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Suspended matter concentrations in coastal waters: methodological improvements to quantify individual measurement uncertainty.

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Abstract

Measurements of total suspended matter (TSM) concentration and the discrimination of the particulate inorganic (PIM) and organic matter fraction by the loss on ignition methods are susceptible to significant and contradictory bias errors by: (a) retention of sea salt in the filter (despite washing with deionized water), and (b) filter material loss during washing and combustion procedures. Several methodological procedures are described to avoid or correct errors associated with these biases but no analysis of the final uncertainty for the overall mass concentration determination has yet been performed. Typically, the exact values of these errors are unknown and can only be estimated. Measurements were performed in coastal and estuarine waters of the German Bight that allowed the individual error for each sample to be determined with respect to a systematic mass offset. This was achieved by using different volumes of the sample and analyzing the mass over volume relationship by linear regression. The results showed that the variation in the mass offset is much larger than expected (mean mass offset: 0.85 ± 0.84 mg, range: $-2.4 - 7.5$ mg) and that it often leads to rather large relative errors even when TSM concentrations were high. Similarly large variations were found for the mass offset for PIM measurements. Correction with a mean offset determined with procedural control filters reduced the maximum error to $<60\%$. The determination errors for the TSM concentration was $<40\%$ when three different volume were used, and for the majority of the samples the error was $<10\%$. When six different volumes were used and outliers removed, the error was always $<25\%$, very often errors of only a few percent were obtained. The approach proposed here can determine the individual determination error for each sample, is independent of bias errors, can be used for TSM and PIM determination, and allows individual quality control for samples from coastal and estuarine waters. It should be possible to use the approach in oceanic or fresh water environments as well. The possibility of individual quality control will allow mass-specific optical properties to be determined with better resolved uncertainties and, hence, lower statistical variability, greatly improving our capability to model inherent optical properties of natural particles and its natural variability, e.g. dependence on particle size and the complex refractive index.

Keywords:

gravimetric techniques
analytical errors
particulate inorganic matter
particulate organic matter
loss on ignition
glass fiber filters

1. Introduction

Natural waters contain a large variety of particles, such as bacteria, phytoplankton, organic and minerogenic detritus. In coastal and estuarine waters but especially in rivers the particle concentrations can be high. The interest in particle mass concentration, its optical properties, and further particle analysis has increased recently to facilitate satellite remote sensing in coastal and estuarine waters (e.g. Babin et al., 2003; McKee and Cunningham, 2006; Tilstone et al., 2012). Errors in the determination of total suspended matter concentration by remote sensing are usually expressed as deviation from the in-situ derived values while their uncertainties are assumed to be of less importance (Global Climate Observing System, GCOS, 2011).

In coastal and inland waters the particle composition is often dominated by minerogenic matter (e.g. Bowers and Binding, 2006). A simple and widely used method to characterise water with respect to the suspended

particles is the determination of the mass concentration of all suspended particles [TSM] and those separated into the suspended particulate inorganic and organic matter concentration, [PIM] and [POM], respectively. The term "total" in TSM is used here with respect to the sum of [PIM] and [POM]. The separation can be done by using the loss on ignition (LoI) technique (Pearlman et al., 1995; see Stavn et al., 2009 for details). The separation can be achieved by volatilising the organics during combustion at ~ 500 °C. To allow collection of large masses in waters with very low particle concentration and subsequent filter combustion, glass-fibre filters are often utilised for this analysis (e.g. Strickland and Parsons, 1968; Trees, 1978).

Together with optical measurements the mass-specific light absorption and scattering is used to characterise the particles (Babin et al., 2003; Bowers and Binding, 2006; Stavn and Richter, 2008; Moate et al., 2012; Neukermans et al., 2012a) for which accurate mass determinations are needed. Standard procedures exist for [TSM] determination in fresh and sea water

(Strickland and Parsons, 1968; Pearlman et al., 1995). Further improvements of these standard procedures have been described and evaluated most recently by Stavn et al., 2009 and Neukermans et al., 2012b. However, no evaluation of the determination uncertainty for individual samples is available. For example, structural water in clays leads to underestimation of [PIM] and consequently overestimations of [POM] in the Lol technique (Mook and Hoskin, 1982). These errors can be corrected (Barillé-Boyer et al., 2003) when the mineral composition is known. Similarly, degradation of carbonates to CO₂ at higher temperatures can lead to an underestimation in the PIM mass determination (Hirota and Szyper, 1975). Water of hydration, e.g. that associated with the remaining salt in the filter is another source for a bias in [PIM] and [POM] (Stavn et al., 2009).

Another well-known bias is the retention of salt in the margins of the filters (Banse et al., 1963; Trees, 1968; Etcheber, 1981). This salt cannot be washed out completely as the margin of the filter is covered by the edge of the filtration funnel during washing. Attempts were made to remove the salt from the margins by rinsing additionally the rim of the filter after the funnel has been removed (Strickland and Parsons, 1968, Tilstone et al., 2002, Neukermans et al., 2012b). The salt water enters the margin by capillary forces, as often the seawater is poured onto dry filters. First attempts to quantify the error were done by Trees (1978) and Etcheber (1981). Recently, Stavn et al. (2009) reported on the salinity dependence of this systematic error for TSM determination of sea water, induced by retention of salt and water of hydration in the filter, and proposed corrections by either determining general salt correction curves or sample individual mass offset with blank filters (procedural control filters) through which only particle-free sample water is passed. The sometimes large statistical variability in these offsets found by Stavn et al. (2009) (max: ± 0.527 mg, see their Table 1) would still represent a significant error source in the total determination even after correction of the salt of retention offset. Rinsing the rim of the filter (Tilstone et al., 2002) and optimizing the filtration volume (Neukermans et al., 2012b) might minimize the error.

In addition, losses of filter material during filtration and combustion represent an additional source for a systematic error (see Stavn et al., 2009 and references therein). Errors related to filter mass losses are assumed to be small, as filters are prepared by pre-washing and pre-combustion that should greatly reduce these losses. However, sample filter weights after combustion were found to be significantly lower than that of the empty filters (pers. observations). The final impact of these material losses on the determination error is unknown for single measurements. The effect would partly be corrected by the approach of Stavn et al. (2009) but would be relevant for freshwater environments as well when salt of retention biases are not expected. It should be noted that the above described errors are real bias errors that, hence, cannot be evaluated from replication of [TSM] measurements with the same volume.

The study presented here examines the possibility of a more accurate and precise determination that allows estimation of the individual error by using several different volumes during sample filtration (Trees, 1978) and analysing the mass over volume relationship, effectively eliminating problems with biases, i.e. systematic filter mass changes. It will be shown that mass concentrations and their individual errors can often be determined very precisely (errors $\ll 10\%$) and that errors associated with the common methods can be very high ($>50\%$).

2. Materials and methods

2.1. Filter types and filter preparation

For most measurements, Whatman GF/F glass-fibre filters (\varnothing 47 mm). In an experiment to assess the extent of the salt retention a similar type from Macherey and Nagel (GF-5) was used with diameters of 45, 47, and 50 mm. Glass-fibre filter are composed of layers of thin, randomly oriented glass fibres forming a net that retains large particles on its surface and small particles in the depths of the filter. The minimum size of particles collected with these filters depends on the filter thickness but also on the filtration force (strength of vacuum, filter loading, etc.) and the combustion; it was determined to be $<0.5 \mu\text{m}$ (e.g. Chavez et al., 1995).

If not stated explicitly, the filters were prepared according to a common practice (van der Linde, 1998). The filters were combusted for 1 h at 500 °C and stored in a vacuum desiccator to gain room temperature. Then, the filters were individually washed by placing them onto a Sartorius 250-ml glass vacuum filtration unit and passing ~ 100 ml purified water through the filter under mild vacuum (less than 200 hPa). The filters were then transferred to plastic PetriSlides™ (Millipore) and dried at 60 °C overnight. Finally the weight of each filter was determined with a Sartorius ME 5-F analytical microbalance (precision: $\pm 1 \mu\text{g}$). The accuracy of the balance was controlled regularly with a 10 ± 0.003 mg certified calibrating mass. The combusted, washed, dried, and weighed filters were stored in the PetriSlides™ before usage. Experiments to assess the performance of the combustion and washing procedure revealed similar results to Stavn et al. (2009): 1) after a combustion phase of 30 min a constant weight was reached, that did not significantly decrease with longer combustion times of up to 6 h. Longer times and higher temperatures were avoided, as filters are known to become brittle, 2) the effect of washing was evaluated and a single wash was sufficient to remove loose particles from the filter. However, longer storage of the filters and using them for suspended matter sampling seems to initiate another weight loss by either combustion or washing (i.e. during sample filtration). These losses can be substantial (>1 mg) and represent a significant error source for the determination of suspended matter (by loss during filtration) and of the inorganic part (by loss during combustion). After experimental treatments or sample filtration the filters were dried at 60 °C for 24 hours, stored in the vacuum desiccator to gain room temperature, and the weights

determined again. When required (e.g. to determine the inorganic part of suspended matter) the filters were combusted at 500 °C for 1 hour, placed in the desiccator, and weighed again.

2.2. Suspended matter concentration

Several cruises with the RV *Heincke* between the years 2011 and 2013 were used to collect surface water samples in the German Bight ($n=434$). Samples were taken from turbid waters close to the coast, in the Elbe Estuary, and from relatively clear offshore waters. To determine [TSM], an appropriate volume (100 ml to several litres) of a sample was filtered under mild vacuum (<200 hPa) onto a filter to which shortly before filtration some ml of purified water was given to saturate the edge of the filter with pure water. – Note that therefore we did not wash the edge of the filter after removing the funnel (Strickland and Parsons, 1968, Tilstone et al., 2002) as this might induce uncontrolled loss of sample material.

Generally, it was intended to filter as much sample volume as possible to gain a maximum mass on the filter and thereby reduce the influence of systematic errors due to retention of salt or loss of filter material. To remove saltwater from inside the filters they were washed immediately after filtration three times with ~50 ml of purified water. The filters were placed back into the PetriSlides™ and immediately dried on air.

A simple correction for salt mass retention in the filter is tested as described by Stavn et al. (2009): a mean mass offset by the retention of salt in the filter was determined from particle-free sample water (filtered through 0.2- μ m membrane filters) that was passed through several blank filters. These procedural control filters were washed and subsequently handled like normal sample filters. For simple calculations of [TSM] and [PIM] the mass gained by sample filtration before and after combustion, respectively, was divided by the sample volume. Correction of the salt retention was done by subtracting the mean mass difference of the procedural control filters before dividing by the volume.

2.3. Statistical analysis and quality control

In some lab experiments and for all natural samples, [TSM] was determined by filtering 3 or 6 different volumes of the sample onto different filters. A linear regression analysis was performed for each set of filters with *Matlab* for volume versus the gained sample mass. This analysis results in a slope and axis intercept determination, their relevant standard errors, and the coefficient of determination. The slope represents the concentration, the intercept the mean mass offset due to salt retention and filter material losses by filtration or, for combusted filters, additional material loss during the final combustion step. The fit accuracy gives information about the determination uncertainty.

When six different volumes of a sample were used, the determination precision is improved by identifying and removing outliers. This was done by determining for each data point of one linear regression analysis the individual residual and the *Cook's* distance with *Matlab*. When both values were more than double the averaged values for the other points, this point was considered to

be an outlier. This procedure was repeated for the remaining points, etc. In most cases one point was removed, and only occasionally two points. In general, removing outliers increased the coefficient of determination (r^2) and decreased the statistical determination error of the concentration and the offset.

The statistics of the linear regression analysis of [TSM] values were used for quality control of the determination for a single sample. Samples with $r^2 < 0.8$ ($n=23$, 5%) were not considered in the following, as here the relative determination error was $>50\%$. In most of these cases ($n=22$) these high errors were observed when using three different volumes. In a few cases the linearity in the three to six values was good but the obtained slope was not significantly different from zero, meaning [TSM] was below the detection limit.

3. Results and discussion

3.1. Salt retention in the filter

A series of simple lab experiments were performed to verify the sources for the mass offset in sample filters and to determine the possible absolute values for this offset. It is assumed that according to reports of Banse (1963) and others (see Stavn et al., 2009 for details) retention of salt in the margin of the glass fibre filters will lead to a positive mass bias. Reduction of the filter weight can occur when filter material is lost during the filtration and combustion procedure. The first occurs probably by mechanically breaking off small pieces of glass fibres that are simply washed out during filtration. Both material losses are normally reduced by the filter preparation (see 2.1).

First, the problem of filter washing to remove seawater is considered. In the following experiments seawater is replaced by a NaCl solution. A 47-mm filter through which a few ml of a 30 g/L NaCl solution is poured, but that is not washed with purified water afterwards, gained ~18 mg of mass. This gain can be explained by a volume of ~600 μ l of the solution remaining in the filter after the filter was removed from the filtration unit. Typically, only a few milligrams of particulate matter are collected on sample filters. Small variations of this salt in the filter are possible and would lead to large errors in the particle mass determination. Therefore filters are typically washed to remove the seawater, but this washing does not appear to be sufficient to remove sea water from the filter margin (Banse et al., 1963, Stavn et al., 2009). Additional washing of the rim did reduce the final filter weights, this is interpreted as being effective in removing salt from the margin (Neukermans et al., 2012b). The effectiveness of washing was tested for filters of different diameters (45, 47, and 50 mm) that were not prepared as usual, but just taken from the package, dried, and weighed. The filters were placed in the same filtration unit such that for a larger filter a larger part of the filter area was covered by the funnel of the filtration unit. A few ml of a 30 g/L NaCl solution were poured onto dry filters, filtered through, and the filters regularly washed with purified water. The mean mass the filters gained by this procedure clearly increased with the

diameter of the filter (Fig. 1) and was on average ($n=5$) 0.34, 1.20, and 2.37 mg for 45-, 47-, and 50-mm filters, respectively.

In a second test the same experiment was repeated but before the NaCl solution was given onto the filter, a few ml of pure water was placed onto the dry filters (Pearlman et al., 1995, Neukermans et al., 2012b) to soak the filter margin with pure water and thereby preventing the salt solution from entering the filter margin. Now the filters did not gain weight, but instead lost weight of between 0.08 and 0.33 mg (Fig. 1). This loss was not correlated by the filter diameter, but the largest loss is found for the largest filter, which also had the highest mass for an empty, unprocessed filter (~145 mg, compared to ~125 and ~120 mg, for 47-mm and 45-mm filter, respectively).

These experiments, admittedly performed under ideal lab conditions with NaCl solution, not with seawater, prove, however, that the salt remaining in the margin of the filter that is covered by the funnel and that cannot be washed out from the margin, is the main source for observed positive mass offsets. Reducing the filter area covered by the filtration funnel reduces this offset. Filling the margin with salt-free water before filtration of the salt solutions reduces this positive offset further, such that the negative offset induced by washing out filter material debris during the experimental procedure is detectable.

Any additional potential source for either positive or negative mass difference is not necessary to explain the above results. Stavn et al. (2009) have shown that the salt related offset is a function of salinity, and might be estimated if the salinity is known. Other dissolved matter in seawater besides salt will be responsible for a positive offset as well but its effect in seawater might be small compared to that of salt alone. The situation in freshwater environments might be different.

Two recommendations for the overall procedure can be given based on these results: 1) the filters should be filled with purified water shortly before the sample is filtered through to avoid sample water filling the margin 2) the filter diameter should be as small as possible for a given filtration unit, to reduce the area covered by the funnel. The first recommendation was implemented in the following experiments and measurements, the second is less easy to implement as a smaller diameter makes exact placing of the filter centrally onto the base of the filtration unit more difficult, increasing the risk for incomplete filtration. Whilst pre-wetting the filter with MQ can be shown to reduce the impact of salt retention on the filter for lab samples, the following measurements for field samples still show positive offset values that are large and probably still attributable to salt retention (though presumably reduced as a result of the pre-wetting).

The following measurements will also show that measurement conditions with natural samples are different from that of lab experiments and that even with these improvements large positive offsets very likely due to salt retention are observed and, hence, are potentially responsible for large errors.

3.2. Analysis of potential errors

This improved procedure together with recommendation of Stavn et al. (2009) was used for the determination of TSM concentrations, [TSM], of samples from coastal and offshore waters of the German Bight. Together with sample collection on filters, a set of ~130 procedural control filters was prepared. The obtained weight changes of these procedural control filters varied between 0.05 and 1.06 mg, with a mean (\pm sd) of 0.52 ± 0.21 mg. No clear variation with salinity was observed but salinity varied only between 28 and 34 PSU. The mean value of this salt retention and its variation is lower than values reported by Stavn et al. (2009) and Trees (1978). As both used filters of the same diameter, this might be due to the improvement applied here (see 3.1). The still relatively large variation of the weight offset in this data set (s.d.: ± 0.21 mg), as well as in that of Stavn et al. (2009), represents a significant source for uncertainty, even if the potential offset is corrected by subtracting the mean offset determined by the procedural control filters.

In [TSM]-measurements with a single volume it is intended to filter a large volume, thus, to collect an optimal mass, thereby reducing the relative error due to salt retention, filter material losses, and the general measurement uncertainties (e.g. Neukermans et al., 2009b). Often, e.g. when the sample contains a larger amount of organic matter, a filter gets clogged before several milligrams can be collected. In all filters through which the largest sample volume had been passed (representing the common measurement approach), the collected mass on the filter varied between 1 and 37 mg. However, for the majority of the samples this mass was between 2 and 5 mg only (Fig. 2). The variation of the weight offset of the procedural control filter is used to calculate potential errors with these filter masses, here considering extreme values by taking two standard deviations (± 0.42 mg). The potential error is below 2% for large collected masses, increases to values >50% for occasionally very low masses, but is still between 10% and 20% for a large part of the samples. These large potential errors can occur despite the efforts taken for filter preparation, blank filter collection, and correction for the salt retention, and might in many cases be a major source for variations in determinations of mass-specific inherent optical properties of suspended matter. The relative error is even larger for the filter weight after combustion and for [POM] determination due to the typical lower masses of PIM and POM. It is shown later that variation of the mass offset between samples is actually much larger than that between procedural control filters, leading to even larger actual errors. A method is therefore considered in the following to further improve precision and accuracy of the [TSM] and [PIM] determination, not to reduce the individual error, but to give exact values of the error for each sample not relying on the calculated potential error.

3.3 Error analysis for individual samples

At the beginning it was considered to determine the offset for each sample individually, not relying on procedural control filters prepared for each sample and the assumption that the offset determined for these

filters is the same as for sample filters. To obtain individual offsets, it is assumed that 1) the absolute weight difference of a filter before and after filtration of the sample aliquot is the sum of the weight of the particles retained on the filter, the weight of the salt remaining in the filter, and the filter material losses by the filtration procedure and combustion (when considering PIM determinations), and 2) that the mass of the particles on the filter varies linearly with the sample volume, whereas 3) the other weight differences (that for salt and material loss) are constant and not influenced by the sample volume (see Stavn et al., 2009). The remaining source of the procedural error is a filter to filter variation of these constant mass differences, considering that all other errors (e.g. that of weight and volume determination) are negligible. Indeed precision of the balance (see 2.2) and that of the measuring cylinders ($\pm 0.5\%$) would lead to errors of maximally 1%, and much care had been taken to keep particles in suspension, not to induce large particle concentration errors due to sedimentation.

To perform such an analysis, a set of filters can be prepared with different volumes of the same sample, as was done by Trees (1978) and a linear regression analysis performed for the correlation of sample volume over absolute filter weight difference (sample minus empty filter). The linear regression statistics will directly give results and errors for the determination of the mass concentration (slope) and the constant mass bias (offset at axis intercept), making the determination of the offset to correct concentration results actually redundant.

Before adopting the method to natural samples, some lab experiments were conducted to determine its potential precision and accuracy. A set of filters was prepared and different masses of a mineral powder were placed directly onto filters and weighed ($n = 25$, in five different weight intervals of 1 – 5 mg, a range chosen to be relevant for samples with largest potential error). The filters had been taken directly from the filter box without the normal filter preparation step to maximise potential uncertainties induced by filter mass losses. The direct placing of the mineral material onto the filter was done to avoid the necessity to keep the material in suspension when determining a sample volume, as the material sinks relatively fast. The mineral powder was prepared from a bulk quartz mineral powder. This bulk material had been sieved through sieves with pore sizes between 20 and 200 μm . A fraction with sizes between 20 and 63 μm was used for the experiment, to reduce the amount of small particles passing through the filter and the number of larger particles that easily fall off the filter. The actual amount of particles passing through the filter was negligible when checked with sensitive turbidity measurements of the filtrate. The mineral powder was also chosen because it did not show any structural water in infrared absorption measurements. This water would be removed by combustion and this would lead to mass losses by combustion. Thus, mass losses by drying at 60 °C and combustion at 500 °C were found to be negligible. The filters with the mineral powder were individually placed in the filtration unit and ~100 ml of either purified water or a dilute NaCl solution (1.5 and 3

g/L) was poured onto each filter and passed through by mild vacuum. The filters were not washed afterwards, the dilute NaCl solution were used to induce a weight offset of ~0.9 and ~1.8 mg by the 1.5 and 3.0 g/L solution, respectively. The filters through which purified water had been passed ('0 g/L' in Fig.3) were afterwards combusted and weighed again. The experiment allows determination of the influence of filter to filter variations on the salt retention and filter mass losses, and any additional error influencing the complete procedure.

For each of the four experiments (pure water (0), pure water then combusted, 1.5, and 3.0 g/L NaCl) the obtained mass difference of a filter was linearly related to the mass deposited on the filters (Fig. 3). Before the final linear regression was performed, a few points were removed as outliers. These outliers showed always an underestimation of the mass and are probably induced by losses of the mineral material when the filters were transported from the balance to the filtration unit, or by larger filter material losses with a few single filters. When these outliers were removed the linear regression showed very high coefficients of determination of 0.991 - 0.997. The observed offset increased linearly with the NaCl concentration of the solution used (Table 1): it was -0.31 mg for pure water, and 1.78 mg for the highest NaCl concentration used. A linear regression for the correlation of the offset vs. NaCl concentration yielded a coefficient of determination of 0.998 ($n=3$). For the combusted filters this offset was -2.15 mg, showing a strong but rather constant filter material loss by combustion. The slope obtained for each experiment should in principal be 1.00. It was close to 1.00 in all cases (Table 1), in three cases it was significantly different from 1.00 by -2% to -4% ($p < 0.001$, t-test).

Table 1.
Results of the linear regression analysis of data shown in Figure 3.

NaCl conc. [g/L]	Slope \pm se	Offset \pm se	r ²	df
0.0	1.00 \pm 0.02	-0.31 \pm 0.05	0.996	19
1.5	1.03 \pm 0.02	0.66 \pm 0.04	0.997	22
3.0	0.98 \pm 0.01	1.78 \pm 0.05	0.996	20
0.0; combusted	0.96 \pm 0.02	-2.15 \pm 0.07	0.991	21

The precision of the slope determination was between 1% and 2%, that of the offset determination between 0.04 and 0.07 mg. This experiment confirms conclusively that filter to filter variations of material losses or gains are relatively small and that the proposed method can be used to determine a mass concentration and might give a good accuracy and precision. The experiments showed acceptable precision errors of $< \pm 2\%$ for the mass concentration, and low errors for the mass offset determination (which, however, is not influencing the concentration error). Accuracy is also shown to be better than $\pm 3\%$ for un-combusted filters and was about $\pm 4\%$ for the single set of combusted filters. Both values are mainly influenced by filter to filter variation of the offset or the full mass, and the results would have been significantly worse if outliers had not been removed. The proposed method allows identification of "bad" filters and removing them from the analysis.

The described method was applied to natural samples, except that the effort was reduced, often only three different volumes are used; for some samples six different volumes are used ($n=79$). In case of three volumes no analysis for outlier can be performed; for those with six volumes removing outliers was very successful in increasing precision. Analysis of these outliers showed that often the values for the highest volume deviated strongest from linearity, indicating that "overloading" the filter should be avoided. In the 79 cases when six filters were used, 13 times two points were removed, 49 times one point, and 17 times none; i.e. $\sim 16\%$ of all measurements ($n= 6 \times 79 = 474$) were identified as outliers. In general a good linear correlation was found for [TSM] and [PIM] measurements. [PIM] measurements were only performed for a limit set of samples ($n = 92$ of 434), but in principal showed the same behaviour regarding precision and number of outliers. In the example shown in Figure 4, - one point was removed as an outlier as indicated - the coefficients of determination were ≥ 0.994 and the obtained errors for the concentrations were ≤ 0.10 mg/L, or on the relative basis 2.4% for the [TSM] and 4.5% for the PIM determination. The observed weight offsets in this example were 0.51 ± 0.13 mg for [TSM] and -0.27 ± 0.21 mg for [PIM]. This example represents a measurement of about average quality: the obtained mass on the filters were rather large (up to 9.7 mg), significantly reducing the general relative errors, but the filter to filter variations were significant, including the one clear outlier.

When considering all samples for which r^2 was >0.8 ($n=411$), r^2 was >0.9975 in about 28% of the samples and then the determination error for [TSM] was $<5\%$. The same analysis performed for the limited set of [PIM] determination showed similar results (data not shown).

The range of the observed offset was analysed for samples for which a [TSM]-determination error of $\leq 10\%$ was obtained (TSM: $n = 273$; PIM: $n = 92$) to avoid large determination errors influencing the analysis. The obtained intercept values of the linear regression were not related to [TSM] nor to the maximum sample mass on the filter, as well as not to the sampling effort, i.e. whether 3 or 6 filters were collected per sample (data not shown). It varied between -2.4 and 7.5 mg (one single sample) for the [TSM] and between -3.4 and 6.2 mg for the [PIM] determination (Figure 5). The mean (\pm sd) value was 0.85 ± 0.84 mg and 0.05 ± 1.10 mg, respectively. The mean offset for [TSM] was, hence, on average higher than the mean offset found above for the procedural control filters and the variations were about four times stronger. The result for [PIM] showed that the final combustion of the filter leads to an additional filter material loss. This had not been considered as an error source yet, as it was believed that filter preparation would avoid this material loss (besides mass losses of structural water in the mineral fraction). A closer look on the loss for the 92 samples showed a rather constant value (offset in [POM]) by combustion of 1.00 ± 0.57 mg (Figure 5, POM), the variations of this loss is lower than for the other two offsets and seems to be purely statistically, no correlation with [PIM], mass on filters, or the [TSM]-offset was observed.

Due to the observed strong variability in the different mass offsets, the actual errors by the common [TSM] method are logically higher than the formerly calculated potential errors, when the correction was done with the mean offset value of the procedural control filter (0.52 mg). Concentrations determined with the different volume approach are now taken as being "true" and used to estimate the error for single volume determinations - note that for this analysis samples were used for which this regression-based determination error estimate was always $\leq 10\%$ ($n=273$). This analysis showed that for 50% of the samples the error is probably $>9\%$ and for 22% the error is between 20% and maximally 77% (Figure 6)

These results are valid for an already improved single volume determination, i.e. when the offset from salt retention is corrected following the approach of Stavn et al. (2009). The errors without such correction for salt retention and filter material loss are much higher (up to several 100% in some single cases), with the error being $>15\%$ in 50% of the samples (Figure 6), proving that the method proposed by Stavn et al. (2009) is reducing the overall error. Calculated relative errors for the [POM] determination are larger due to very small values in most of our samples. Uncorrected [POM] values were systematically overestimated due to filter material loss in [PIM] measurements by on average 50% (range 10% – 230%). The associated error with [TSM] determination when only a single volume is filtered can, thus, be quite high.

Better estimation of the determination error is very useful for data assessment. Previous determinations of mass-specific light absorption coefficients have to date failed to consider that variation in the coefficient could be mainly attributable to large determination errors of the [TSM]. Similarly, a large part of variations in the ratio of POM/PIM might be induced by these errors as well. The same problem is often neglected when in-situ [TSM] measurements are compared to satellite derived data. The method proposed here needs greater effort for the measurement procedure but gives more accurate determination errors and allows a final quality control of the measurement.

The results of all samples are now analysed for the determination error. Please note that the errors are sometimes relatively high but that each error can be considered as an error determined for each sample not just estimated from general methodological errors (and actually unknown) as done in the above consideration and is normally the case when using the standard approach. The analysis of the error as a function of [TSM] showed no strong correlation with [TSM] or the maximum sample mass on the filter (data not shown). It seems to be only dependent on the sample, but we do not yet know the exact physical reasons for the extent of the offset, i.e. the property that influences the effectiveness of the washing.

The determination error ranged from below 1% to up to $\sim 40\%$ in a few cases (Figure 7). Note, that 23 samples were ignored as r^2 was <0.8 and, hence, for these the relative error would be much higher. The error histogram in Figure 7 showed that the majority of the error values was below 10%. Measurements with six

different volumes always showed errors below 25%. But even for samples with low concentrations when only three different volumes were used, a high precision was obtained in most cases. The range of TSM concentrations is well within that observed by others (e.g. Babin et al., 2003) and the values ranged over two orders of magnitude from very low concentrations below 1 mg l⁻¹ to up to 72 mg l⁻¹.

There seems to be no lower limit for accurate TSM determination, however, sample volumes needed here were up to 10 l. The sometimes larger errors found when only three different volumes are used are not surprising, as a single filter weight that deviates from linearity disturbs the whole determination. With just three filters an outlier cannot be identified but should be expected in 36% of all cases (see section 3.3). As filter to filter variations can be large, e.g. see results for the blank filter offset, larger errors were expected. Hence, it was surprising that errors below 10% could often be obtained. When six different volumes are analysed the outliers can be removed and the overall error can be reduced. This can clearly be seen in Figure 7 when comparing the results with different number of volume used. As often only one outlier was identified in a set of six filters, 4-5 different volumes might be sufficient for a precise analysis.

Measurements were done mainly in coastal waters, but included a few samples from offshore waters of the central North Sea, where [TSM] was very low. Oceanic waters will have even lower concentrations, and large volumes are normally needed for a reasonable [TSM] determination. Considering the potential large mass offset, [TSM] determination in such oceanic waters are probably susceptible to a very large error, as final masses on filters even when filtering more than 10 l might still often be <1 mg and, hence, in the range of the blank filter offset variation.

From the results presented here it seems possible that distributing a large sample volume over different filters (with different volumes onto each filter) has advantages over filtering repetitively the same total volume through the filters. For coastal and estuarine waters the proposed method offers a very good way to do precise and accurate [TSM] and [PIM] measurements. It is out of the scope of this paper but similar methodological problems are expected for fresh water environments, except that the positive mass offset due to dissolved matter should be much lower.

4. Conclusions

A method is presented that allows accurate estimations of the individual errors in [TSM] and [PIM] measurements in seawater. It is shown that the main error sources are a very variable, sample-dependent positive mass bias by salt retention in the filter margin and negative mass biases due to filter material losses during filtration and filter combustion. However, filter to filter variations in these biases are often small enough to allow precise and accurate determinations. Error analysis for the common TSM and PIM method showed that very large errors can occur. These errors can be reduced to be <60% by subtracting a mean offset

determined with procedural control filters as advised by Stavn et al. (2009). These large errors might be one significant source for variations in mass-specific optical properties of TSM in many studies. The proposed methodology will allow an individual quality control of the determination and can be used to examine variations in suspended matter concentration and its mass-specific optical properties in more detail.

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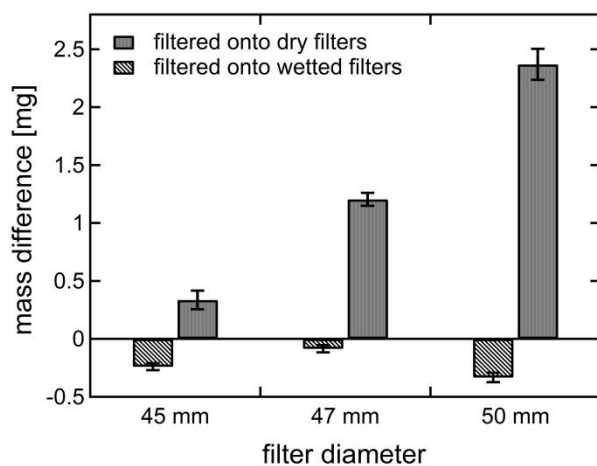


Fig. 1. Mass difference of filters after filtration of a 30 gL^{-1} NaCl solution and washing three times with purified water as a function of the filter diameter. Filtration was done onto dry filters and onto filters wetted with purified water. Shown are mean values of $n=5$ measurements and error bars indicate one standard deviation.

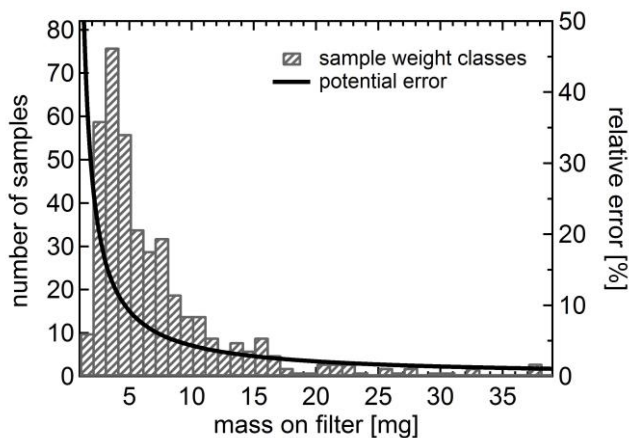


Fig. 2. Potential error as a function of the mass on filters, calculated from the maximum mass variations in the procedural control filters. The error is plotted on top of the histogram for the highest obtained sample mass in measurements of natural samples ($n = 422$).

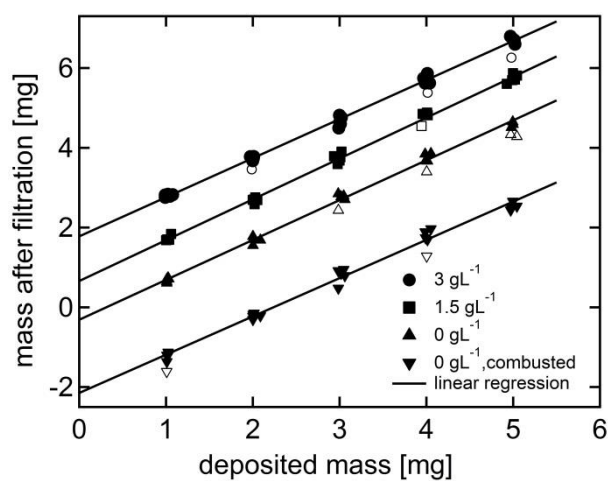


Fig. 3. Mass retention on filters after filtration of solutions of 0, 1.5, and 3 g/L NaCl as a function of mass deposited on the filter before filtration. Additionally shown are the results of the same filters with 0 g/L after combustion. Indicated are the linear slopes of a regression analysis. The results of the regression analysis are shown in Table 1. Open symbols indicated filters that were identified as outliers.

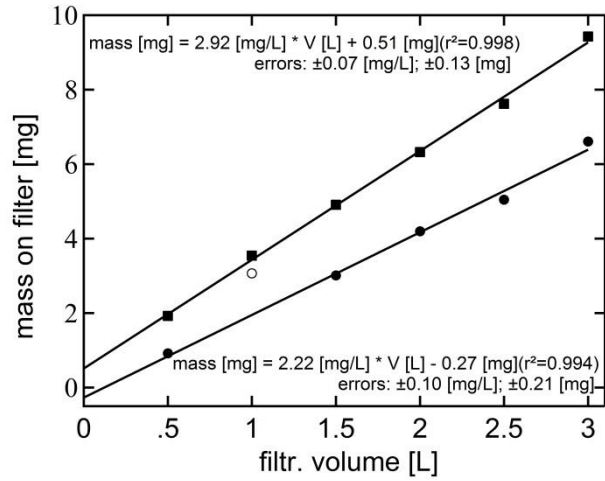


Fig. 4. One example for the suspended matter analysis: sample mass on filter as a function of filtered sample volume before (squares) and after combustion (circles) of the filters. Open symbols indicate points identified as outliers. Shown are the results of a linear regression analysis (solid lines).

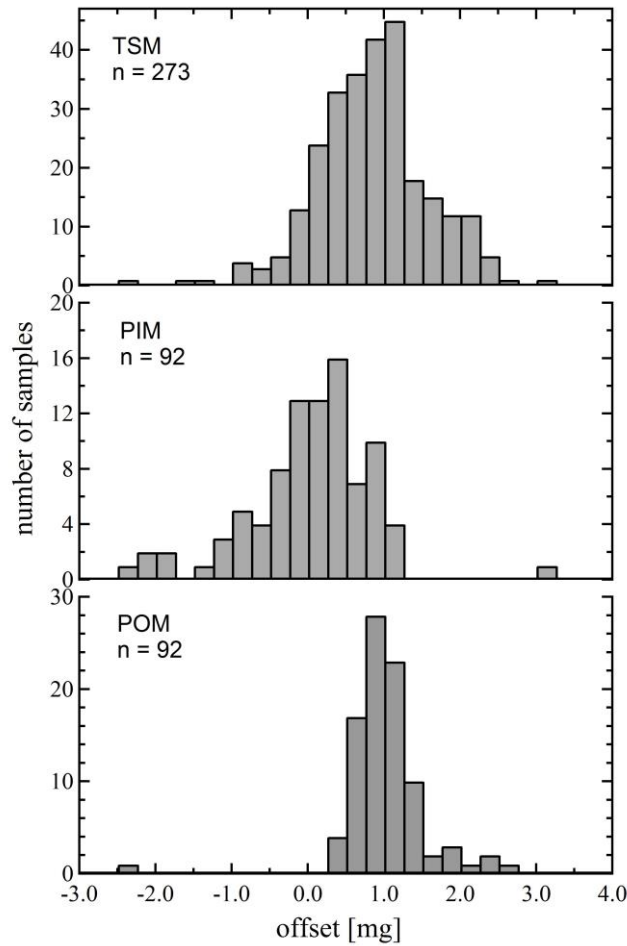


Fig. 5. Number distribution of the axis intercept values for linear regression analysis of [TSM], [PIM] and [POM] measurements, representing the mass offset due to salt retention and filter material loss. Single extreme values for TSM (7.5) and PIM (-3.4 and 6.2 mg) are not shown.

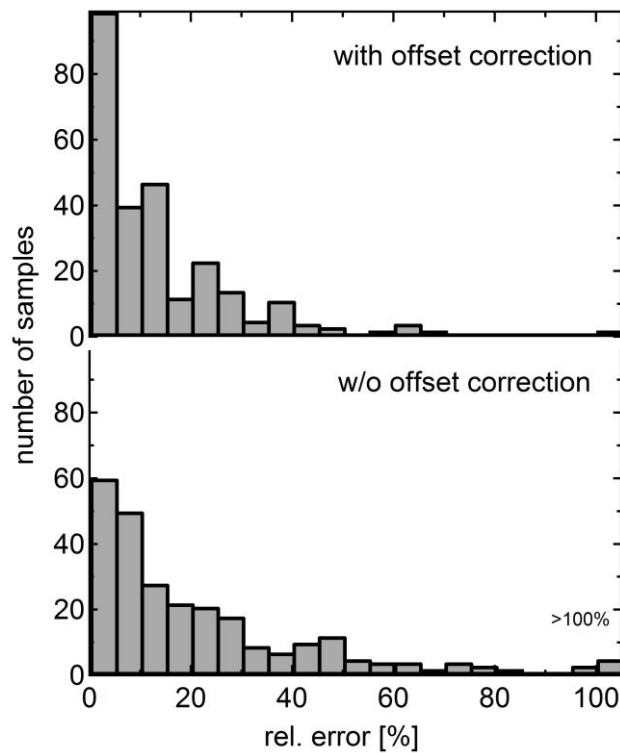


Fig. 6. Calculated error for the common [TSM] determination using a single filter (the filter with the largest volume in the set), with and without a correction by a mean salt retention offset. The calculations are based on all samples for which the real determination error was $\leq 10\%$ ($n=273$).

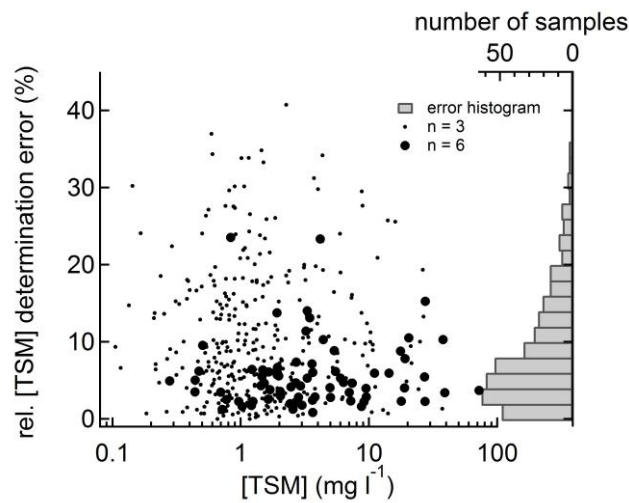


Fig. 7. [TSM] determination error as a function of [TSM] (symbols) and the corresponding error distribution (bars). Separately shown are results when using three (dots) and six (closed circles) different volumes per sample.