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

Rüdiger Röttgers*, Kerstin Heymann, Hajo Krasemann

Helmholtz-Zentrum Geesthacht, Center for Materials and Coastal Research, Institute for Coastal Research, Remote Sensing, Max-Planck-Str. 1, D-21502 Geesthacht, Germany

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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.

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

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* Corresponding author.
E-mail address: rroettgers@hzg.de (R. Röttgers).

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separation can be achieved by volatising 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 LoI 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 CO_2 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, 1978; 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 prewashing 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.

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

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

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 <<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 (ø 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 μm (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: ±1 μg). 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 h, 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 h, 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.