Correcting the Errors from Variable Sea Salt Retention and Water of Hydration in Loss on Ignition Analysis: Implications for Studies of Estuarine and Coastal Waters

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Abstract:
The standard technique of determining the concentrations of total suspended solids (TSSs), particulate inorganic matter (PIM), and particulate organic matter (POM) by filtration with glass fiber filters is subject to an error or bias from sea salt plus water of hydration retention, when applied to saline waters. The sea salt plus water of hydration retention by the filters occurs even after washing the filter with 300 ml of deionized water, a greater volume than any wash recommended in the literature. We determined that the mass retention on a glass fiber filter, at a given salinity, is essentially constant, no matter the volume of seawater passed through the filter. We also determined that the sea salt plus water of hydration retention on glass fiber filters is directly proportional to the salinity of the seawater filtered. Sea salt plus water of hydration retention causes an overestimate of TSS; sea salt retention causes an overestimate of PIM; volatilization of water of hydration causes an overestimate of POM. Thus a correction curve is required for sea salt and water of hydration errors in the determination of TSS and PIM. Corrected POM comes from the difference between the two. Also, filter blanks (procedural control filters), run with deionized (DI) water rather than the seawater sample, are required to correct for possible filter mass loss during the analysis. We demonstrate correction curves for sea salt plus water of hydration retention for Whatman GF/F filters, 47 mm diameter, utilizing the methods of the APHA Manual, Standard Methods for the Examination of Water and Wastewater. Application of other glass fiber filter types or an analytical technique differing significantly from that employed here requires a different correction curve for retention of sea salt and water of hydration. These methods can be used to reanalyze older data on PIM, POM, and TSS.

We apply these corrections to PIM and POM data from the northern Gulf of Mexico and examine the interactions of these filter corrections with corrections for structural water volatilization from suspended clay minerals in the determinations of PIM and POM. We analyze published data on PIM and POM determinations and their application to remote sensing. We conclude that sea salt and water of hydration retention on filters has an adverse effect on remote-sensing algorithms inverting radiance reflectance to estimate concentrations of suspended matter.

INTRODUCTION

There is increasing interest in determining the nature of suspended particulate matter in natural waters and especially the coastal ocean and estuaries. There is a need to partition the Total Suspended Solids (TSSs) in water, determined by filtration and gentle drying, into at least the suspended Particulate Inorganic Matter (PIM), and suspended Particulate Organic Matter (POM). The loss on ignition technique (LOI), which accomplishes this partition, has been described in the American Public Health Association manual on Standard Methods for Analysis of Water and Wastewater (Pearlman et al., 1995), henceforth referred to as Standard Methods. There has long been an interest in POM in coastal regions committed to oyster culture (Eisma et al., 1991 and Barillé-Boyer et al., 2003). Lately, recognition has been given to the importance of the PIM concentration in coastal waters (Lund-Hansen, 2004; Stavn, 2005 and Bowers and Binding, 2006; Mckee and Cunningham, 2006; Snyder et al., 2008 and Stavn and Richter, 2008). Much of this interest is based on the need for accurate and efficient remote-sensing algorithms to interpret the remote sensing data of the coastal ocean (Bukata et al., 1995; Binding et al., 2003 and Binding et al., 2005; Wozniak and Stramski, 2004; McKee and Cunningham, 2006) to assess sediment loading, chlorophyll concentration, and detrital organic matter of coastal waters. Since the suspended mineral and organic components have significantly different refractive indices, they have different effects on the remote sensing signal. All of these relate to the importance of suspended particulates in the geochemical cycles of many elements and compounds in the ocean (Anderson et al., 1991). The dynamics, transformations, and fluxes of suspended particulates have a direct impact on the concentrations of the dissolved component of ocean water (Feely et al., 1991).

Given the increasing attention to PIM and POM determinations, knowledge of sources of error and bias in the LOI technique is becoming very important. Barillé-Boyer et al. (2003) report on many studies of bias in the LOI technique and on the serious bias associated with the structural water associated with clay minerals. The error or bias associated with clay minerals is generated by the loss of structural water of clay minerals in the ashing step of the LOI technique which causes an underestimate of PIM, when clay minerals are important constituents, and an overestimate of POM. They did not, however, consider the error associated with sea salt retention on the glass fiber filters used in the LOI technique. Sea salt retention in the LOI technique has not been adequately covered in the Standard Methods because this volume considers the determination of suspended solids in sewage treatment plants treating freshwater (Trees, 1978). Sea salt retention on glass fiber filters has been reported by many (Armstrong, 1958, Strickland and Parsons, 1968, Etcheber, 1981, Bishop, 1991 and Feely et al., 1991). Trees (1978) and Etcheber (1981), however, reported on the quantitative mass retention of glass fiber filters. Each author investigated this retention at one salinity only.

The purpose of this investigation is to look further into the error or bias associated with sea salt retention on glass fiber filters in the LOI technique. Since previous investigations were made at only one salinity level, we have performed quantitative investigations of mass retention of dissolved solids and associated material on glass fiber filters at several salinity levels. The questions we asked were 1) Is the mass of sea salt retained by Whatman GF/F glass fiber filters independent of the volume of seawater passed through the filter and 2) Is the mass of sea salt

retained on the glass fiber filters a constant or does it vary with the salinity of seawater passed through the filter?

MATERIALS AND METHODS

Generation of particle-free seawater

Seawater was collected from clearer offshore waters of the Gulf of Mexico, stored, and made particle-free at the University of Louisiana at Lafayette (ULL), Lafayette, Louisiana, USA. The seawater was filtered in a Sartorius plate filter apparatus under positive pressure through a 90 mm Whatman GF/C filter, nominal pore diameter of 1.2 μm, and a 100 mm Schleicher and Schuell OE 66 membrane filter, nominal pore diameter 0.2 μm. Dilution of particle-free seawater from salinity of 33 to 29, 25, 20, and 15 was accomplished with NANOpure water (Barnsted NANOpure Diamond system with D50281 NANOpure Diamond cartridge and D 3750 hollow fiber end filter). Salinity was measured using the Practical Salinity Scale.

Loss on ignition method

All filtrations and drying/ashing analyses were conducted at the Naval Research Laboratory (NRL), Stennis Space Center, Mississippi, USA. We utilized Whatman GF/F glass fiber filters, 47 mm diameter, nominal pore diameter 0.7 μm. In actual application the effective pore diameter decreases from the nominal value upon filtration until the filter is clogged (Sheldon and Sutcliffe, 1969 and Sheldon, 1972). All filters were prepared by an initial wash of 20 ml deionized (DI) water and then ashed at 550 °C for 15 min. After ashing the filters were cooled for half an hour in a vacuum desiccator. The filters were then weighed and ashed again. The process of ashing, cooling, and weighing continued until a constant weight was obtained. Constancy was defined as having subsequent weights agree to within 2 standard deviations, 0.04 mg, of the accuracy of the analytical balance (Ohaus Analytical Plus, Model AP250D). Usually, only 3 cycles were required to achieve constancy but occasionally a fourth cycle was required. This resulted in a total ashing time of usually 45 min. Some protocols state that ashing of filters will go overnight. We do not recommend this as the filters become brittle, hard to handle, and prone to large filter mass loss during the LOI technique (Feely et al., 1991).

The filtration was effected by a 250 ml Millipore apparatus with an applied vacuum of 300–400 mmHg. The particle-free seawater samples were utilized in volumes of 100 ml, 500 ml, 1000 ml, 2500 ml, 4000 ml, and 8000 ml. Initially a salinity of particle-free seawater was chosen for filtration and each experimental volume was passed through an ashed and pre-weighed filter. Each volume was filtered in triplicate. After the chosen volume of seawater passed through the filter, three 100 ml aliquots of DI water, each under vacuum, were run through the filter as a wash. The aliquots were added continuously, one on top of the other, to ensure the integrity of the applied vacuum. Washing was completed after the application of the three aliquots and the vacuum was stopped. The outer edge of the filter that was under the rim of the filter funnel was then thoroughly wetted with DI water to flush possible diffused salt (Strickland and Parsons, 1968). Three hundred ml of DI water wash is near the wash water volume recommended by Sheldon (1972), 250 ml, but rather greater than that recommended by Trees (1978), 50 ml, and Pearlman et al. (1995), 30 ml.

The filters were then dried at 103 °C for 2 h and put in a vacuum desiccator for half an hour to cool to room temperature. Again, 3 cycles were usually sufficient to achieve constant weight, a

total of 6 h drying time, but occasionally a fourth cycle was needed. When dry weight was deemed constant the filter was ashed at 550 °C for 15 min, put in a vacuum desiccator for half an hour, and weighed. Here, too, three cycles were usually sufficient, a total of 45 min ashing, but a fourth cycle was used occasionally. The mass retained on the dried filter was simply the difference in weight between the pre-washed, pre-weighed filter and the dried filter. The mass retained on the ashed filter was then the difference in weight between the ashed filter and the pre-washed, pre-weighed filter. The mass volatilized was the difference in weight between the dried filter and the ashed filter. Thus the pre-washed, ashed, and pre-weighed filter weight serves as a tare for the weights recorded on the subsequently dried and ashed filters.

A series of filter blanks, often termed procedural control filters, were also run in which the filters were treated exactly as above with the exception that 1 l of DI water was run through the filter rather than particle-free seawater. This filter blank (procedural control) is necessary to account for loss of glass fiber filter mass with the loss-on-ignition technique and its processes of drying and ashing of filters (Feely et al., 1991). The process is mitigated somewhat by weighing to constancy during the ashing and pre-weighing of glass fiber filters but it is not eliminated (Feely et al., 1991). The filter blanks are subjected to every condition experienced by the experimental filters except for the sample of particle-free seawater. A series of filter blanks run with each sample series will additionally control for any extreme variations in humidity, also affecting the recorded weights since glass fiber filters are hygroscopic (Strickland and Parsons, 1968, Fleer and Bacon, 1991, Landing and Lewis, 1991 and Trefry and Trocine, 1991).

Identification of mass retained on filters
The nature of the material retained on the glass fiber filters was determined with selected filters run through scanning electron microscopy (SEM) and electron dispersive spectra (EDS). The setup for EDS runs suppressed peaks associated with water. The sample was carbon coated with approximately 250 Å of carbon under a vacuum of 1×10^{-15} torr. An AMRAY 1820 digital SEM was used in the study and operated at an acceleration potential of 20 kV. A working distance of 18 mm, a sample tilt of 25°, and a final aperture size of 300μm were used to obtain the images as well as the EDS spectrum. Image and spectrum were generated via EDS 2008, an integrated software package by IXRFSYSTEMS, Inc. The image was captured at a resolution of 1024×1024 pixel and converted to a TIF image.

Volatile component of retained mass
A series of experiments were conducted to determine the possible nature of the retained mass, from the drying step, that was volatilized from the filter during the ashing step. The retention of sea salt on the glass fiber filter is most likely an adsorptive phenomenon and the residual sea salts on the filter are known to be hygroscopic (Sherrell, 1991). Thus, the question arises about what the nature of the volatilized mass in the ashing step might be. A selected set of the ashed filters used in the experiments outlined above was carefully rewetted with DI water and air dried overnight in a refrigerator. The rewetted filters were dried at 103 °C for 2 h and put into a vacuum dessicator for half an hour to cool to room temperature. The rewetted filters were reweighed and the process continued through 4 drying cycles. This process regenerated the original dry weights of the filters. The filters were ashed again through 4 cycles and the weights compared with the original ashed weights.

Statistical analysis

The equality of the masses retained on the glass fiber filters from the various volumes filtered (constant salinity) during the drying and ashing steps of the LOI was tested with one-way analysis of variance. The inequality of the masses retained on the glass fiber filters from the different salinities examined was also tested with one-way analysis of variance. The mean masses retained by the glass fiber filters, at the different salinities examined, were regressed against the salinities of the particle-free seawater filtered. Masses retained on the glass fiber filters during the drying step were compared with the dried masses of rewetted glass fiber filters using a paired sample t-test, double-sided. All statistics were performed on the Lotus 123 spreadsheet program.

RESULTS

Mass retention: varying filtration volumes – constant salinity

The mass retention of the GF/F filters after the drying step of LOI is shown in Table 1. The condition illustrated is salinity 33 and varying volumes were filtered, 0.1–8 l. The data from Table 1 are analyzed in Table 2 by one-way analysis of variance (ANOVA). The ANOVA indicates that there is no significant difference between the retained masses, from 100 ml filtered to the maximum of 8 l filtered. This constancy of retained mass on the GF/F filters, regardless of volume of seawater filtered, occurred for all salinities of particle-free seawater tested. The pattern of mass retention, for all salinities, was an apparent maximum retained at 100 ml of particle-free seawater filtered. This apparent maximum was never statistically significant.

Table 1: Salt + water of hydration mass retained by GF/F glass fiber filters, salinity 33, various volumes of particle-free seawater filtered.

|	Volume filtered (ml)					
	100	**500**	**1000**	**2500**	**4000**	**8000**
Mean mass (mg)	**1.359**	**0.851**	**1.172**	**1.289**	**0.977**	**0.956**
Std. dev.	*0.090*	*0.415*	*0.527*	*0.202*	*0.328*	*0.403*

Table 2: Analysis of variance (one-way) of salt + water of hydration mass retained on GF/F filters, salinity 33.

Source of variance	Sums of squares	Degrees of freedom	Estimated STD	$F_{5,12}$	$F_{5,12}$ ($p = 0.05$)
Between treatment	0.647	5	0.1293	**1.0093**	3.11
Sampling error	1.537	12	0.1281		
Total	2.184	17			

Mass retention: varying salinities

The mean mass retention of the GF/F filters, after the drying step of LOI, at varying salinities of particle-free seawater, is illustrated in Fig. 1a. The mass retention of the filters is proportional to the salinity: less mass retention as the salinity decreases. The regression of the mean mass retention against salinity, forced through zero, is $y = 0.34x$, where y is the mass retention, in mg, per filter and x is the salinity of the particle-free seawater filtered. The $R^2 = 0.961$.

Figure 1: Mean mass retentions by GF/F glass fiber filters. a) Mean mass retention (sea salt + water of hydration) by a GF/F glass fiber filter dried according to the technique described in Section 2.2. Regression shown here is the mass retention correction curve determined by our research group. Regression not forced through the zero point. b) Mean sea salt retention by a GF/F glass fiber filter ashed according to the technique in Section 2.2. Regression shown here is the mass retention correction curve determined by our group. Regression not forced through the zero point. The mean water of hydration volatilized from the ashing step is the difference between regression curve of Fig. 1a and this regression curve. Mass retention correction curves should be determined for the specific technique utilized by a research group.
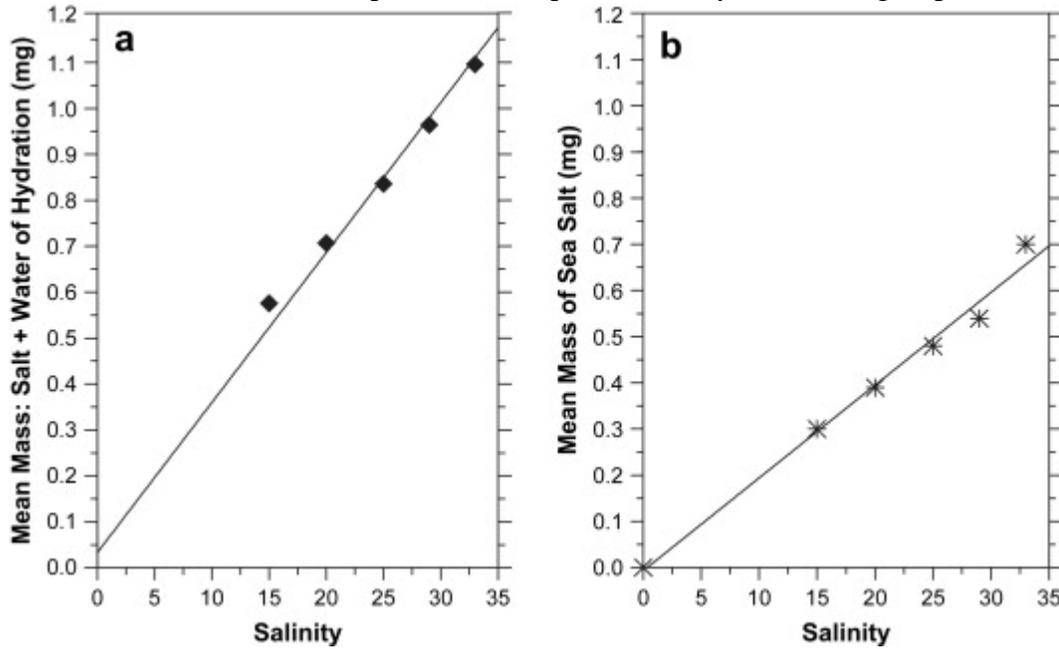

The mean mass retention of the GF/F filters, after the ashing step of LOI, at varying salinities of particle-free seawater is illustrated in Fig. 1b. The mass retention trend, with salinity, of the ashed GF/F filters is the same as that demonstrated for the dried filters. However, the retained mass on the ashed filters was about 50% of the mass retained after the drying step throughout all of the salinities examined. The regression relation of the ashing step, forced through zero, is $y = 0.0199x$, where y is the mass retention, in mg, per filter and x is the salinity of the particle-free seawater filtered. The $R^2 = 0.990$.

Mass retention: identification of component on filter
A typical SEM of a dried glass fiber filter is shown in Fig. 2a. The filter illustrated was used to filter particle-free seawater of salinity 29. Fig. 2a, at fairly high resolution, indicates a well-formed crystal. The EDS scan of the crystal in Fig. 2b indicates peaks of sodium and chloride, sea salt.

Figure 2: Identification of material retained on GF/F filter. a) SEM image of dried filter from filtration of particle-free seawater, salinity 29. Filtration residue indicates crystalline material. Marked crystal subjected to an EDS scan. b) EDS scan of particle marked in Fig. 2a. The *x*-axis scaled in keV. The sodium peak at 1 keV and the chloride peak at 2.75 keV clearly indicate sea salt.
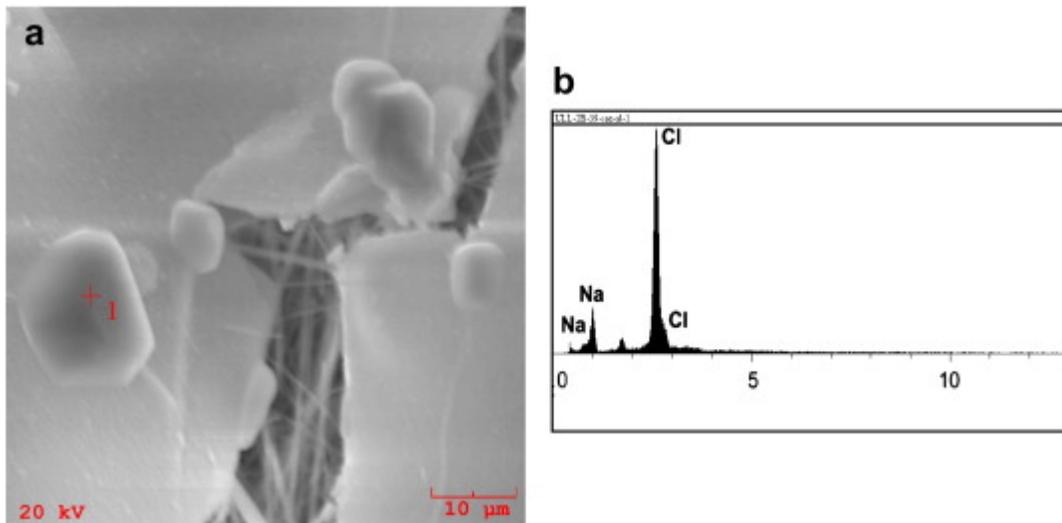
Mass retention: volatilized component

The weight of the ashed GF/F filters that were rewetted with DI water was compared with their previous dried weight. A double-sided *t*-test for matched pairs at the 5% level indicated that the rewetted ashed filters did not differ significantly from their previous dried weight.

DISCUSSION

We have established that, in the initial sample filtration and drying of GF/F filters for LOI, mass retention by the filter is independent of the volume of seawater of constant salinity passing through the filter (Table 1). The characteristic mass retained by the filter is established after only 100 ml of seawater has passed the filter. We have also demonstrated that the mass retained on the GF/F filters is directly proportional to the salinity of the seawater filtered (Fig. 1a). The glass fiber filter is a depth filter (Feely et al., 1991). A depth filter works on the principle of being relatively thick and provides many tortuous pathways through it, as is seen with the complex network of fibers in a glass fiber filter. Particle retention is primarily by adsorption on the glass fibers (Feely et al., 1991). Therefore, an increase in salinity of seawater filtered means more sites on the filter will be occupied by dissolved salt adsorbing and crystallizing out. Furthermore, the results from rewetted filters establish that the retained mass volatilized from the GF/F filter in the ashing step is water of hydration, representing a little less than 50% of the initially retained mass (Fig. 1a,b). What remains on the filter after ashing is sea salt (Fig. 2a,b). This leads to two errors of overestimation in the LOI technique. PIM is estimated by the difference in weight between the pre-weighed filter and the ashed filter. Since the ashed filter has a sea salt residue in addition to the mass of suspended inorganic matter, this results in an overestimate of PIM. POM is estimated by the difference in weight between the dried filter and the ashed filter. Organic matter is volatilized in this step and so is the water of hydration. Thus POM is also overestimated. Our results on the mass retention capability of glass fiber filters allow investigators utilizing the LOI

technique to determine a sea salt and water of hydration correction for studies of PIM, POM, and TSS concentrations.

Comparison with other studies of mass retention on glass fiber filters
Trees (1978) reported a mass retention of 1.25 mg per filter, dried Gelman Type A/E glass fiber filters, 47 mm diameter, 1.0 μm nominal pore diameter. This mass retention on the dried glass fiber filter was attained after filtering 100 ml of particle-free seawater, salinity 19. Fig. 1a shows about 0.65 mg mass residue on a dried GF/F filter for salinity 19 particle-free seawater. Recall that the mass retention of a glass fiber filter is independent of the volume of seawater filtered and that the mass retention, for a particular salinity, is established at about 100 ml of seawater filtered. Etcheber (1981) reported a mass retention of 0.2 mg per filter on dried Whatman GF/C glass fiber filters, 25 mm diameter, 1.2 μm nominal pore diameter. This retention on a dried filter was from filtering a liter of particle-free seawater, salinity 34. Fig. 1a shows about 1.1 mg mass retention on a dried GF/F filter for a salinity of about 34. The difference in mass retention reported here for GF/F filters and by Etcheber for GF/C filters cannot be explained by differences in the diameter of the filters. All of these results represent different techniques of filter preparation and drying. Therefore, each group of investigators will have to establish their mass retention curves based on their own adaptation of LOI techniques.

The mass retention characteristics of glass fiber filters immediately lead to the question of what magnitude of error these demonstrated mass retentions represent. We have been sampling, with NRL and NASA, the PIM and POM concentrations of the northern Gulf of Mexico, associated bays and estuaries, and the mouth of the Mississippi River for the past several years. When we consider the suspended particle mass retained by the filters and ignore the division of suspended particle mass by the volume filtered to determine the concentration of suspended matter, the maximum mass of suspended mineral matter is 10 mg per filter and the maximum volatilized mass, assumed suspended organics, is 2 mg per filter. Thus, at higher salinities, a potential overestimate of PIM is about 10% and a potential overestimate of POM is 25%, considering the maximum masses obtained per filter. Potential errors will be greater, POM especially, with lower masses of suspended matter filtered. The problem in the coastal ocean and estuaries is that with variable salinity the error from mass retention on the glass fiber filter will vary with the salinity of the sample area.

Analysis of corrections needed in LOI determinations
We have a representative series of data on PIM and POM collected at Mobile Bay, Alabama, USA, by the NRL in May of 2002. We analyze here the effect of the mass retention by glass fiber filters on our estimates of PIM and POM in Mobile Bay and the associated sounds. We also consider the corrections proposed by Barillé-Boyer et al. (2003) based on the clay content of the PIM. They have reported that the loss of structural water from clay minerals during LOI analysis causes a PIM underestimate and a POM overestimate. This phenomenon will, of course, interact with the mass retention and volatilization of water of hydration by the glass fiber filters. We apply the Barillé-Boyer et al. corrections in the later stages of this analysis. We estimate the clay content of the PIM residue from the data of Doyle and Sparks (1980) from Mobile Bay: clay fraction 85% consisting of kaolinite 67%, illite 20%, montmorillonite 13%.

The first comparison we made was the effect of ignoring the retention of sea salt and water of hydration by the glass fiber filters when estimating PIM and POM in Mobile Bay and the northern Gulf of Mexico. We have a regression of uncorrected values of PIM against the corrected values of PIM in Fig. 3a. The regression of corrected and uncorrected estimates has a slope of essentially 1.0 and a displacement of the uncorrected PIM values upward by an intercept value of 0.286 ± 0.183 (95% c.i.) mg l^{-1}. This displacement represents an overestimate of PIM ranging from about 19% at the lower end of the PIM range to about 1.4% at the upper end of the PIM range (20 mg l^{-1}). We then have a regression of uncorrected values of POM against the filter-corrected POM in Fig. 3b. The regression of corrected and uncorrected estimates has a slope of essentially 1.0 and a displacement of the uncorrected POM values by an intercept value of 0.747 ± 0.284 (95% c.i.) mg l^{-1}. The POM overestimate then ranges from about 93% at the lower range of POM concentration to 15% at the upper range of the concentration. If the suspended matter of Mobile Bay did not include clay minerals, then the errors of overestimation from mass retention by glass fiber filters would be quite significant.

Figure 3: Comparison of PIM and POM estimates, Mobile Bay, Alabama, USA, with and without the filter mass retention corrections of Fig. 1. a) Regression of corrected and uncorrected PIM estimates $y = 0.286 + 0.988x$, y is uncorrected PIM concentration and x is the filter-corrected PIM concentration. $R^2 = 0.997$ and $n = 24$. PIM estimate of 20 mg l^{-1} is not shown to emphasize the y intercept. b) Regression of corrected and uncorrected POM estimates $y = 0.747 + 1.06x$, y is uncorrected POM concentration and x is filter-corrected POM concentration. $R^2 = 0.948$ and $n = 24$.
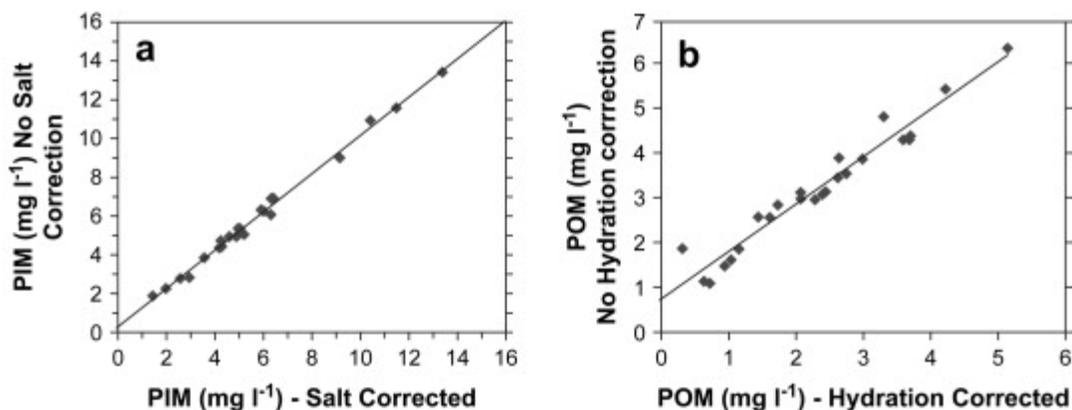
We then added in the Barillé-Boyer et al. corrections for clay mineral content and its associated structural water to the corrections for mass retention by the glass fiber filters and investigated the effect of neglecting filter corrections. That is, PIM values uncorrected for mass retention by the filter were corrected for clay mineral structural water and were regressed against filter-corrected PIM values further corrected for clay mineral structural water (Fig. 4a). Then POM values without the filter corrections but corrected for clay mineral structural water were regressed against filter-corrected POM values further corrected for clay mineral structural water (Fig. 4b). The regressions of Fig. 4 are similar to Fig. 3 but there are interesting differences. The y intercept of the PIMreal (Barillé-Boyer et al. notation) plot, not filter-corrected, is comparable to that of

the uncorrected PIM plot in Fig. 3a, 0.312 ± 0.200 (95% c.i.) mg l^{-1}. The two intercept values strongly overlap. Thus, the Barillé-Boyer et al. corrections for clay structural water applied to the PIM estimates without the filter correction include the overestimates from the sea salt retained on the filter. Thus we have an overestimation of PIMreal, about 20% at the lower PIMreal concentrations and about 1.4% at the higher PIMreal concentrations (22 mg l^{-1}). However, when we examine the values of POMreal estimates from the Barillé-Boyer et al. clay and structural water corrections, with and without the filter corrections, there appears to be a good correspondence between the POMreal values with the filter corrections and the POMreal values without the filter corrections (Fig. 4b). The downward displaced y intercept value of -0.0411 ± 0.016 (95% c.i.) mg l^{-1} in the comparison plot (Fig. 4b) falls easily within the measurement error range of the electrobalance used in this study. Apparently the overestimate from the clay structural water correction overwhelms the water of hydration correction for the glass fiber filters as can be seen by the POM estimates, maximum estimated value 5.2 mg l^{-1} for filter-only corrections and then 3.3 mg l^{-1} for estimates including filter corrections plus clay structural water corrections (Figs. 3b and 4b). Thus, the PIMreal determined from the Barillé-Boyer et al. corrections, without filter corrections, will include an error of overestimation from the sea salt retained by the glass fiber filter, significant at the lower concentrations of PIMreal. An estimation of POMreal with the Barillé-Boyer et al. corrections without a filter correction will be acceptable, however.

Figure 4: Comparison of PIM and POM estimates, Mobile Bay, Alabama, USA, Barillé-Boyer et al. corrected values (designated PIMreal and POMreal), with and without filter corrections. a) Regression of PIMreal estimates $y = 0.312 + 0.988x$, y is uncorrected PIMreal concentration and x is filter-corrected PIMreal concentration. $R^2 = 0.9969$ and $n = 24$. PIMreal estimate of 22 mg l^{-1} is not shown to emphasize the y intercept. b) Regression of POMreal estimates $y = -0.0411 + 1.01x$, y is uncorrected POMreal concentration and x is filter-corrected POMreal concentration. $R^2 = 0.9997$ and $n = 24$.
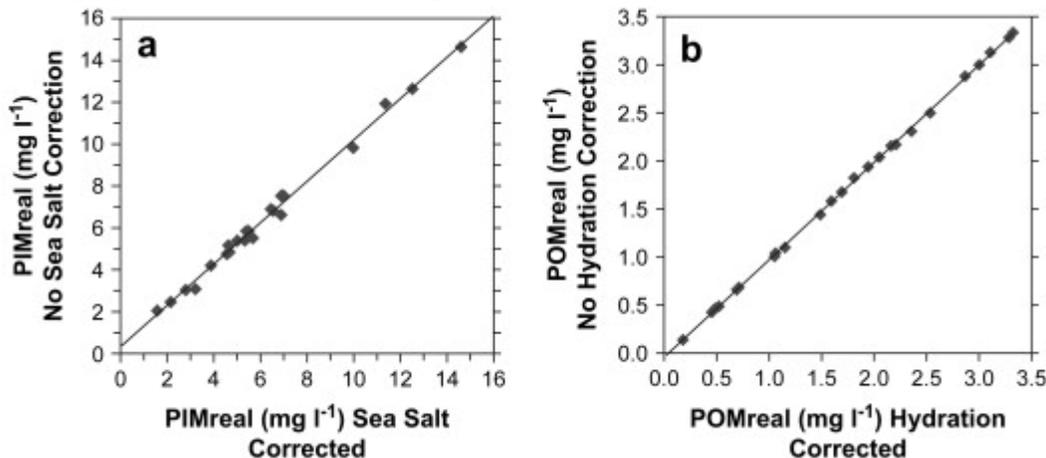
Comparison with other studies of PIM and POM

We feel that the results presented above allow us to analyze other published studies of the occurrence of PIM, POM, and TSS in the coastal ocean and estuaries. Gallegos (2005) noted that determinations of TSS in the St. Johns River estuary, Florida, USA, were highly variable and that it was difficult to compare the analytical results that two different laboratories performed for

the study. The investigators sampled a steep gradient of environmental properties in this river, from freshwater to near oceanic water salinities and it is tidally influenced throughout its length. Given the steep sampling gradient and the significant tidal changes reported in this estuary, values of TSS estimated from GF/F filters would be expected to have a highly varying amount of associated mass retention error. If the two different labs did not have a well-defined series of filter blanks (procedural control filters) or mass retention correction curves as part of their analytical protocol they would certainly have differences in their reported analyses of TSS. A significant number of TSS masses were reported in the range of 5 mg l^{-1}, definitely within the concentration range liable to the filter mass retention errors reported here.

Binding et al. (2003) attempt to produce algorithms for predicting PIM concentration (MSS concentration in their notation) from the remote sensing reflectance at 665 nm, R_{665}, in the Irish Sea. In their figures 4 and 6 when the R_{665} value is plotted against the PIM concentration its zero point does not end up at the zero point of the PIM axis but rather at about the 1 mg l^{-1} point of the PIM axis. This PIM concentration for the zero value of R_{665} is a reasonable value for the mass retention of glass fiber filters in high salinity water (Fig. 1a,b). Further confirmation of this comes from Binding et al. (2005) in their figure 3. In addition, an attempt by Binding et al. (2005) to relate the PIM concentration to the scattering coefficient at 665 nm, b_{665} m^{-1}, also had the consequence of b_{665} going to zero not at the zero point of PIM but rather at the 1 mg l^{-1} point of the PIM axis (their figure 6). One of the consequences of this is a difficulty to make modeled R_{665} values match measured R_{665} values, figure 4 in Binding et al. (2005). The concentrations of PIM they reported in the Irish Sea were 4–6 mg l^{-1}, well within the range of values subject to significant filter mass retention from seawater. It would appear that in the studies enumerated above careful attention to the mass retention qualities of glass fiber filters relative to salinity would improve efforts at modeling and algorithm construction involving PIM, POM, and TSS.

CONCLUSIONS AND RECOMMENDATIONS
We have highlighted a potential source of error in studies of PIM and POM concentration in coastal and estuarine waters: the tendency of glass fiber filters, even when thoroughly rinsed, to retain quantitative masses of sea salt and water of hydration. This error is compounded by tendencies of glass fiber filters to lose quantitative portions of their mass in the LOI technique (Bishop, 1991 and Feely et al., 1991). We have endeavored to follow the techniques of Standard Methods (Pearlman et al., 1995) as much as possible. Obviously, we would not need to make this report if Standard Methods covered the issues we have investigated here. It is also true that there is a great deal of variability in the LOI techniques applied by various research groups (Barillé-Boyer et al., 2003). We feel that a good start toward generating comparable PIM and POM results from different groups will be the careful attention to maintaining an adequate tare for these determinations. The corrections we have described ensure that the pre-weighed mass of a glass fiber filter can be adjusted to produce an adequate tare.

Correction curves for mass retention on glass fiber filters
Filter blanks (procedural control filters) are a must for ensuring that the initial weights of the glass fiber filters used in LOI will serve as an adequate tare in the determination of the mass of suspended matter filtered from a seawater sample. This is also true for determining a salinity correction curve to account for mass retention of sea salt and water of hydration on the filter. The

filter blanks account for the mass loss from glass fiber filters in the drying and ashing steps of the LOI technique.

In the determination of the sea salt plus water of hydration correction curves, Fig. 1a,b implies that only a few salinity points for particle-free seawater are required. Any convenient volume of particle-free seawater can be used. The filters for the salinities chosen are treated by the same technique as samples would be and a set of filter blanks is also included. The filter blanks (procedural control filters) have a liter of DI water run through them and are then treated the same as the other filters. The filter blanks account for mass loss and also for any extreme changes in humidity during the experimental run that can affect the weight of the filters.

When the correction curves are determined, an analysis at any given station will require recording the salinity for each sample collected and a set of 3 filter blanks (procedural control filters) for the station. Additionally, the practice of filtering samples and freezing them during a research cruise to await final processing will further damage the filters and these changes in the filter mass will also be corrected with the filter blanks (procedural controls). The procedure of determining filter blanks and filter correction curves for mass retention can be utilized to reanalyze older sets of data that have been gathered previously if the salinity is known for the previously collected samples.

Absolute procedural control

It is possible to forego the correction curves for mass retention delineated above by running a comprehensive set of absolute procedural controls, i.e. a filter blank to accompany every sample filtered. Filter blanks, prepared and treated experimentally in an identical fashion to the sample filters, have particle-free seawater samples run through them. The particle-free seawater comes from the sample filtered of its suspended matter for analysis. This is a more difficult and time, space, and resource consuming process than that outlined above, given time and space limitations on shipboard, etc.

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