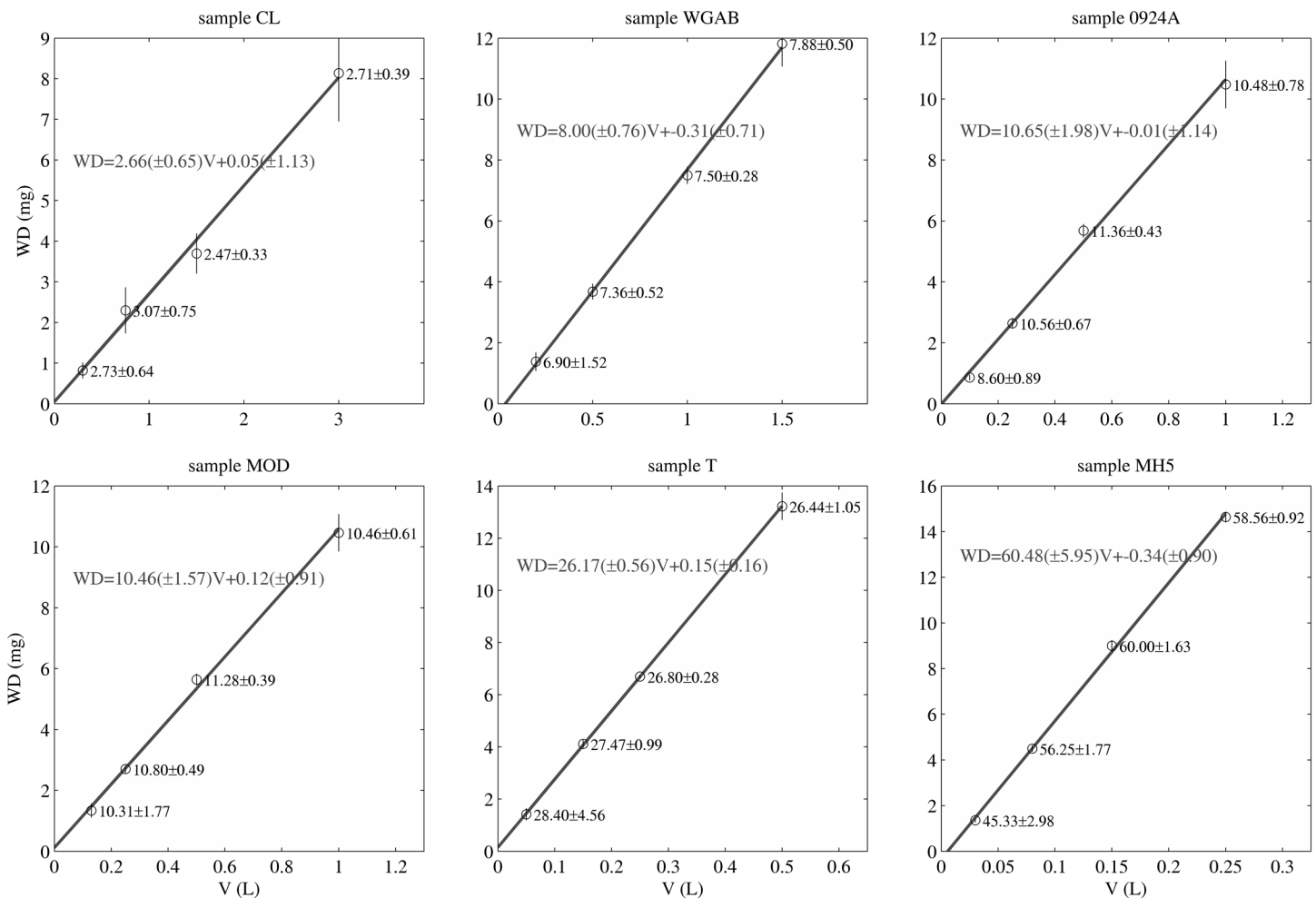


Fig. 9. Scatterplots of particulate dry mass ($WD = w_a - w_b$) versus filtrate volume, V . The error bars denote the standard error on WD obtained from 5 replicates. The mean and standard error of [SPM] are also shown for each filtration volume. Shown in red are the regression line and its equation with 95% confidence intervals of the coefficient estimates.

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