

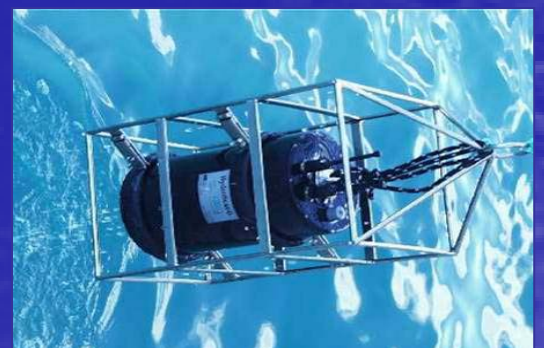
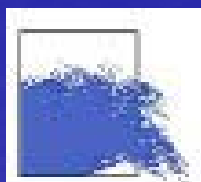
Regional Validation of MERIS Chlorophyll products in North Sea coastal waters.

Proposal: EVG2 – 2001 – 00009

Contract: EVG1 – CT – 2001 – 00049

REVAMP Inter-calibration Report

G. H. Tilstone, G. F. Moore, K. Sørensen, R. Röttgers, P.V.
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Development of Generic Earth Observation Technologies

REVAMP
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Inter-calibration report document

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Jørgensen⁴, V. Martinez Vicente¹, K. G. Ruddick⁵, 2002.

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Based on MERIS and REVAMP protocols

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Executive Summary of the inter-calibration workshop

Measurements of *in vivo* phytoplankton absorption (Pabs), backscatter coefficient (bb), absorption of coloured dissolved organic material (CDOM), Chlorophyll a concentration by high performance liquid chromatography (HPLC), spectral sky radiance and total suspended matter concentration (TSM) were compared between five laboratories. The inter-comparisons consisted of both laboratory experiments and measurements at sea and were conducted at Plymouth Marine Laboratory, from 17 to 21 June 2002 during cruise Belgica 200-14 organized by MUMM, and from 4 to 6 November 2002 at GKSS. The field inter-comparisons were carried out at 2 to 3 stations off Plymouth Sound, UK and at 17 stations between Ostende, Belgium and Harwich, UK in the North Sea.

Chlorophyll a concentration by high performance liquid chromatography showed the lowest variability between laboratories (~9 %), followed by *in vivo* phytoplankton absorption (~14 %) and the backscatter coefficient (~13 %). The absorption of coloured dissolved organic material and total suspended matter concentration showed the highest variation between laboratories (~22 %). For CDOM this was attributed to unequal degradation of CDOM in shipped samples and for TSM incomplete washing procedures.

From the laboratory experiments a number of recommendations were made to reduce the variability between laboratories. For CDOM the spectrophotometer should be regularly calibrated, the reference blank should be auto-zeroed against air, the purity and quality of the reference MilliQ should be monitored regularly and samples collected at sea should ideally be analyzed immediately after collection to avoid CDOM degradation. CDOM degradation in specific regions should be checked so that guidelines can be drawn up for safe sample storage for specific areas. It was also found that humic acid salt suspended in MilliQ could be used as a standard for data quality control. For TSM further improvements of the rinsing technique are necessary which should include the rinsing of the filtration apparatus. It was also found that Formazin in distilled water could be used as standard for quality procedures in determining TSM concentrations.

In-vivo Absorption Spectra of pigmented and non pigmented Particulate Matter - $a_{pm}(\lambda)$ (m^{-1})

Introduction

Prior to the inter-calibration exercise held at Plymouth Marine Laboratory, a number of experiments were conducted to assess the following aspects of *in-vivo* particulate matter absorption:

- *Instrument performance and accuracy*
- *De-pigmentation agent*
- *Blank Filter*
- *Data processing*

The results from these experiments were presented at the inter-calibration workshop (11 to 14 June 2002) to scrutinize the current methodologies and are documented in the Appendices of the REVAMP protocols document.

Particulate matter absorption spectra inter-comparison

Three replicate samples were filtered from three stations; L4, Mayflower (MF) and Barnpool (BP). In addition, three blanks per station were prepared using the filtrate from seawater that had passed through the 0.7 μm GFF filters. The samples were run according to REVAMP protocols. GKSS use a Perkin Elmer Lambda 19 spectrophotometer with a 60 mm spectralon integrating sphere. NIVA use a Perkin Elmer Lambda 40 with a 20 mm Labsphere RSA-PI-20 and PML use a Perkin Elmer Lambda 800 spectrophotometer with a 60 mm spectralon integrating sphere. To avoid differences between laboratories as a result of data processing, one laboratory (GKSS) processed all of the data. The results are given in Fig 1. For all stations the difference between labs was small, $\sim 14\%$ over MERIS bands 412 to 664 nm. In general NIVA data was 18 % higher than the GKSS & PML data (Fig 1 b & d). For the L4 sample, there was a 20 % difference between labs over MERIS bands (412-664 nm). The difference between PML & GKSS was 2 % and the difference between GKSS & NIVA was 28 %. For Barnpool, the difference between labs was 5 % over the MERIS bands. The variation between PML & GKSS data was 3 % over MERIS bands and the difference between PML & NIVA was 4 %. The Mayflower samples exhibited the highest phytoplankton absorption the difference between labs was 16 % over MERIS bands.

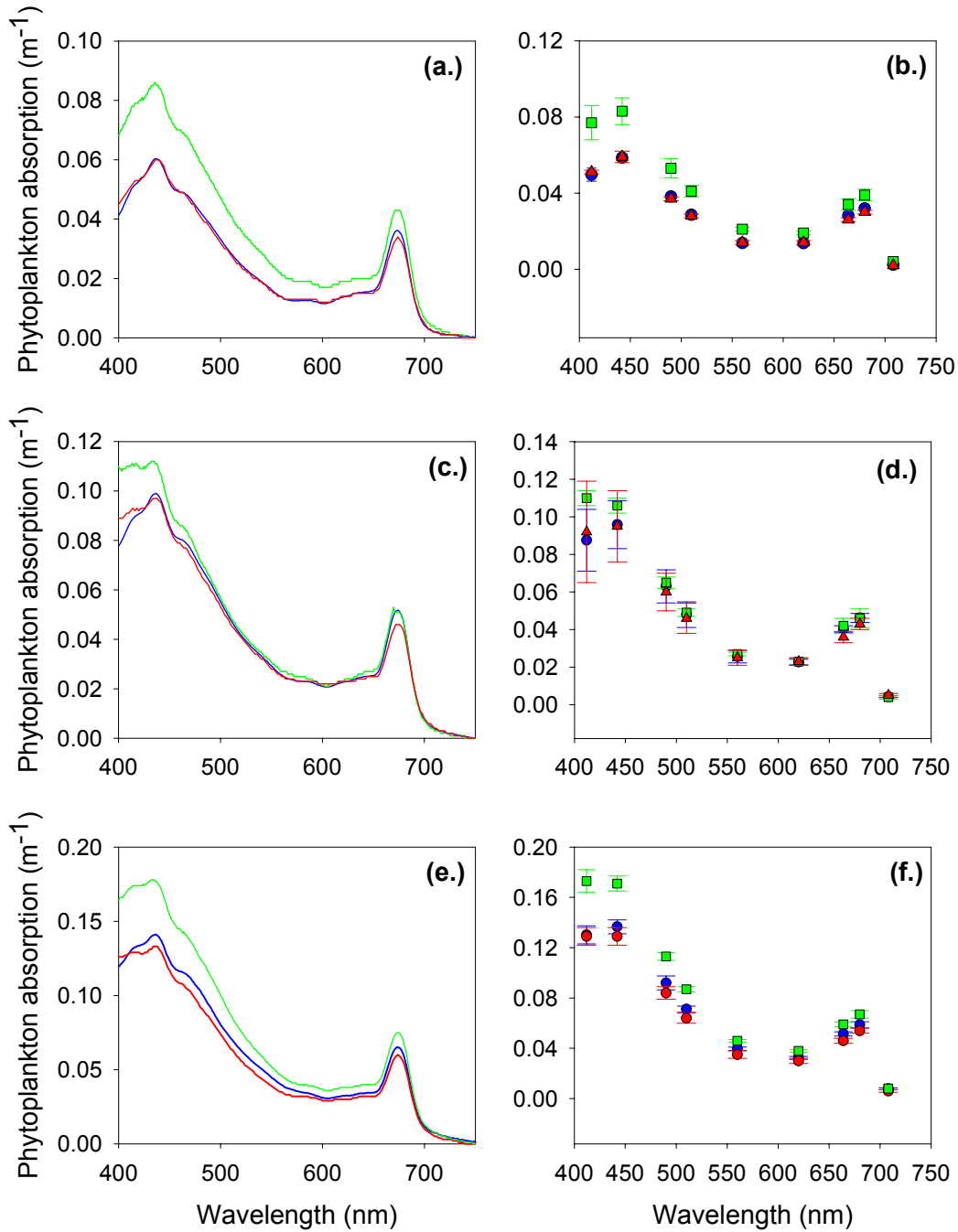
Conclusions and Recommendations

The difference between labs for *in vivo* phytoplankton absorption coefficients for three stations at MERIS bands 412 to 664 nm was low, $\sim 14\%$ and the differences observed were not statistically significant; L4 – $F_{2,26} = 0.96$, $P = 0.39$; BP - $F_{2,26} = 0.071$, $P = 0.93$; & MF – $F_{2,26} = 0.44$, $P = 0.64$.

The differences could be due to different methods of calculating α for the derivation of τ or differences in measurements as a result of instrument differences. Using data from one laboratory (PML), we compared absorption coefficients derived from the two methods of calculating α but the difference was not significant. We found

that filter reflectance and sample transmission measurements caused the variation in absorption coefficients between laboratories, which was largely due to differences in instrumentation and possibly due to differences in integrating sphere configuration and / or baseline variation between the different spectrophotometers.

Fig 1. Comparison of phytoplankton absorption spectra (m^{-1}) between GKSS (red lines and symbols), NIVA (green lines and symbols), PML (blue lines and symbols) at L4 (a. & b.), Barnpool (c. & d.) and Mayflower (e. & f.).



Backscatter coefficient, $\beta(\theta,\lambda)$ (m^{-1})

Two large inter-calibration workshops (PlymCal-1 & 2) were conducted at Plymouth Marine Laboratory (PML) as part of the MERIS calibration/validation work within ESA's MAVT (MERIS & AATSR Validation Team) group in 2001 and 2002. In this paper the results from PlymCal 2 are presented as well as measurements from two cruises made within the framework of the REVAMP project funded by the EU.. Four institutes participated in PlymCal 2 when different versions of the Hydrosat backscattering instrument were inter-compared. Two of the instruments measured the backscattering coefficient (bb) at six different wavelengths, one at 4 wavelengths and one at two wavelengths (Table 2). During PlymCal-2 measurements were made at sea, in both Case 1 and Case 2 waters and in the laboratory in tank experiments. The results were encouraging. In particular, the PML and GKSS instruments compared favourably. The NIVA and DMI instruments were slightly higher, but in good agreement with the other instruments in the blue and green regions of the spectrum. However, the NIVA instrument seemed to overestimate bb around 620 nm, and the DMI was completely off in the red 676 nm channel. This was also confirmed during two cruises in April and June 2002. Fortunately, this overestimation seems very stable and the correlation between GKSS and DMI instruments is excellent.

Introduction

As part of REVAMP, the PlymCal-2 workshop was held at PML from 10-15 June 2002. A number of instruments were compared including Hydrosats, AC-9's and spectro-radiometers. Also water samples were taken for comparison of water constituents concentration. The backscattering measurements are reported here. These were made at sea in both Case 1 and Case 2 waters, and in the laboratory with a controlled experiment in a tank.

Four institutions participated with Hydrosat instruments: the Danish Meteorological Institute (DMI), the Institute for Coastal Research (GKSS), the Norwegian Institute for Water Research (NIVA) and the Plymouth Marine Laboratory (PML). The various Hydrosats vary in age; they are from 1997-2002 and number of channels, with either two, four or six wavelengths.

In addition, a number of measurements were made during two REVAMP – cruises. The first one was conducted in April 2002 with R/V Heincke mainly in the German Bight and the central North Sea with the participation of GKSS and DMI, and one in June 2002 with R/V Belgica in Belgium coastal waters and the English Channel with the participation of PML and DMI.

Table 2 below shows the configuration of the various Hydroscats, including year of purchase and wavelength channels.

Table 2: Hydroscat Configurations

Wavelength (nm)	415	440 442	488	510	550 555	620	671 675 676	852
Institution								
DMI HS2-1999			√				√ (676)	
GKSS HS4-1997	√	√ (440)		√			√ (675)	
NIVA HS6-2001		√ (442)	√	√	√	√	√ (676)	
PML HS6-2002		√ (442)	√		√	√	√ (671)	√

Method

3.1 Principle of backscattering measurement

The principle of the Hydroscat is to estimate the total backscattering from a measurement of scattering at 140° (Maffione & Dana 1997) as described in eq.1 (spectral notation omitted for simplicity):

$$b_b = 2\pi \cdot \chi(\theta) \cdot \beta(\theta) \quad (1)$$

where b_b is the total backscattering coefficient and $\beta(\theta)$ the volume scattering function (VSF). θ is the scattering angle. The function $\chi(\theta)$ depends on sensor geometry and varies linearly around 120° (Oishi 1990), and the measurement at 140° can therefore be used with a great deal of confidence as it is not too far from the 120°. Both Maffione & Dana (1997) and Oishi (1990) find $\chi(140^\circ) = 1.08$.

As the light is attenuated while travelling between the emitter and receiver of the instrument, a sigma-correction is used to compensate for this effect, which would otherwise lead to an underestimation of backscattering. The sigma-correction, as currently implemented in the Hydroscat controlling software, Hydrosft2.5x is estimated by eq.2:

$$\sigma = k_l \cdot e^{(k_{\text{exp}} \cdot K_{bb})} \quad (2)$$

k_l is a calibration parameter that compensates for the attenuation in water. k_{exp} is a calibration parameter which is specific to the instrument, and K_{bb} is the attenuation coefficient of light travelling through the instrument's sensing volume, which depends on

local water properties. Calculation of sigma requires that K_{bb} is measured or estimated using, eq.3:

$$K_{bb} = a + 0.4 \cdot \frac{b_b}{b_b^{\sim}} \quad (3)$$

In which, b_b^{\sim} is the backscattering ratio (the ratio of backscattering to total scattering) is estimated from the raw backscattering measurement or specified by the user, default $b_b^{\sim} = 0.015$, and a is the absorption coefficient modelled by, eq. 4:

$$a(\lambda) = a_w(\lambda) + \left[0.06 \cdot a_{ph}^*(\lambda) \cdot C^{0.65} \right] \cdot \left[1 + 0.2 e^{(-S_{ys} \cdot (\lambda - 440))} \right] + a_d(400) \cdot e^{(-S_d(\lambda - 400))}$$

In which a_w is the absorption of pure water, a_{ph}^* the specific phytoplankton absorption coefficient, C the chlorophyll concentration, a_d the detritus absorption coefficient and S the exponential slope value for yellow substance (S_{ys}) and detritus (S_d), respectively.

Default values are: 0.014 and 0.011 for S_{ys} and S_d , respectively, $C = 0.1$ and $a_d(400) = 0.01$. These can be adjusted, as can the spectra for a_w and a_{ph}^* .

3.2 Deployment during PlymCal-2

The first part of PlymCal-2 was carried out onboard R/V Squilla on a relatively cloudy and misty day. The Case 1 station was approximately 15 km outside Plymouth harbour and the Case 2 stations only a few km from the harbour close to the coast. Three of the Hydroscats were mounted vertically on the same horizontal crossbar about 30 cm apart, while the last (GKSS) instrument was lowered off a separate frame, 1-2 meters away from the crossbar. At the Case 1 station measurements were carried out for 22 minutes, while data for 7 minutes were collected at the Case 2 station. Data were processed to insure accurate cut-off of data collected while lowering and retrieving the instrument. In addition, in order to filter out extreme spikes in the data, data outside +/- 3 standard deviations from the mean were excluded.

The second part of PlymCal-2 involved measurements carried out in a tank in the laboratory. The tank was 1 x 1 x 1 m. The instruments were deployed separately and data were recorded for 2 minutes, firstly with a TSM (total suspended matter) concentration of 1 mg/l, and a secondly with a concentration of 5 mg/l. A pump was used to circulate / mix the water and keep the material in homogenous suspension, but care was also taken to avoid creating too many bubbles.

3.3 Deployment during REVAMP cruises

During two REVAMP cruises in April and June 2002, on R/V Heincke and R/V Belgica, respectively, deployments were carried a few meters apart on separate frames. During the Heincke cruise the DMI-HS2 instrument measured profiles at discrete depth, of 1, 3 and 5

meter, for approx. 30 sec. at each depth, while the GKSS-HS4 was installed on the CTD-frame making profiles from the surface to the bottom, (~20-30 mts). Figure 2 shows the stations visited during the Hencke cruise mainly in the German Bight and Central North Sea.

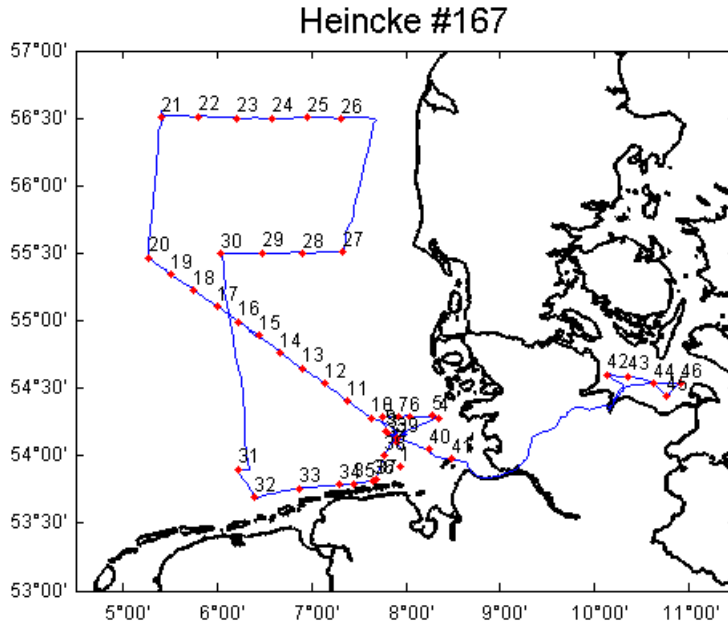


Figure 2: R/V Heincke cruise-plan April 2002 (Courtesy : Wolfgang Schönfeld, GKSS)

In the section below, the average DMI values from 3-6 meters are compared to the average GKSS values from 1-10 meters at each station.

During the Belgica cruise, conducted by the MUMM- institute the PML-HS6 and DMI-HS2 instruments were lowered simultaneously and the data were recorded every 2 mins at 1, 3, 5, 7 and 9 meters depth at the stations shown in Fig 3.

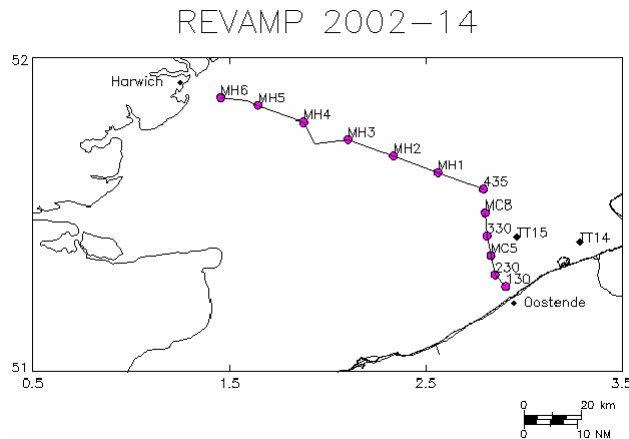


Figure 3: R/V Belgica cruise-plan June 2002 (Courtesy: Kevin Ruddick, MUMM)

Figure 4 shows an example of a b_b -data file before processing. The instrument is switched on and off on the deck which causes the major spikes at the beginning and end of the cast in Figure 4. These are filtered out by selecting only data below 0.5 – 1.0 m.

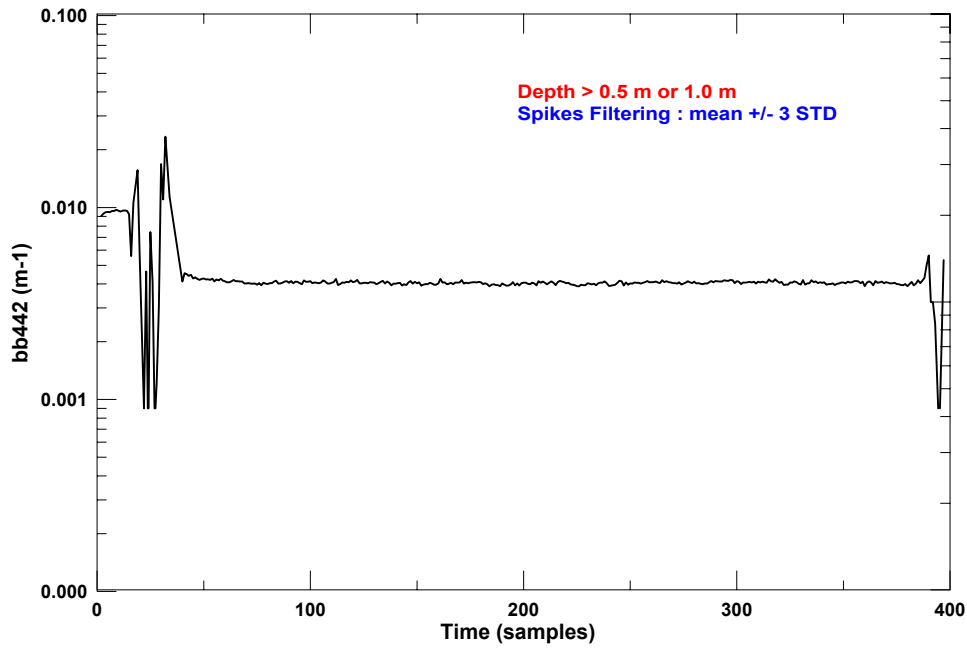


Figure 4 : Raw b_b -data file before cut-off in the beginning and end of the cast.

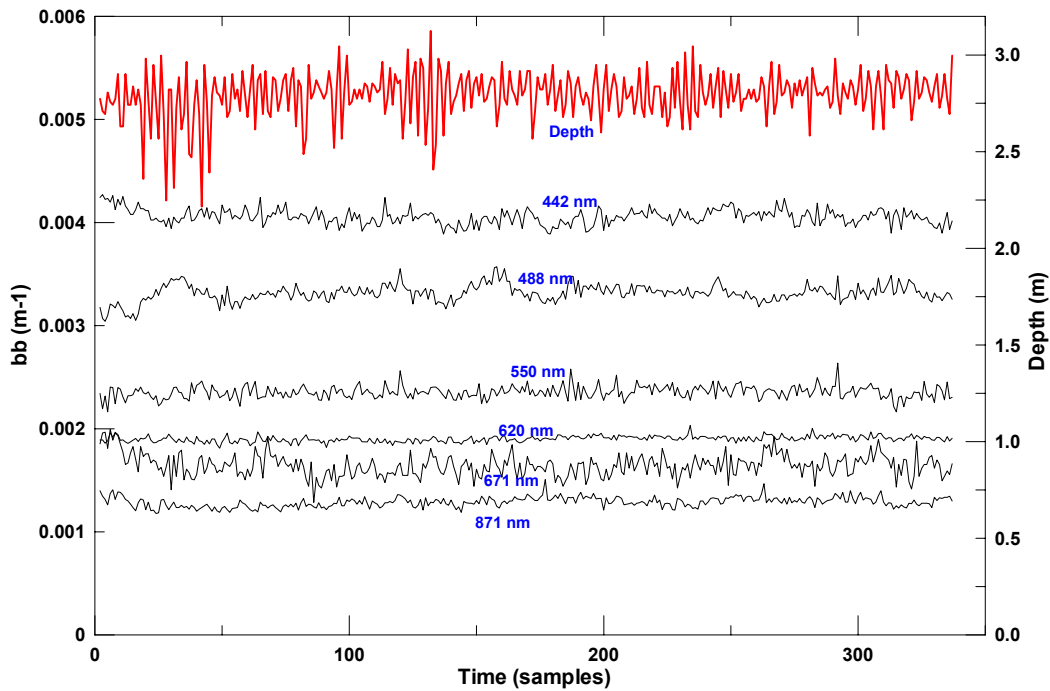


Figure 5: Example of b_b -data file from a HS-6 during PlymCal-2 after cut-off and spikes filtering.

Hereafter, any remaining major spikes are removed by selecting data within +/- 3 standard deviations from the mean. Figure 4 shows the example of a HS-6 file from PlymCal-2 after this filtration. The motion of the ship can be seen as variations in depth from approximately 2.2 – 3.1 m during the entire 20 minutes cast. Most of the time, the variations are smaller, from approximately 2.6 – 3.0 m. All six $b_b(\lambda)$ recordings are quite stable, with only minor variations, and b_b decreases slowly from 442 nm to 871 nm.

Results

4.1 Results from PlymCal-2 – Mean values of b_b .

Table 1 shows the mean depth and mean b_b - values at 488 and 676 nm recorded by the various instruments at the Case 1 station which were the wavelengths that all instruments measure, except for GKSS, which does not have a 488 nm channel, so the value at 488 nm has been interpolated from the 440 and 510 nm channels. Also, it should be noted that the exact position of the red channel varies, so that DMI and NIVA records at 676 nm, PML at 671 nm and GKSS at 675 nm. No corrections have been applied to account for the minor differences caused by this.

Table 2: Case 1 station – Mean Depth and b_b – values (22 min. of measurements)

	DMI	GKSS	NIVA	PML
Depth [m]	3.3	3.0	3.4	2.8
b_b (488) [m^{-1}]	0.0036	0.0035	0.0038	0.0033
b_b (676) [m^{-1}]	(0.0030)	0.0017	0.0019	0.0016

Depth recordings range from 2.8 – 3.4 meters. The DMI values are known to be accurate, so the PML depth may be a bit low. GKSS instrument was on a separate frame so the 3.0 m value may be correct. b_b (488) values are in very good agreement ranging from 0.0033 – 0.0038. b_b (676) values of GKSS, NIVA and PML are in good agreement while the DMI value of 0.0030 is nearly a factor two higher (therefore the parenthesis). The 676 nm channel of the DMI instrument is generally suspicious; for instance it broke down shortly after the instrument was acquired. Table 3 shows the same as Table 2 for the Case 2 station.

Table 3: Case 2 station – Mean Depth and b_b – values (7 min. of measurements)

	DMI	GKSS	NIVA	PML
Depth [m]	1.2	1.0	1.2	0.8
b_b (488) [m^{-1}]	0.0390	0.0295	0.0405	0.0338
b_b (676) [m^{-1}]	(0.0506)	0.0259	0.0284	0.0250

The results in Table 3 show that there was a difference of factor of 10-15 in backscattering between the two sites depending on wavelength. Depth values show the same picture as Table 2. b_b (488) shows somewhat larger differences than in Table 2, but again DMI and NIVA values are slightly higher than the NIVA and GKSS values. b_b (676) values have smaller variations, except again the DMI value of 0.0506.

4.2 Results from PlymCal-2 – Spectral variations of b_b .

Figure 6 shows the spectral variations of the data from both the Case 1 and Case 2 stations. In general the Hydrosat are in reasonably good agreement. PML and GKSS results show the same spectral shapes, while NIVA is similar except for the 620 nm channel. Also both NIVA and DMI values are slightly higher in all channels and again the red DMI channel at 676 nm seems to be far off compared to the others.

The results from the tank experiment in the laboratory are shown in Figure 6. Much of the same tendencies are seen for both the TSM concentrations of 1 and 5 mg/l, but the scatter between the instruments is larger. This was somewhat unexpected, since the controlled environment should have resulted in smaller deviations. The reason for this may be reflections from the sides and bottom of the relatively small tank. A future additional experiment with a larger tank would be preferable in order to confirm this. In addition, two of the six channels of the NIVA instrument saturated, so data from four channels only were available from this instrument.

4.3 Results from REVAMP cruises

During the Heincke-cruise, simultaneous data-recordings with the DMI-HS2 and the GKSS-HS4 were made at 17 of the 40 stations. Scatterplots of b_b (488) and b_b (676) are shown in Figure 8 and 9. It should be noted again that the GKSS values were interpolated from values at 440 and 510 nm. However, there is excellent agreement between the two even over nearly 3 orders of magnitude in absolute range. Correlation coefficients are $r^2 = 0.972$ and $r^2 = 0.989$ for b_b (488) and b_b (676) respectively. The DMI values are consistently higher than the GKSS values which confirms the results from the PlymCal-2 intercalibration. The DMI blue channel is 23 % and the red is off by 85 %, but apart from this large offset due to calibration, the effect is stable over the entire range.

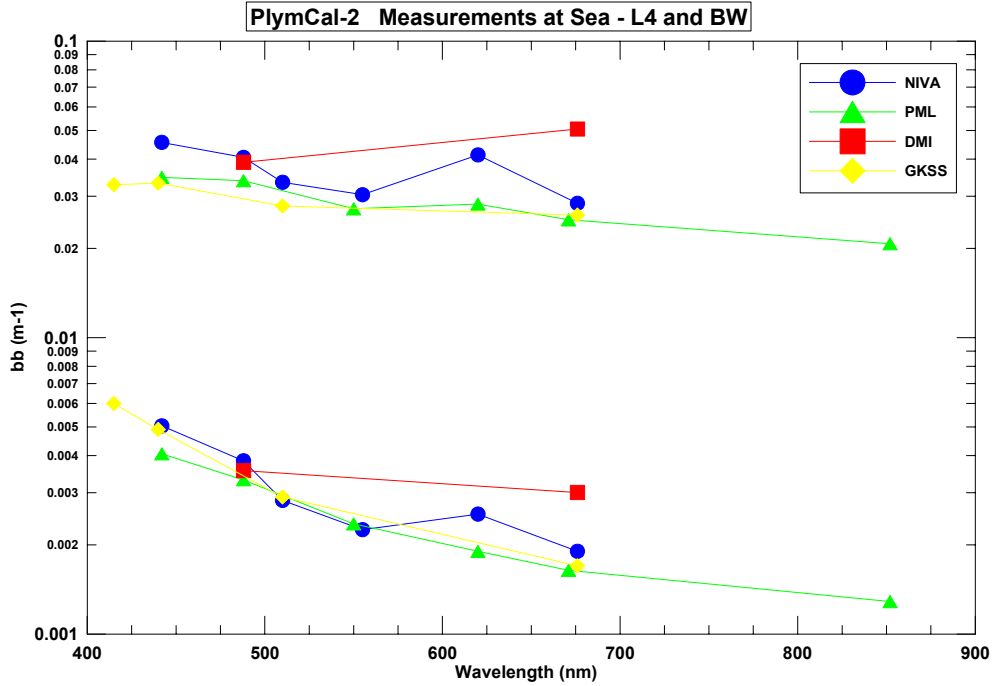


Figure 6: Spectral variations in measured b_b at the Case 1 and Case 2 stations

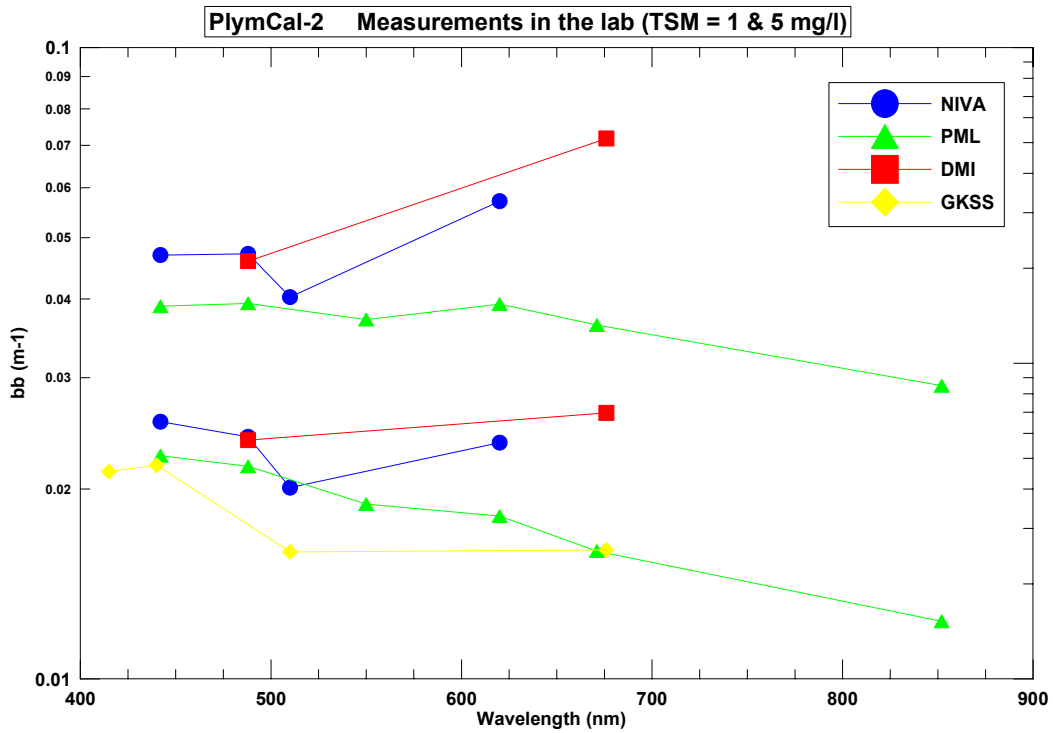


Figure 7: Spectral variations in measured b_b during the laboratory experiment

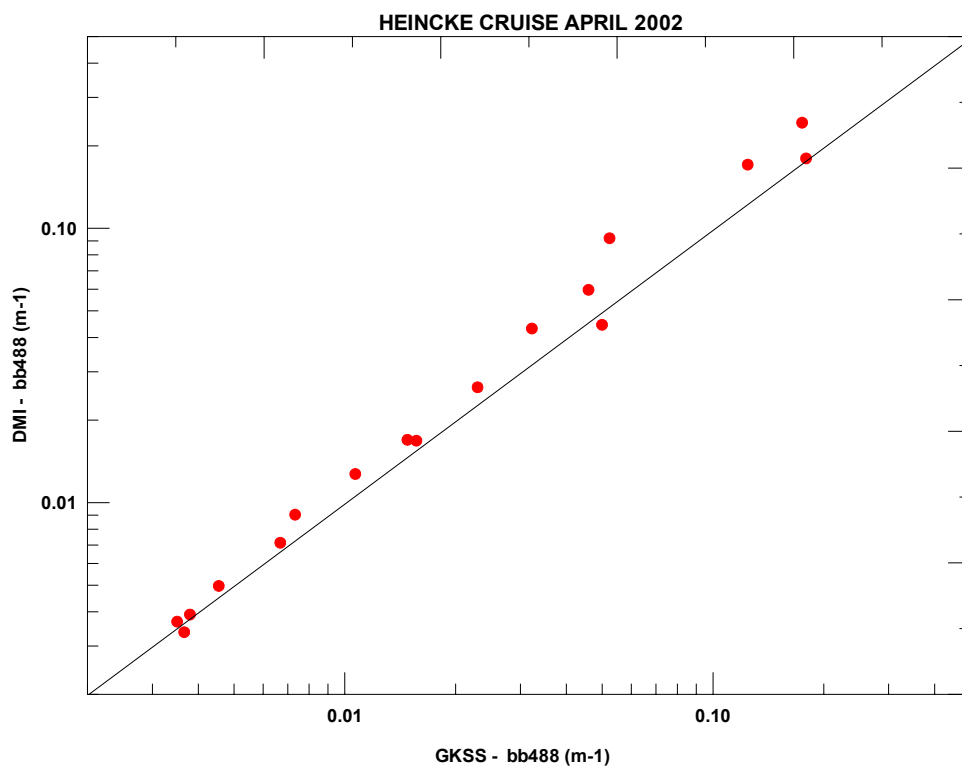


Figure 8: Scatterplot of GKSS and DMI values of b_b at 488 nm (m^{-1})

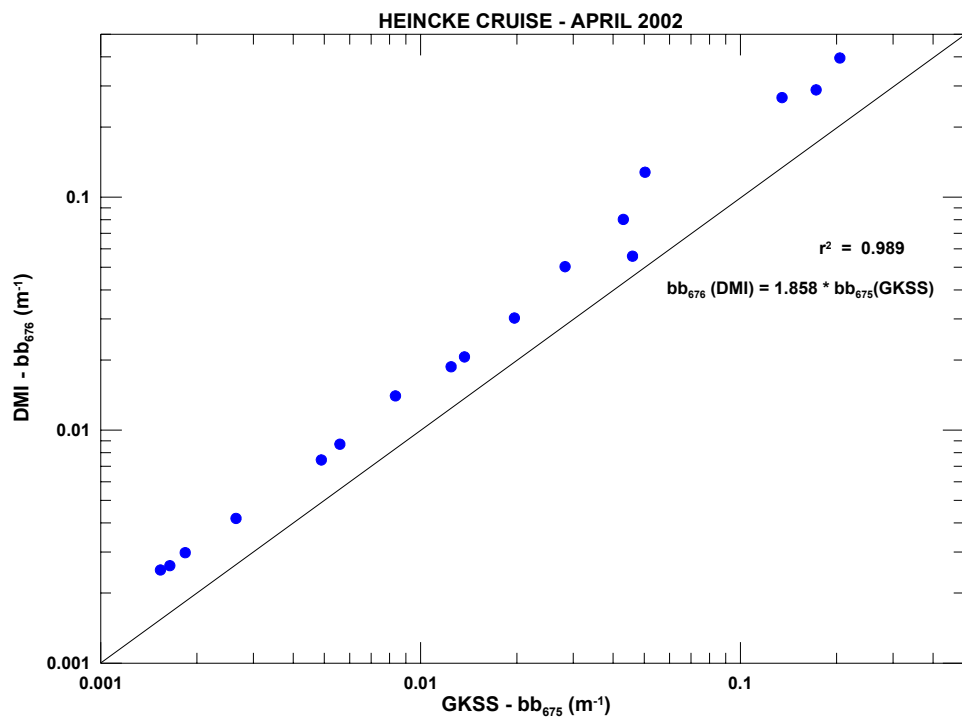


Figure 9: Scatterplot of GKSS and DMI values of b_b at 676 nm (m^{-1})

It should still be noted that the GKSS data were not sigma-corrected, and this accounts for 5.2 % of the observed differences. Exact values applied in the sigma-correction are given in Table 4.

Table 4: Applied Sigma Correction Parameters

	Hydroscat Default	DMI	GKSS	NIVA	PML
$a_d(400)$	0.01	1.0	-	0	0.01
$b_b(\lambda)$	0.015	0.015	-	0.015	0.015
C (CHL-Conc.)	0.1	0.1	-	0	0.1
S_d	0.011	0.011	-	0	0.011
S_{ys}	0.014	0.014	-	0	0.014
Γ	4.32	4.32	-	4.0	4.32
χ	1.08	1.08	-	1.08	1.08

During the R/V Belgica cruise in Belgian coastal waters and the English Channel, simultaneous measurements with the PML-HS6 and the DMI-HS2 were made. Many stations were made with the PML-HS6, but unfortunately the cable on one of the DMI instruments was damaged on the first day of deployments, so data from only three stations were collected with both instruments. These measurements are shown in Figure 10.

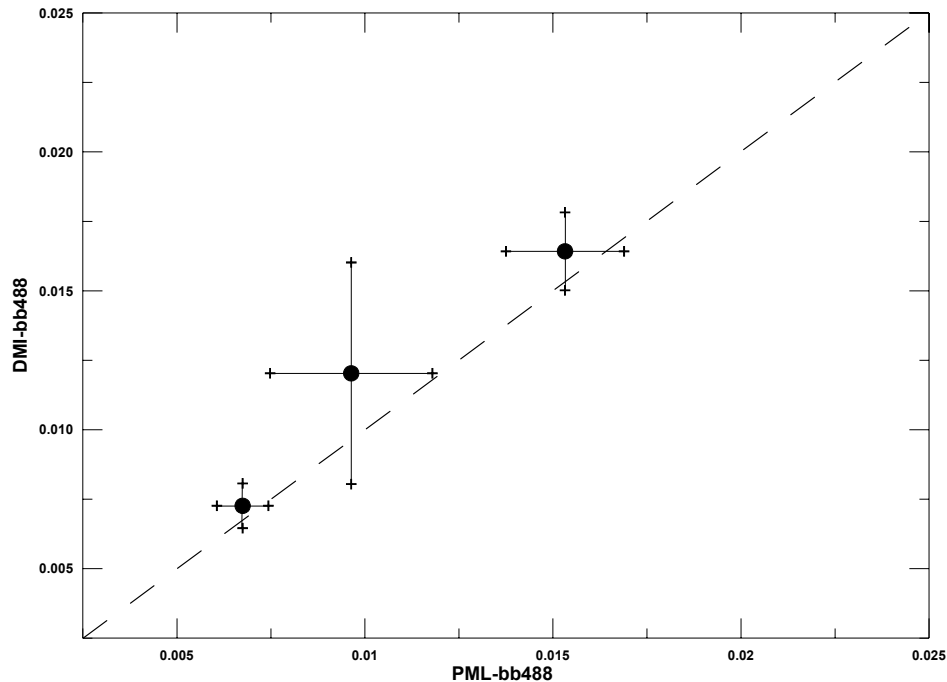


Figure 10: Scatterplot of PML and DMI values of b_b at 488 nm (m^{-1}) from R/V Belgica cruise including mean values and standard deviations

The overall results are the same as in the PlymCal-2 and the Heincke cruise analysis; the agreement between the two is good and DMI values are somewhat higher. The station where data from the two instruments deviate the most from each other also has the highest standard deviations. The fact that the standard deviation is nearly equally large in both directions suggests that the water was very heterogeneous. The fact that the two instruments were lowered separately a few meters apart means that there were small differences in actual depth and therefore the actual water masses recorded and that the variation in b_b (488) was due to fluctuating densities of particulate matter.

Conclusions and Recommendations

In general, the Hydrosat are in reasonably good agreement with each other both spectrally and in absolute values with a few exceptions. The GKSS and PML agree the best, while the DMI and NIVA instrument show slightly higher values. In addition the red DMI channel at 676 nm is far off compared to the others and requires calibration. The NIVA 620 nm channel, also seem to overestimate.

Signal variations are higher during the laboratory experiment than during the measurements at sea, possibly due to noise originating the scattering by the walls and bottom of the tank.

Results from the REVAMP cruises (GKSS-R/V Heincke) and (MUMM-R/V Belgica) confirms the PlymCal-2 results tendencies (DMI higher than both GKSS and PML), but underlines also the excellent correlation between the instruments.

The application of varying sigma-correction accounted for up to 5 % of the differences observed. Even though this is a small correction, realistic sigma-correction values should be applied, particularly in turbid and/or highly absorbing waters (Case 2 waters), and also in any future b_b inter-comparisons.

References

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Oishi, T. (1990): Significant relationship between the backward scattering coefficient of sea water and the scatterance at 120°. *Applied Optics, Vol.29*, 4658-4665.

Coloured dissolved organic material (m^{-1})

Introduction

Prior to the inter-calibration exercise held at Plymouth Marine Laboratory, a number of experiments were conducted to assess the following aspects of the measurement protocol of CDOM absorption:

- *Sample preparation*
- *Filter type*
- *Filter preparation*
- *Sample storage*
- *Reference baseline*
- *Temperature control of blanks and samples*

The results from these experiments were presented at the inter-calibration workshop (11 to 14 June 2002) to scrutinize the current methodologies and are / will be documented in the Appendices of the REVAMP protocols document.

Reference blank

The greatest difference in measurement protocols between laboratories was the use of reference blanks. GKSS and NIVA autozero the spectrophotometer using MilliQ in the sample cell and air in the reference cell. The absorbance of MilliQ against air was recorded followed by the sample against air. The two spectra were then subtracted to give the absorbance of the sample. PML autozero the instrument using MilliQ in both sample and reference cells and then the sample was run against MilliQ to give the absorbance of the sample directly.

During the inter-calibration workshop, an experiment was designed to investigate the effects of differences in reference blank on CDOM absorption. Natural seawater samples were taken from two sites close to Plymouth Sound, with varying CDOM concentrations (L4 and Mayflower) and reference blank methods were used to analyse the samples.

Table 5. YS Inter-comparison; air versus MilliQ reference blank.

MERIS Band	Mean L4 Ref - air	Std dev L4	Mean L4 Ref - MQ	Std dev L4	Mean MF Ref - Air	Std dev MF	Mean MF Ref - MQ	Std dev MF
412	0.252	0.016	0.290	0.020	0.652	0.085	0.703	0.091
442	0.161	0.014	0.194	0.019	0.459	0.079	0.506	0.084
490	0.082	0.015	0.115	0.019	0.296	0.071	0.347	0.075
510	0.064	0.014	0.100	0.017	0.258	0.067	0.310	0.071
560	0.041	0.012	0.072	0.016	0.201	0.060	0.251	0.064
620	0.027	0.013	0.056	0.013	0.159	0.054	0.210	0.055
680	0.014	0.008	0.042	0.012	0.133	0.051	0.182	0.050
708	0.002	0.004	0.028	0.008	0.112	0.048	0.162	0.047

Fig 11. CDOM absorption coefficient of samples from L4 and Mayflower using different reference blanks. Red line – sample run against air; Blue line – sample run against MilliQ.

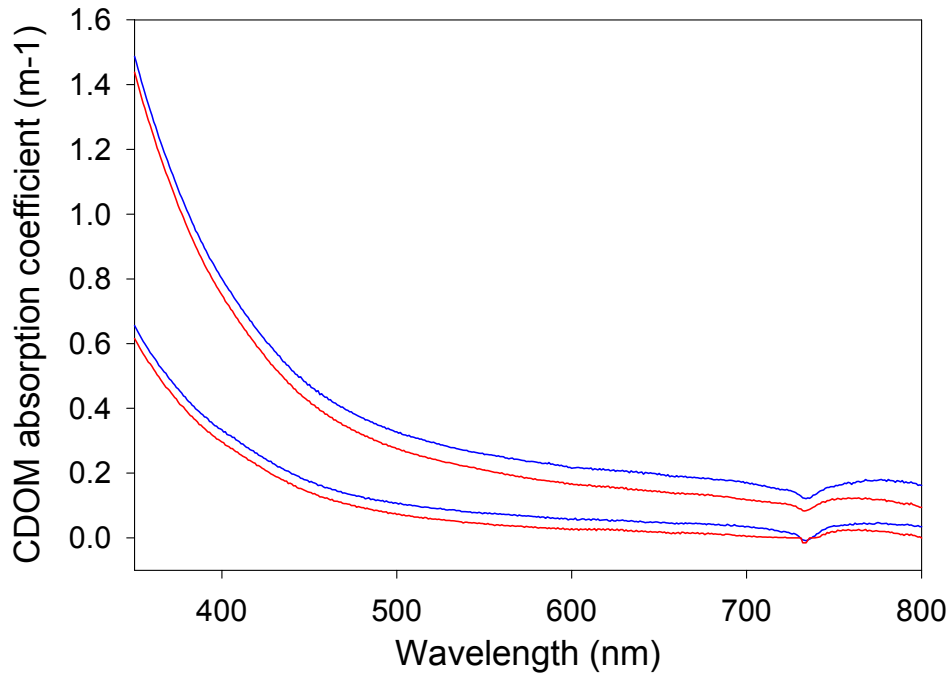
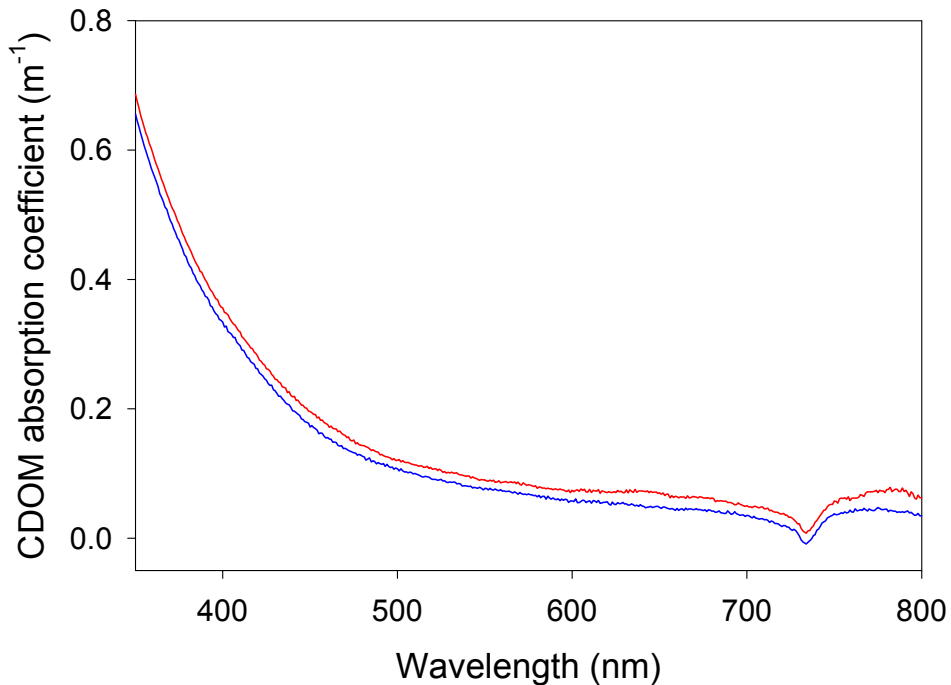


Fig 11 illustrates the difference between samples using air and MilliQ reference blanks. Over the whole spectrum there was a 21 % difference between samples. The difference was greater at lower CDOM absorption coefficients (e.g. L4 – 29 %) compared to higher CDOM concentrations (e.g. MF – 14 %). For the 442 nm MERIS bands there was a 20 % difference in CDOM absorption for the L4 sample and a 10% difference for Mayflower and the standard deviation for both samples was low indicating little difference between replicates. The percentage difference over blue to green MERIS wavebands (412 to 620 nm) increased (Table 1) to 48 % for L4 and 19 % for Mayflower and showed that at longer wavelengths the effect of the reference blank on CDOM absorption increased.

The effects of sodium azide on CDOM absorption

Different protocols have suggested different methods of preserving CDOM samples. NASA found that samples can be stored in a refrigerator for 4 to 24 hrs with no adverse effects on CDOM absorption (Mitchell et al. 2000). For longer term storage, the addition of 0.5 ml solution of 10g/l of NaN_3 per 100 ml of sample has been suggested, to prevent the degradation of CDOM (Ferrari et al 1996). To check the effects of NaN_3 on the resulting absorption coefficient fresh seawater samples from L4 were spiked with NaN_3 were compared with fresh samples that had not been spiked with NaN_3 . There was a 10 % difference between CDOM absorption coefficients (Fig 12) at 442 nm and a 14 % difference over MERIS wavebands. Overall the difference between samples spiked and non-spiked was relatively low, however to reduce analytical errors in MERIS data validation, it is recommended that CDOM samples should be run fresh whenever possible.

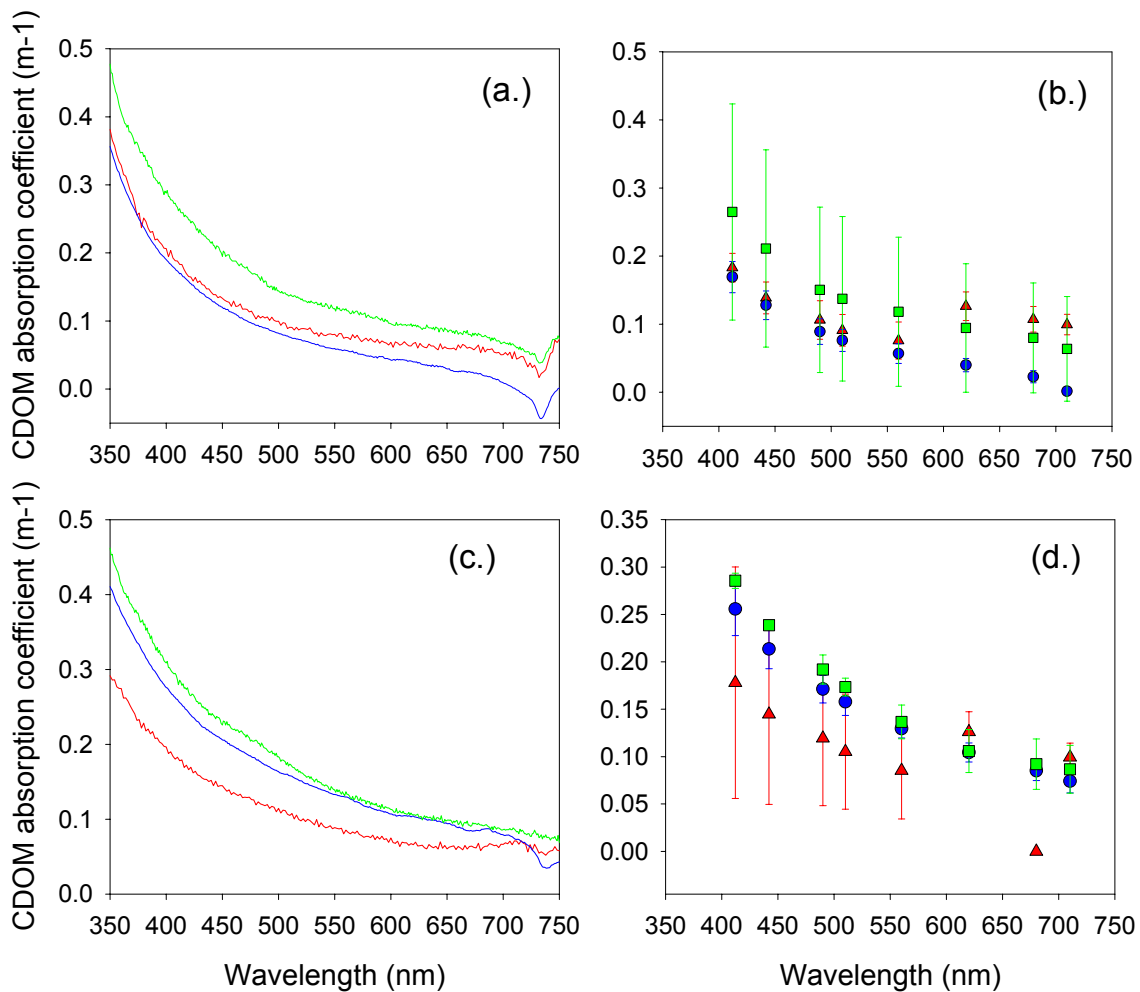
Fig 12. The effect of sodium azide on CDOM absorption. Red line – mean of three replicate natural seawater samples with sodium azide. Blue line - three replicate natural seawater samples without sodium azide



CDOM inter-calibration 1

On 29 July 2002, a water sample from L4 was collected in 2.5l dark acid cleaned bottle. The sample was filtered through 0.2 μm polycarbonate filter (as per REVAMP protocols) and the filtrate was decanted into 125 ml dark storage bottles. Three replicate samples were prepared for each partner laboratory (GKSS, NIVA & PML). In addition to natural seawater samples, a 1% solution of Aldrich humic acid sodium salt was prepared and aliquots of the standard were added to MilliQ to give absorbance values of 0.11 and 0.055 at 442nm. Three replicates of these respective solutions were prepared for shipment to each laboratory. The natural seawater samples, humic acid solutions and MilliQ samples were stored in polystyrene containers surrounded by ice packs and shipped to the respective laboratories within 24 hrs of filtration. The samples were analyzed at approximately the same time, two days later, on 31 July 2002.

Fig 13. Comparison of CDOM absorption coefficients for L4 (a.) & (b.) and humic acid sodium salt with optical density of 0.055 at 442 nm (c.) & (d.). Red line and triangles – GKSS; Green line and squares – NIVA; Blue line and circles - PML.

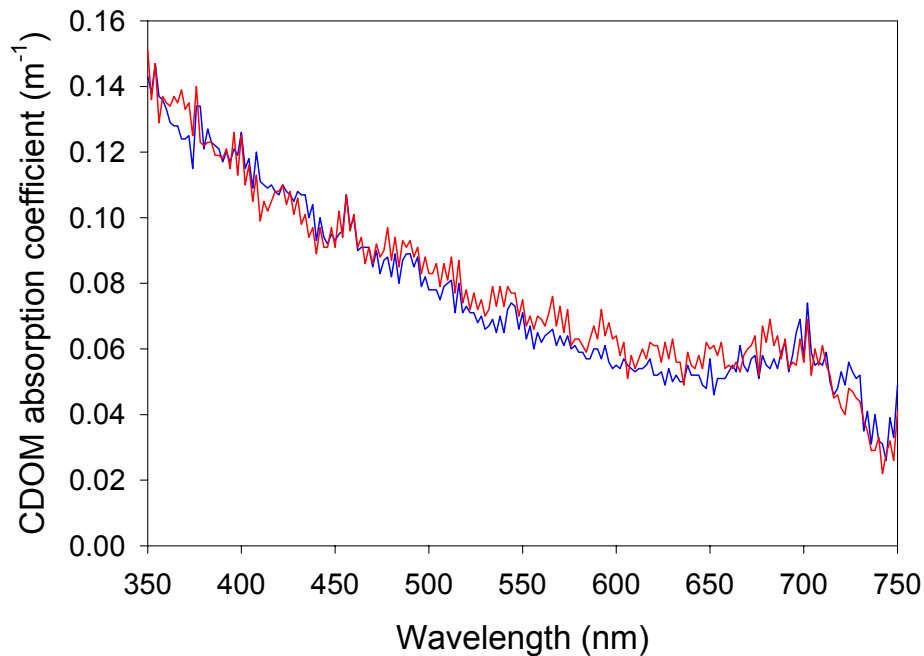


For both the natural water sample and the humic acid solution there was a large offset between laboratories which resulted in a high percentage difference between some laboratories (Fig 13 a & c). At MERIS band 442 nm there was a 39 % difference between NIVA and PML, whereas the difference between GKSS and PML was only 8%. For the humic acid standard the difference between NIVA and GKSS was 32% and between PML and NIVA 11%. The variation between replicates was high for NIVA for the natural sea water sample and for GKSS for the humic acid solution. The large offset between samples may have been partly due to the following:

Impurities in reference MilliQ.

The MilliQ water that was sent with the samples showed a high variation compared with MilliQ derived from GKSS indicating some impurities in the MilliQ sent with the samples (Fig 14). The MilliQ system was subsequently serviced and one of the components was replaced which may have been shedding fine particles into the recirculating water.

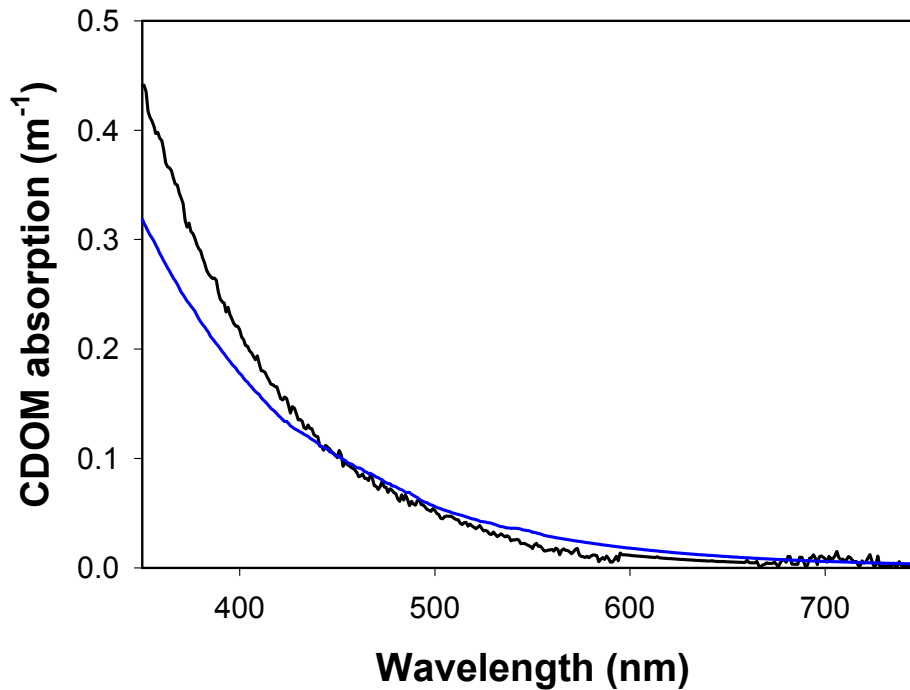
Fig 14. Inter calibration MilliQ (sample cell) measured against GKSS MilliQ (reference cell).



Degradation of humic acid.

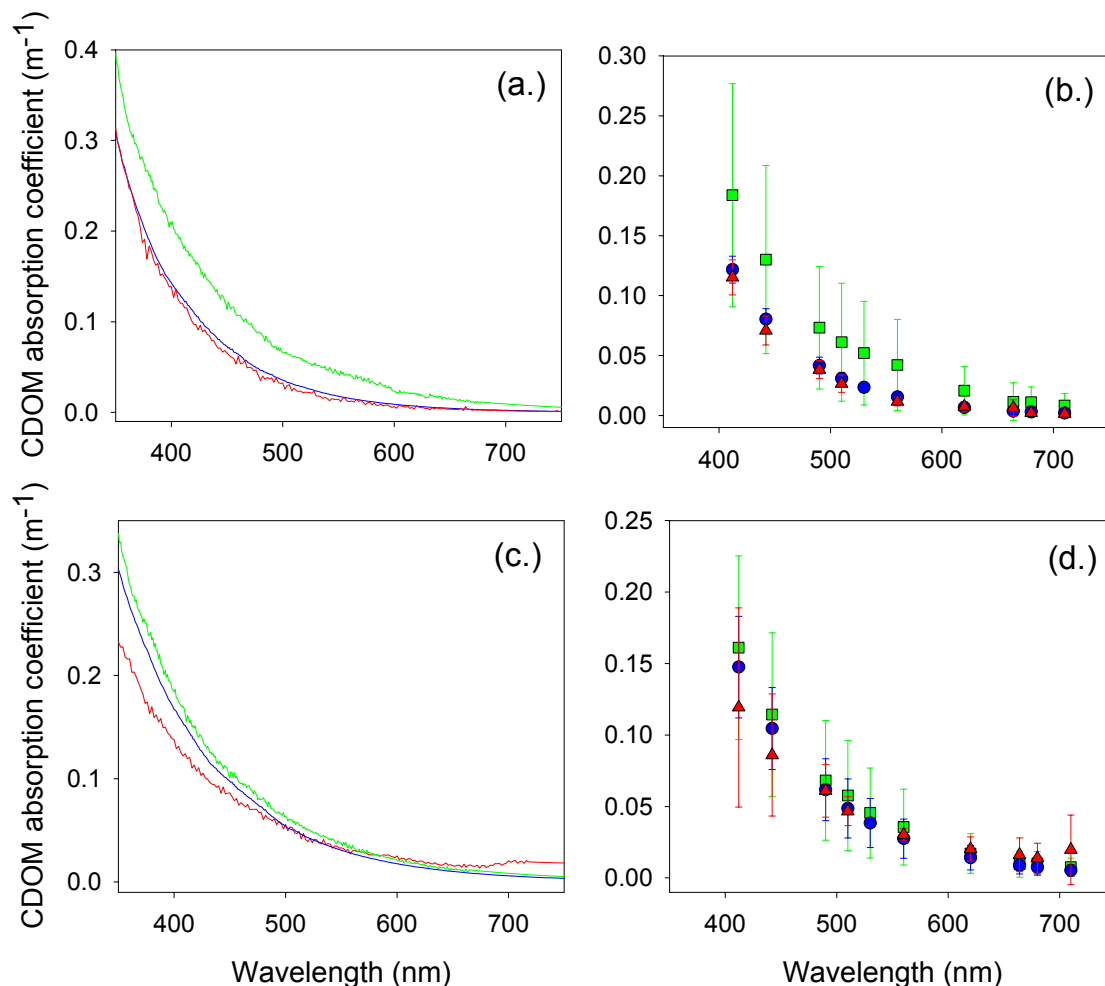
There were differences in the fresh humic acid solution prepared on 28 July and the solution measured two days later on 31 July (Fig 15). Between 350 and 500 nm the difference was 13% whereas at 442 nm there was only a 1% difference between CDOM absorption coefficients.

Fig 15. Comparison of CDOM absorption in fresh (black line) and two day old (blue line) 0.11 OD₄₄₂ humic acid solution.



In order to remove the effect of the offset between samples the raw data was processed using an offset correction (Fig 16). However this only had a significant effect on the humic acid samples when the % difference between NIVA and GKSS was reduced to 25% and between PML and NIVA to 9%. Over the MERIS wavebands (412 to 560 nm) the over all difference between labs was greater for the natural seawater sample from L4 (37%) than for the humic acid solution (14%). For the L4 sample alone there was almost a 50% difference in absorption between GKSS and NIVA. The largest difference for the humic acid solution was 19%.

Fig 16. Comparison of CDOM absorption coefficients for L4 (a.) & (b.) and humic acid sodium salt with optical density of 0.055 at 442 nm (c.) & (d.). Data same as Fig 5, but reprocessed to remove the influence of baseline offset between laboratories. Red line and triangles – GKSS; Green line and squares – NIVA; Blue line and circles - PML.



CDOM inter-calibration 2

The CDOM intercalibration was therefore repeated on 18 November 2002 to check the effect of impurities in MilliQ and degradation of humic acid solution. Samples were collected from two sites (L4 and Barnpool) off Plymouth Sound. In addition, a 1% solution of Aldrich humic acid sodium salt was prepared and aliquots of the standard were added to MilliQ spiked with phosphoric acid to prevent CDOM degradation. The humic acid standard gave absorption coefficients of 0.2 m^{-1} at 442nm. Three replicate samples were prepared for each partner laboratory (GKSS, NIVA & PML) and the samples were stored in polystyrene containers surrounded by ice packs and shipped to the

respective laboratories within 36 hrs of filtration. The samples were analyzed at approximately the same time three days later on 21 November 2002.

The results of the inter comparison are given in Fig 17. Over all, the difference between labs for MERIS band centres 412 to 560 nm was 22 %. The variation between labs was lower at low CDOM concentrations and increased with increasing CDOM absorption. The difference between labs over MERIS bands (412 to 560 nm) was lowest at L4 (10 %), when the absorption coefficient at 442 nm was 0.1 m^{-1} , and highest at Barnpool (43 %), when the absorption coefficient was 1.0 m^{-1} . For the humic acid standard, the difference between the labs was 14 % and the absorption coefficient was 0.2 m^{-1} . For the L4 sample, the standard deviation for all labs was small (Fig 7b). Similarly for the humic acid standard the standard deviation was generally low but for the PML data increased in the red end of the spectrum. For the Barnpool sample, PML showed higher variation in standard deviation than the other labs, indicating large differences in CDOM concentration between samples. For the L4 sample at MERIS band 442 nm there was only a 1% difference between each of the labs. For the humic acid standard at 442 nm the difference between GKSS & NIVA was 6 % and between PML & GKSS, 18%. For the Barnpool sample GKSS & NIVA exhibited a difference of 10 %, whereas the difference between PML and GKSS was $> 50\%$. Compared to the fresh sample which were run on the day of sample collection (18 November 2002), L4 and the humic acid standard exhibited a difference of 17 & 15 % respectively at 442 nm, but for Barnpool the difference was 54 % at 442 nm, indicating high degradation of CDOM in this sample.

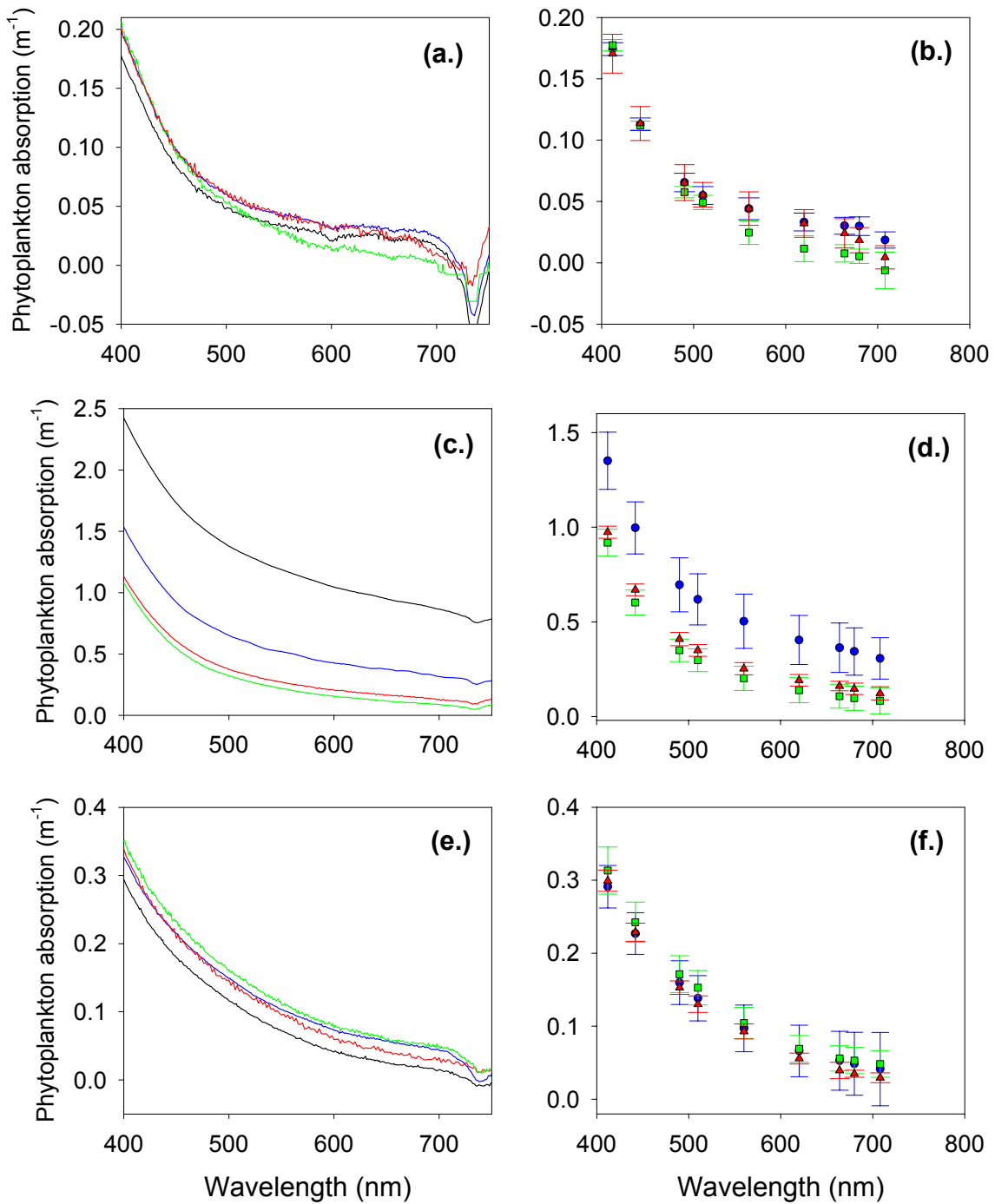
Differences in storage conditions may account for the difference in CDOM absorption between the three labs especially at Barnpool, where the absorption of CDOM was ten times higher than L4 and is attributed to outflow of the River Tamar. Although care was taken to eliminate differences in filtration, storage, protocols, instruments between labs, and even though the samples were in the same insulated packaging, the GKSS & NIVA were transported and therefore the package would have been at a colder ambient temperature for a longer period of time than the PML samples which were kept in the laboratory. This may have increased the degradation of the CDOM in the PML samples especially for the high CDOM sample Barnpool. The relatively high variability in CDOM results between labs illustrates the necessity for accurate determination for this parameter.

Conclusions and recommendations

There was a 22 % difference between laboratories for the absorption coefficient of CDOM in artificial and natural sea water samples. For the artificial sample the difference was 14 % and for the natural seawater samples the difference was 30 %. The following recommendations were made to reduce the variability between laboratories:

- *The spectrophotometer is regularly calibrated,*
- *The reference blank is auto-zeroed against air,*
- *The purity and quality of the reference MilliQ is monitored*
- *Samples are analysed immediately after collection to avoid CDOM degradation.*
- *Humic acid salt suspended in MilliQ can be used as a standard for quality control between laboratories.*

Fig 17. Comparison of CDOM absorption coefficients for L4 (a.) & (b.) Barnpool (c.) & (d.) and humic acid standard (e.) & (f.). Red line and triangles – GKSS; Green line and squares – NIVA; Blue line and circles – PML; Black line and circles – fresh samples. Note fresh samples are not plotted on (b.), (d.) & (f.).



Pigments Concentration by High Performance Liquid Chromatography [mg m^{-3} or $\mu\text{g l}^{-1}$].

Inter-comparison of detection of chlorophyll a using HPLC

An inter-comparison of detection of chlorophyll-a between 3 European labs (GKSS, NIVA and PML) was performed at the inter-comparison workshop on 12 June 2002. Between 0.5 and 1 l of seawater was filtered through Whatman 24 mm GFF filters and frozen in liquid nitrogen following MAVT and REVAMP protocols. To remove uncertainties in filtration between laboratories, the same person filtered all samples. Samples were transported to the respective laboratories on dry ice and were then transferred to liquid nitrogen or a -80°C freezer. Chlorophyll a was measured using HPLC; each lab used a slightly different extraction procedure and measurement protocol. The differences between experimental procedures are documented in the MAVT chlorophyll-a intercomparison report (Sørensen, et al. 2003). NIVA also measured chlorophyll a using spectrophotometric methods for reference purposes. This method uses no correction for pheopigments and only a monochromatic determination with a extinction coefficient of 91.1 in 90% acetone.

Samples were derived from three different stations (time series station Plymouth Sound – L4; Barnpool – BP; Mayflower – MF) in triplicate. A summary of the three replicates from each of the labs and the spectrophotometric results from NIVA are given in Table 5.

Table 5. Chlorophyll a concentration ($\mu\text{g/l}$) measured by HPLC by different laboratories.

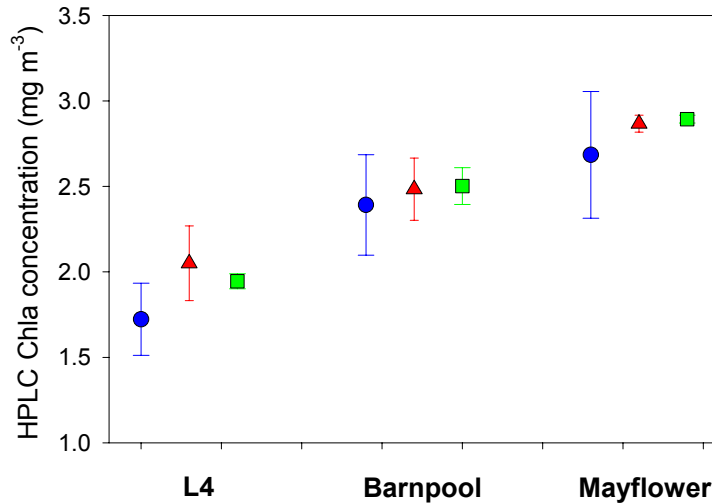
		GKSS	NIVA	PML	NIVA sp
L4	1	2,30	1,90	1,77	1,94
L4	2	1,90	1,98	1,49	2,02
L4	3	1,95	1,97	1,91	2,07
BP	1	2,63	2,50	2,06	2,94
BP	2	2,54	2,61	2,48	2,70
BP	3	2,28	2,40	2,63	2,56
MF	1	2,89	2,88	2,26	3,08
MF	2	2,81	2,92	2,93	3,12
MF	3	2,90	2,88	2,87	3,06

In Figure 18 the results from the different labs are presented. Each point represents the mean and standard deviations for the different labs and for the overall measurement are summarised in Figure 18 and Table 6.

Table 6. Mean and standard deviation in % of mean for the three replicates for individual laboratories and overall.

		GKSS	NIVA	PML	Overall
Mean	L4	2,05	1,95	1,72	1,91
% St.dev	L4	11 %	2 %	22 %	35 %
Mean	BP	2,48	2,50	2,39	2,46
% St.dev	BP	7 %	4 %	22 %	22 %
Mean	MF	2,87	2,89	2,68	2,81
% St.dev	MF	2 %	1 %	23 %	23 %

Figure 18. Chlorophyll a concentration for each laboratory. The results represent the mean of the replicates, and the error bars represent the standard deviation. Blue circles – PML; Red triangles – GKSS; Green squares – NIVA.



The percentage difference between all labs was small (~9 %). For the L4 sample NIVA and GKSS results showed good agreement (Table 5 & Fig 18), while the results from PML were between 13 and 19 % lower. For the Barnpool and Mayflower results, the PML results were always lower and showed a higher standard deviation although the differences were not significant. For the Barnpool sample the difference between NiVA/GKSS and PML was 4 % and for the Mayflower sample the difference was 7 %. During previous inter-comparisons (e.g. PlymCal I), the results from NIVA and PML were within 4-10 % of each other (GKSS did not participate). In the first round of MAVT inter-comparisons (arranged by NIVA), the percentage standard deviation from the mean was 4-24 % for 9 of the 10 samples between the three participants. For the sample with the lowest chlorophyll a content, the standard deviation was 50 % between the three participants and GKSS always reported higher chlorophyll a concentrations than NIVA and PML.

The small differences observed may be due to methodological differences in sample analysis. The principal differences between laboratories are that PML employs sonication for 20 s for pigment extraction whilst GKSS and NIVA soak the samples for 24 hours and GKSS use a temperature of -30°C and NIVA use room temperature

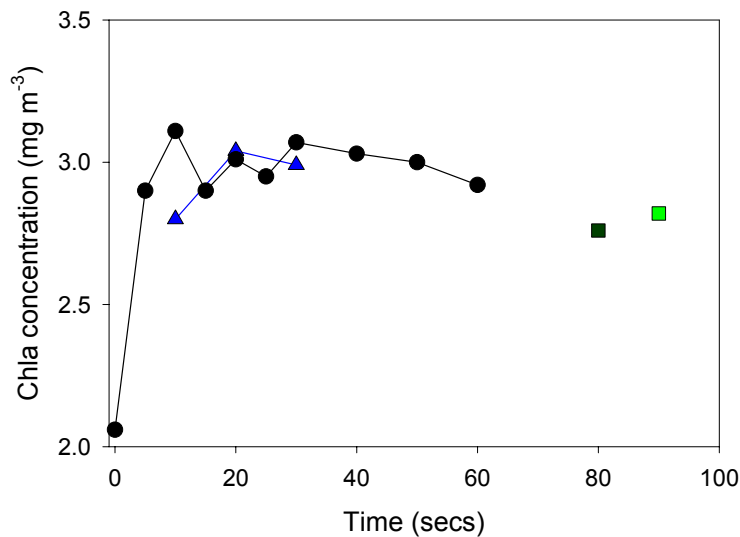
Inter-comparison of extraction techniques

An experiment was designed using phytoplankton cultures of *Isocrysis* to investigate –

- The extraction kinetics of sonication.
- The comparative extraction response of sonication and extraction in a fridge or deep freeze for 24 hrs.

It was found that 20 to 30 seconds was the optimum response time for extracting Chla and that soaking the filters in acetone in a fridge or freezer (20°C) for 24 hrs resulted in lower Chla concentrations (Fig 19).

Fig 19. Chla extraction efficiency using different sonication times (black circles) without an internal standard (blue triangles), 24 hr extraction in the fridge (black square) and in a freezer (green square).



These results indicated that extraction procedure is not the principal reason for the small differences observed between laboratories. From the data given in Fig 2 the GKSS & NIVA data should have been lower than PML data, but we found the reverse trend. Other differences in instrumentation such as differences in columns and auto analysers may be the cause of the differences found. PML uses a C8 column, whereas GKSS and NIVA use a C18 column.

Conclusions and Recommendations.

The differences found between laboratories was small (9 %) and differences in instrumentation may have lead to the differences observed.

References:

Sørensen, K. Grung. M., Röttgers, R. An intercomparison of in vitro chlorophyll-a determinations – preliminary results. ESA publication 2003.

Surface Downwelling Spectral Irradiance, $E_s(\lambda)$ ($\text{W m}^{-2} \text{nm}^{-1}$)
Subsurface Downwelling Spectral Irradiance, $E_d(z,\lambda)$ ($\text{W m}^{-2} \text{nm}^{-1}$)
Subsurface Upwelling Spectral Radiance, $L_u(z,\lambda)$ ($\text{W m}^{-2} \text{nm}^{-1} \text{sr}^{-1}$)
Surface Downwelling Diffuse Spectral Irradiance over Direct Spectral Irradiance $r(\lambda)$

Above-water Water Leaving Radiance, L_w ($\text{Wm}^{-2}\text{nm}^{-1}\text{sr}^{-1}$) and Downwelling Irradiance, E_s ($\text{W m}^{-2}\text{nm}^{-1}$)

This report summarises the activities of an inter-calibration workshop of measurements of optical sensors and held at Plymouth from 11 to 14 June 2002 during the REVAMP inter-calibration workshop (PlymCal 2). Laboratory radiometric inter-calibrations of in-water radiometers, irradiometers, above-water down-welling solar irradiance sensors and multi-spectral radiance sensors were performed and field measurements of AOP instruments were compared at a Case 1 and Case 2 water sites near to Plymouth Sound.

Introduction

During a previous inter-calibration PlymCal 1 at PML from 13 to 17 August 2001, eight laboratories participated in an inter-calibration at which Bio-spherical, PR650, Satlantic, SIMBADA, SPMR, TACCS and TRIOS were compared. PlyMCal I was designed as a common bench test for the MERIS validation instruments. The TACCS showed a small deviation from the other instruments (2 %) with better agreement in the blue than in the red. The NIVA instrument showed no error since all the results are within the uncertainty of the calibration lamp (+/- 2%). The IVM instrument showed a constant offset of around 4% with a small trend from blue to red similar to the TACCS. The SPMR showed a strong trend from blue to red with errors increasing to around 7%. The TRIOS instruments showed an offset decreasing blue to red from around 10% to zero. The IOW TRIOS instrument showed an average offset of 5%.

In general, the band pass instruments were closer to the manufactures' specification than the spectral instruments in PlyMCal 1. The main cause of calibration differences is likely to be the calibration lamp; however the PML lamp used was calibrated at a SIRREX inter-comparison and had less than 20 hours use after this. Further it was found to be reliable for the COLORS intercomparison the previous year. It therefore seems unlikely that the errors were due to the lamp ageing as ageing results would result in an offset and irradiance decrease at blue wavelengths and the opposite trend to that observed.

The objective of PlymCal 2 was to calibrate radiometric sensors to within ± 1 to 2 % and to perform an instrument inter-comparison both in the laboratory and at sea. During PlymCal 2 the laboratory facilities and calibration standards were upgraded following a grant from SWRDA. In order to reduce the uncertainty in lamp calibration, a new NIST lamp was used.

A number of problems were encountered during the inter-comparison; different laboratories produced different results when referenced to the same lamp (91739 from SIRREX 3) using identical geometries. PlymCal 2 validated the PML setup and back traced the PlymCal 1 radiometric standards to the new NIST lamp.

Radiometric Calibrations

In a previous inter-calibration, SIRREX 5, organised by NASA as part of the SeaWiFS project in which 8 laboratories from different countries participated, there was a 2 % difference between radiometric sensors. During the EU COLORS inter-calibration the difference between sensors was 2 % except for the PML 412 channel which had a low output due to the configuration of the sphere. During the PlymCal 1 calibration the IVM calibration was within 4 %, the NIVA bio-spherical calibration was within 1 % and the MUMM calibration was from 0 to 10 % (Table 7). During PlymCal 2 a new plaque and new NIST lamp were used and a TRIOS radiometer from MUMM was re-calibrated.

Table 7. In air calibration at SeaWiFS and MERIS bands during PlymCal 1 (percentage difference with respect to PML standard).

Below Surface Radiance

MERIS Band	TACCS	IVM	IOW TriOS	MUMM LU_8068	MUMM LU_806B	NIVA ¹	SOTON
412	-0.97	-3.47	8.89	9.64	9.97	-0.12	-2.23
442	-1.83	-3.96	7.34	8.19	8.56	0.06	-2.36
490	-2.05	-3.89	5.44	6.35	6.62	0.17	-0.21
510	-2.03	-4.16	4.65	5.52	5.85	0.95	.1.71
[555]	-2.74	-4.10	2.01	2.85	3.15	0.30	
560		-4.39	1.95	2.78	3.07		2.65
620	-3.74	-4.00	1.11	1.95	2.29	² 1.31	-5.69
665		-4.90	0.47	1.23	1.54	-1.02	2.36
[670]	-3.92	-5.16	0.42	1.14	1.47		
685		-4.55	0.17	0.83	1.17		
709		-5.01	-0.25	0.32	0.68		

Calibration of the TRIOS instrument

Comparison of the stability of the MUMM TRIOS radiometers is given in Fig 20 & 21. In these figures the ratio of the radiance or irradiance reaching the sensor as calculated from the lamp output and plaque reflectance data supplied by PML is compared to the radiance or irradiance measured by the sensor using nominal calibration coefficients derived from a calibration by the instrument manufacturer in April 2001. This ratio is presented to study long-term calibration drift, though it is noted that the Plymcal-2 calibration and not the April 2001 calibration is used for MERIS validation measurements. Similarly measurements for wavelengths less than 410nm are included to show more clearly the spectral behaviour of discrepancies but such wavelengths are not used for MERIS validation. The TRiOS instrument was stable between PlymCal 1 & 2 but there

was a slight shift during PlymCal 1 with increasing error from red to blue. During PlymCal 2, the TRIOS head was referenced against the new NIST lamp, but there was still a progressive drift in the blue end of the spectrum. Since the two radiance sensors had the same sensitivity during Plymcal-1 and Plymcal-2, the difference between Figures 20 and 21 cannot be attributed to the sensors but must be attributed to one or more of the following factors: lamp, shunt or plaque. Once this effect is accounted for there is still a difference for the irradiance sensor between Plymcal-1 and Plymcal-2, which we believe to be the result of degradation of the cosine collector (see below).

Fig 20. Calibration of MUMM TRIOS sensor during PlymCal 1.

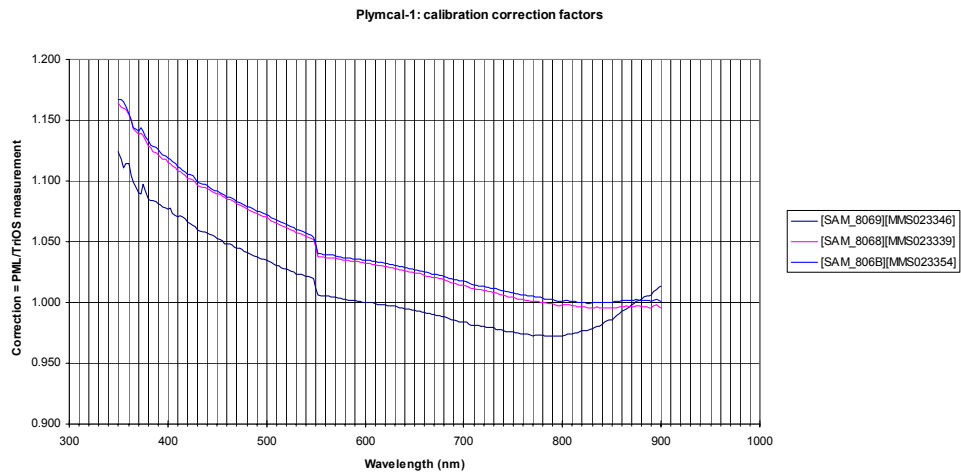
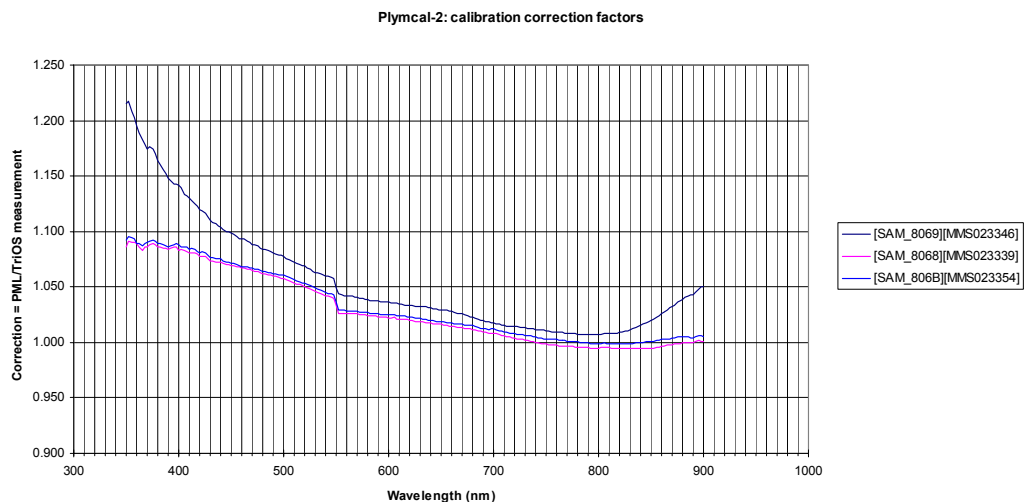


Fig 21. Calibration of MUMM TRIOS sensor during PlymCal 2 with new NIST lamp.



Potential Sources of Error in TRIOS Calibration

In order to investigate the different measurements of the two TriOS radiance sensors which are supposed stable between Plymcal-1 and Plymcal-2 further investigations of the calibration equipment were made. Since geometric error is non spectral any potential problems with calibration would be due to:

- the lamp (verified using a new NIST calibrated standard)
- the shunt (verified against NPL standard)
- or the plaque (verified against a newly calibrated Labsphere plaque and against absolute reflectance method).

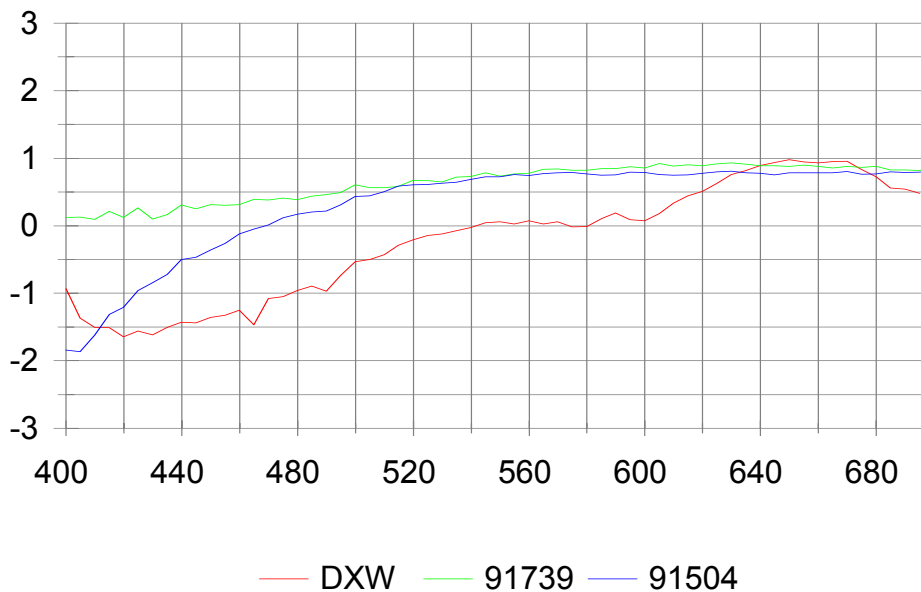
SIRREX lamp transfer

On average lamps have been changed every 4.5 yrs in the PML calibration facility and during the PlymCal 2 inter-calibration the performance of the TRIOS heads was checked against a new NIST lamp standard to eliminate the possibility of differences in lamp transfer. The following lamps have been used by PML for routine radiometric calibrations since 1984.

- 1) *Optronix DXW – UV Group* 1984
- 2) *91739 - Sirrex 3 – Reference* 1996
- 3) *91504 – Working Standard* 1997
- 4) *NIST FEL New Reference* 2002

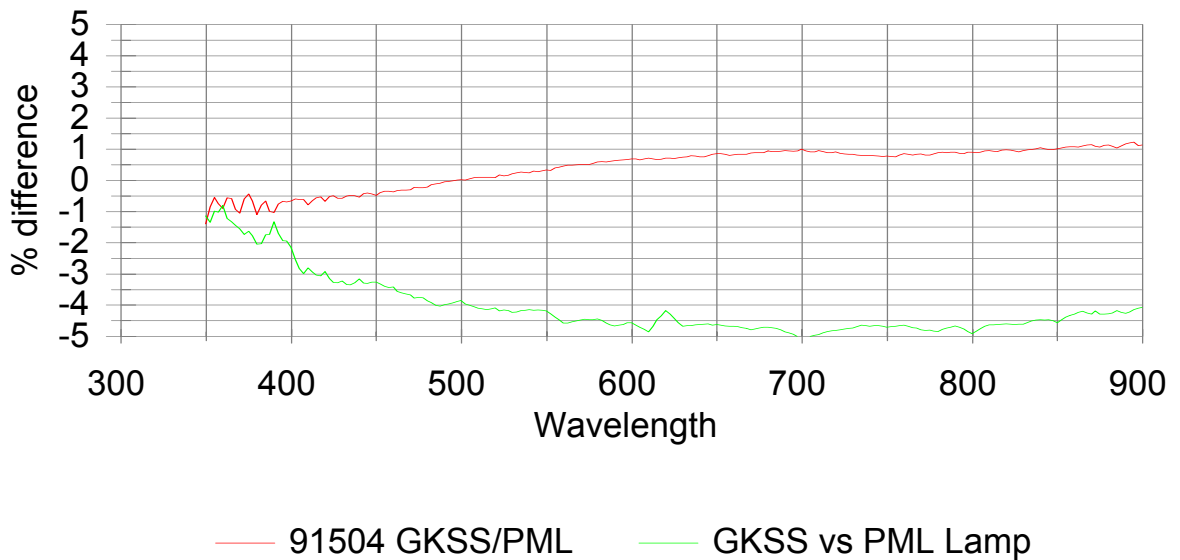
Lamp transfers were cross referenced to the new NIST lamp. Fig 22 shows the spectral response of the 2 lamps. The green line is the NASA SIRREX lamp which was spectrally stable to within 1 to 2 %. All lamps were found to be ± 1 to 2 %.

Fig 22. Lamp transfers cross referenced to NIST lamp. (Lamps are referred to above).



Further to the radiometric calibrations made at PML, a facility inter-calibration was made at GKSS from 2 to 4 November 2002 to check the effect of physical setup, power supplies and shunts, between the two laboratories. A Trios irradiance sensor was used at the laboratories, the sensor was pre and post calibrated at PML. The output of the PML lamp when measured using the GKSS facility shows 1 % or less difference (Fig 23). There was a 4-5 % difference between laboratories, but this is acceptable within the SeaWiFS and MERIS validation protocols.

Fig 23. Comparison of power supplies, shunts and lamps between GKSS & PML. Red line PML lamp output measured at both PML and GKSS. Green line output of GKSS lamp compared to that of PML lamp at GKSS.



Shunts

Using a lamp current that is different from that at which the lamp is calibrated by the manufacturer can produce significant changes especially at blue wavelengths. PML used the following shunts:

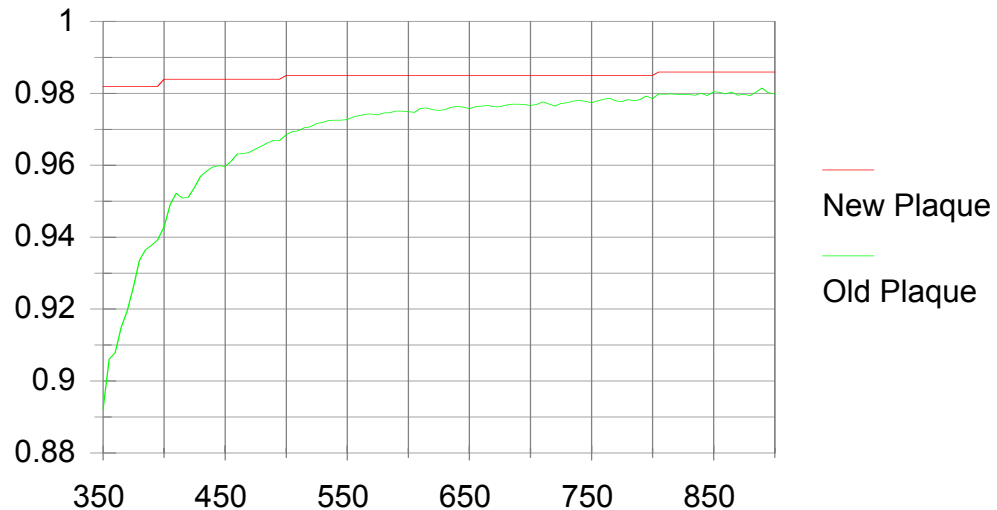
- 1) 0.3A 10 Ω – Reference - NPL Calibrated 1980 (0.01%)
- 2) 20A 0.7.. Ω – Intercompared at Sirrex 4 (0.2%)
- 3) 10A 1.0 Ω - New Purchase (0.01%)

Shunt 2 was used in PlymCal 1 and shunt 3 was used in Plymcal 2. The shunts were compared with the reference shunt and found to be within the nominal value, thus eliminating this as a possible cause of the discrepancy between PlymCals 1 and 2.

Plaque validation

A new plaque was purchased and compared to the old plaque used for PlymCal 1 and the TRIOS calibration. Absolute reflectance was determined by the use of an integrating sphere calibrated by the duel sphere method. It was found that due to ageing and discolouration of the old plaque there was a large difference in the blue to blue – green (Fig 24). The worst case scenario however was only 3% at 412nm, which does not explain the differences observed in the TRIOS data.

Fig 24. Comparison of plaques used in the TRIOS calibration.



Following the validation of the lamp standards, shunts and plaques, the TRIOS calibration data was reprocessed taking into consideration the differences in TRIOS response due to these components. The reprocessed data is given in Fig 25 in which TRIOS is compared against other sensors, however a significant drift in the blue was still observed (Fig 26) and there was still a response change in the instrument and a drift in the irradiance sensor due to degradation of the spectralon head. However this was only about 1 %. As a result of the inter-calibration workshop the manufacturers have traced the discrepancy and will be confirmed during a further inter-cal between PML and the manufacturers. The differences observed in PlymCal 1 & 2 were previously due to lamp transfer errors. Using the Plymcal standards for calibration the uncertainty associated with radiometric calibration within REVAMP will now be less than 5%.

Fig 25. Spectral percentage difference with respect to the PML standard for different radiometers. R68 and R6b are radiance sensors, E69 is the irradiance sensor.

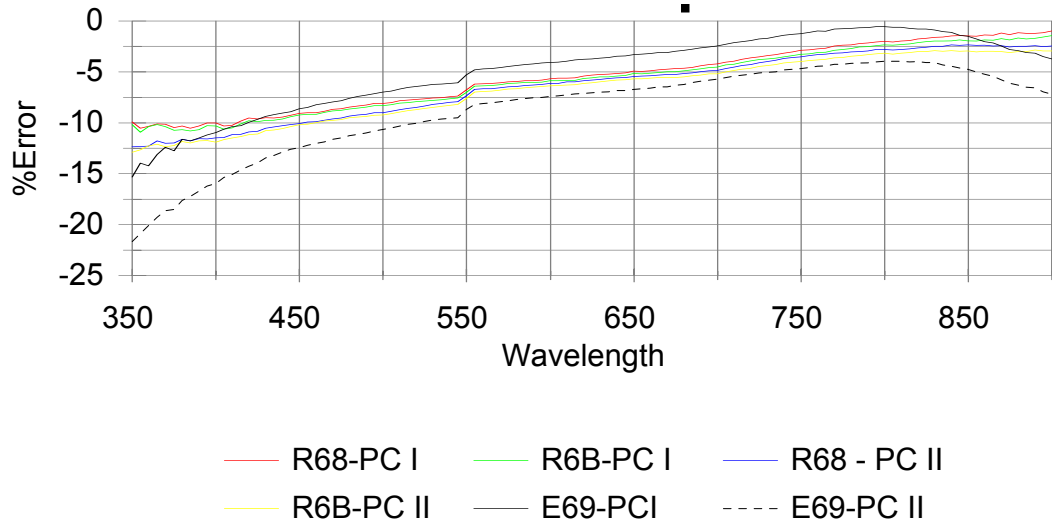
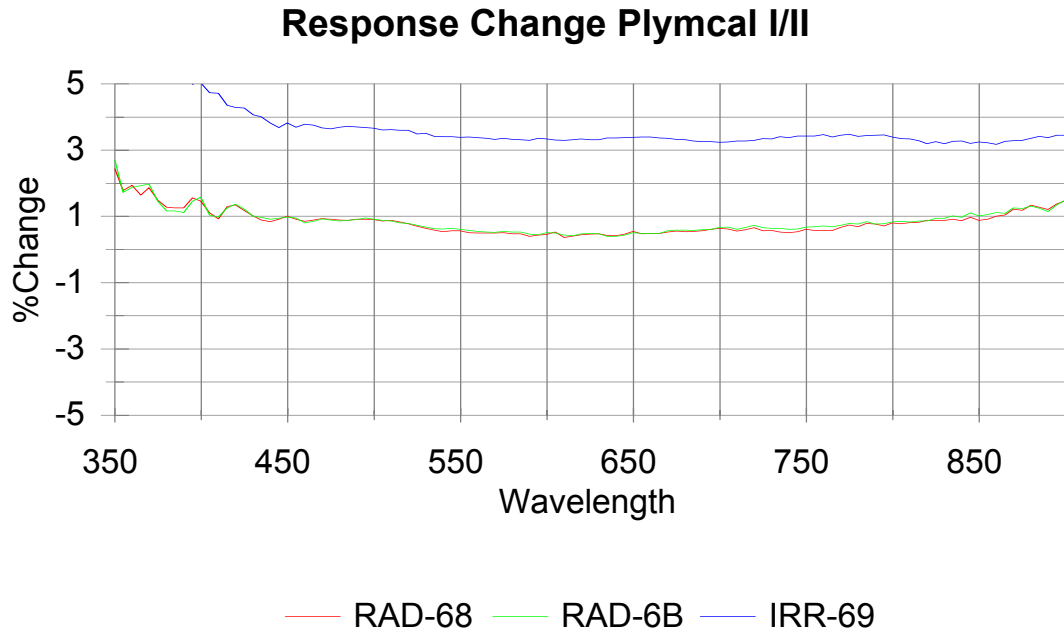


Fig 26. Response change of PlymCals 1 and 2. Key as in Fig 25. R68 and R6b are radiance sensors, E69 is the irradiance sensor.



These results show that there has been no significant change (generally less than 1%) in the response of the TRIOS radiance sensors between PlymCal 1 & 2. There has been a

degradation of about 3.5% rising to 4.5% at 412nm for the irradiance sensor. This is thought to be due to the cosine collector ageing in field deployments.

Summary / Conclusions for Trios Sensors

- Lamps were within +/- 2%
- Shunts were within 0.2%
- Plaque had degraded in blue
- Discrepancies in radiance calibration explained entirely by plaque degradation
- Discrepancies in irradiance sensor explained by change in irradiance head material

Conclusions and Recommendations

The expected error for radiometric calibrations is 2% and we would expect 5% between labs and sensors. PlyMCal 1 & 2 radiometry were referenced to a new NIST lamp and new plaque and the result was radiometry performance of between +/- 2%. A comparison of TRIOS radiance sensors above indicates that after full correction the experiments were reproducible at the 1% level for MERIS bands and with the exception of the TRIOS, the factory calibrations for all participants matched the PML standard to within 5% or better . The TRIOS instruments have been recalibrated using the PML standard for use within REVAMP and the matter is being investigated with the manufacturer to improve the standardisation of future calibrations.

Total Suspended Matter - TSM (g m⁻³)

Introduction

During the PlymCal II workshop in Plymouth in June 2002 the TSM methods were tested according to REVAMP and MAVT protocols. Three laboratories GKSS, NIVA and PML participated in the inter-comparison which consisted of determining total suspended particulate concentrations from natural and artificial samples.

Natural samples

Seawater was collected from station L4, MF and BP on 11th June, transported to PML and filtered the same day. A representative from each laboratory filtered their own samples onto pre-weighed filters. The same filtration volume was used by all laboratories; 2 liters for stations L4 and 1 liter for stations MF and BP.

Artificial samples

A solution of Formazin used for the calibration of turbidity meters (NIVA) was added to both MilliQ and seawater to test the effect of rinsing the filters. A solution of 4000 FTU (Formazin Turbidity Units) was diluted to a concentration of 10 FTU. The seawater used was the filtrate from the HPLC and particle absorption filtration (GFF filters). From the stock solution of 10 FTU 300 ml was used in the test.

In addition a clay mineral was tested to check if this could be used as a standard. A stock solution containing 10 mg/l stock solution was prepared and 300 ml of the solution was filtered. For these additional tests the same person filtered all samples for all labs. For PML one other person filtered an additional set of filters.

Analytical methods

The methods reported in the MAVT-protocol were used, but following the results from the MAVT PlymCal I workshop, the rinsing method was improved by using 3 * 50 ml of MilliQ water, followed by removing the funnel and rinsing the rim 3 times (approx. 3*5 ml).

For the natural water samples the different laboratories filtered their own samples and the sequence of filtration was PML, NIVA then GKSS. The seawater samples were mixed continuously and sub-samples for each lab were taken from the same bottle. For the artificial samples the same person filtered all samples. In addition a different person filtered an extra set of filters for reference comparison. In the test the same 3 filtration units were used (1,2,3) which corresponds to sample replicates 1, 2 and 3 (see tables). The same vacuum was also applied to all filters using a Millipore filtration manifold.

The analytical differences between the three labs was as follows;
PML use a Sartorius R200D semimicrobalance (DL 10 µg) and follow the methods of Van der Linde (1998), with the exception that the filters are dried at 65 ° C for 4 hours and are then cooled in a dessicator.

NIVA use a Sartorius microbalance type SC 2 (DL 0.1 µg) with a Polonium-210 static eliminator (Static Master model 1U400). The filters were prepared according to van der Linde (1998) and were fired at 450 °C, soaked in distilled water, dried at 75 °C for 1 hour and weighed after cooling in a dessicator. The same drying procedure was also used for the samples.

GKSS use a Sartorius type BP210D semi-microbalance (DL 10 µg). The filters were prepared according to van der Linde (1998) and were fired at 450 °C, soaked in distilled water, dried at 75 °C for 2 hours and are then weighed after cooling in a dessicator. The same drying procedure is used for the samples.

Results

Natural samples

The results from the TSM test from the three seawater stations are shown in Tables 1 & 2. TSM concentration at Station L4 was below 1 mg/l and Stations MF and BP about 3-4 mg/l. The variation in replicates between labs varied from 28 to 33% for L4, from 4% to 15% for MF and 9 to 25% for BP. The total % variation of the 9 replicates was highest for L4 (34%) and 15% for MF and BP.

For the individual stations, GKSS showed 45 % higher values than NIVA and PML for L4 and PML had 19 % lower values than GKSS and NIVA for MF. For station BP the differences was negligible. All labs had outliers at one or more stations (Fig 1 & 2).

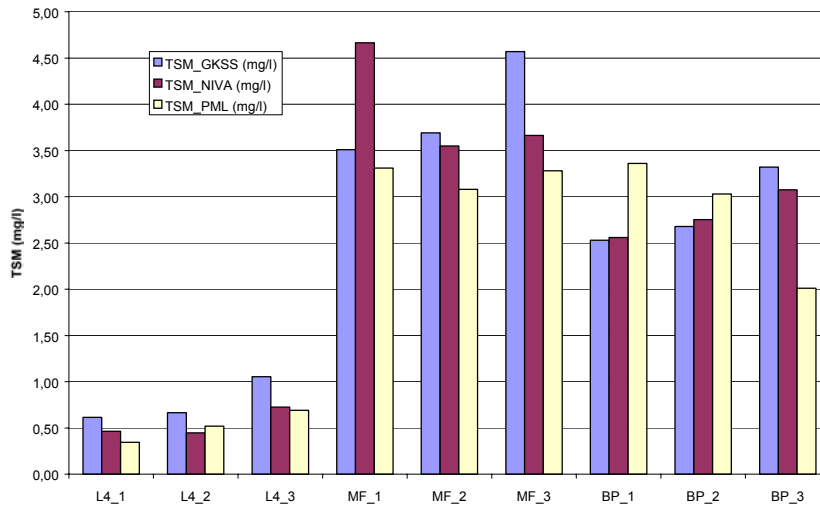
Table 8. Results from TSM test on natural water samples for all the three labs.

Station	Replicate	GKSS (mg/l)	NIVA (mg/l)	PML (mg/l)
L4	1	0,62	0,46	0,35
L4	2	0,67	0,45	0,52
L4	3	1,06	0,73	0,69
MF	1	3,51	4,67	3,31
MF	2	3,69	3,55	3,08
MF	3	4,57	3,66	3,28
BP	1	2,53	2,56	3,36
BP	2	2,68	2,75	3,03
BP	3	3,32	3,08	2,01

Table 9. Mean and % standard deviation for all the labs and for the overall for all labs.

	Station	GKSS	NIVA	PML	Overall
Mean (mg/l)	L4	0,78	0,55	0,52	0,61
% St.dev	L4	31,0 %	28,6 %	33,3 %	33,9 %
Mean (mg/l)	MF	3,92	3,96	3,22	3,70
% St.dev	MF	14,5 %	15,5 %	3,9 %	15,0 %
Mean (mg/l)	BP	2,84	2,80	2,80	2,81
% St.dev	BP	14,8 %	9,3 %	25,1 %	15,3 %

Figure 27. Comparison of Total Suspended Matter between GKSS, NIVA & PML in water samples taken at L4, Mayflower (MF) and Barnpool (BP). Three replicates were analyzed per station.



In addition to the inter-comparison carried out during the June workshop, further inter-comparisons were conducted during the field campaign BG2002-14 (16 – 20 June 2002) between PML and MUMM. Four replicate samples (three samples + one blank) were determined at 17 stations. 91 % of the variation between laboratories could be explained (Fig 29) and overall there was a 24 % difference in station means.

Figure 28. As Fig 27 but average total suspended material concentrations. The average standard error was $\pm 15\%$ around the mean of the three laboratories.

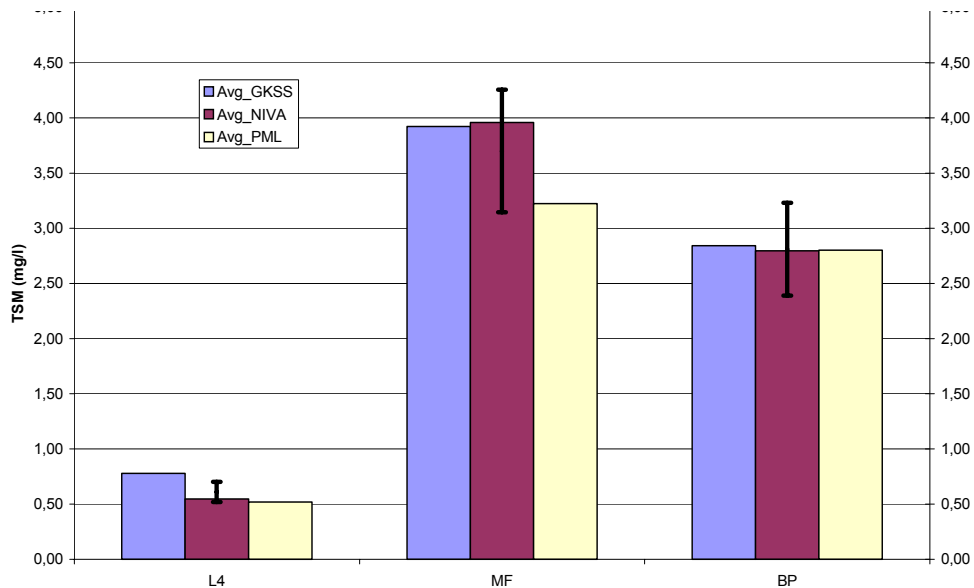
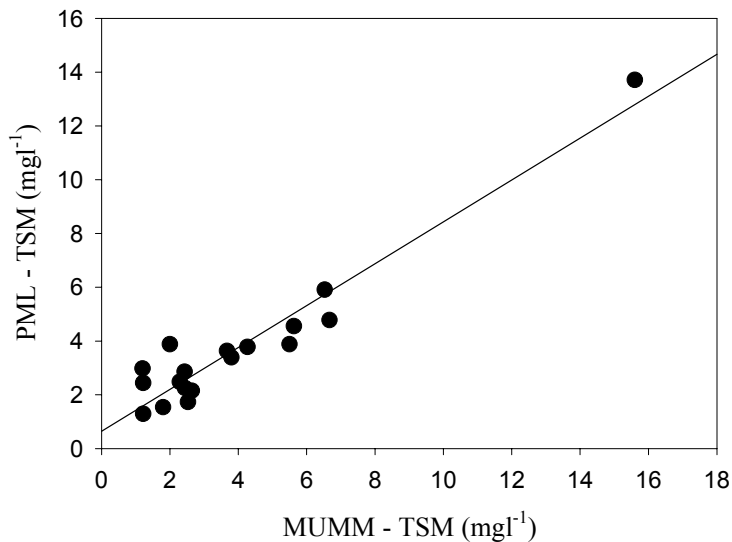


Fig 29. Comparison of TSM concentrations (mg/l) from North Sea samples (Transect: Ostende to Harwich) determined by MUMM & PML on cruise BG2002-14.



Artificial samples

The results from the experiment with Formazin and clay are given in Tables 3 & 4). The test with Formazin in distilled water showed a low variation both within ($< 6\%$) and between (7%) laboratories. For both the test (B and C) in seawater the variation

increased to between 6 and 24 % for the individual labs and to 20 % for all the labs. The data indicates that rinsing may be the main problem in determining TSM concentrations and that the rinsing procedure is still insufficient to reduce the variation between laboratories.

During filtration of PML samples A (J), the beaker and the funnel were also rinsed, which may explain why these results are higher than the PML samples A (K). However, compared with GKSS & NIVA the PML were 6.5% lower, indicating that the rinsing of the funnel and beaker does not explain the difference between labs. The differences between labs for artificial samples were small compared to the error found for the sea water samples (Table 9 & 10).

Table 10. Results from the TSM test with Formazin in distilled water (A) and in seawater (B) as well as the test with clay mineral (C) in seawater.

Sample A - Formazin in distilled water		Sample B - Formazin in seawater		Sample C - Clay mineral in sea water	
Sample-Lab filter- Filtered by	TSM (mg/l)	Sample-Lab filter - Filtered by	TSM (mg/l)	Sample-Lab filter - Filtered by	TSM (mg/l)
A1-GKSS (K)	5,60	B1-GKSS (K)	7,93	C1-GKSS (K)	7,80
A2-GKSS (K)	5,30	B2-GKSS (K)	6,93	C2-GKSS (K)	7,17
A3-GKSS (K)	5,37	B3-GKSS (K)	6,80	C3-GKSS (K)	8,53
A1-NIVA (K)	5,20	B1-NIVA (K)	5,74	C1-NIVA (K)	8,31
A2-NIVA (K)	5,54	B2-NIVA (K)	5,08	C2-NIVA (K)	8,56
A3-NIVA (K)	5,37	B3-NIVA (K)	4,32	C3-NIVA (K)	9,35
A1-PML (K)	4,57	B1-PML (K)	5,93	C1-PML (K)	9,90
A2-PML (K)	4,93	B2-PML (K)	5,23	C2-PML (K)	7,87
A3-PML (K)	4,70	B3-PML (K)	8,20	C3-PML (K)	11,53
A1-PML (J)	5,07	B1-PML (J)	6,00	C1-PML (J)	6,43
A2-PML (J)	5,33	B2-PML (J)	4,87	C2-PML (J)	5,17
A3-PML (J)	4,73	B3-PML (J)	6,43	C3-PML (J)	6,53

Table 10. Mean and standard deviation (%) for sample A, B and C and overall.

Mean and % stdev sample A	TSM (mg/l)	Mean and % stdev sample B	TSM (mg/l)	Mean and % stdev sample C	TSM (mg/l)
Mean A GKSS	5,42	Mean B GKSS	7,22	Mean A GKSS	7,83
%Stdev A GKSS	2,89	%Stdev B GKSS	8,58	%Stdev A GKSS	8,73
Mean A NIVA	5,37	Mean B NIVA	5,05	Mean A NIVA	8,74
%Stdev A NIVA	3,10	%Stdev B NIVA	14,15	%Stdev A NIVA	6,20
Mean A PML (K)	4,73	Mean B PML (K)	6,46	Mean A PML (K)	9,77
%Stdev A PML (K)	3,92	%Stdev B PML	24,02	%Stdev A PML (K)	18,81
Mean A PML (J)	5,04	Mean B PML (J)	5,77	Mean A PML (J)	6,04
%Stdev A PML (J)	5,96	%Stdev B PML (J)	14,03	%Stdev A PML (J)	12,60
Mean overall sample A	5,14	Mean overall sample B	6,12	Mean overall sample C	8,10
%Stdev overall sample A	6,63	%Stdev overall sample B	19,53	%Stdev overall sample C	21,03

Figure 30. Total suspended matter of Formazin in distilled water.

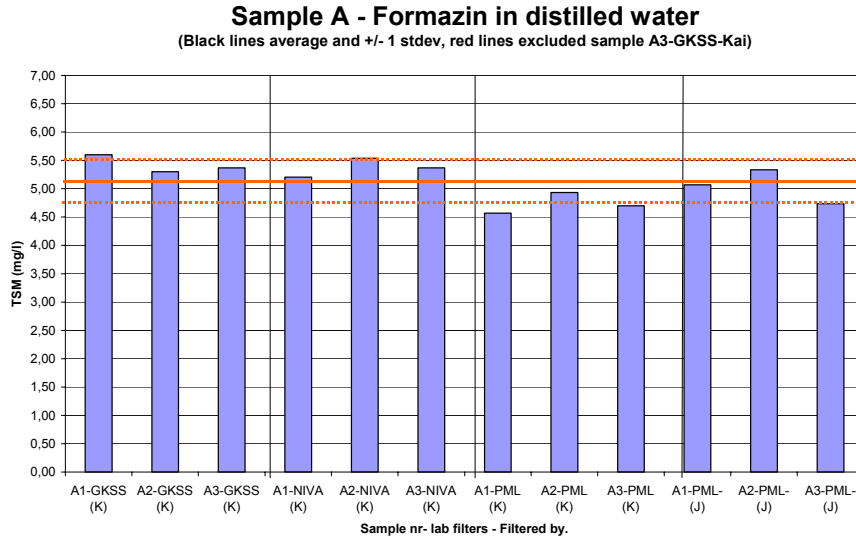


Figure 31. Total suspended matter of Formazin in seawater.

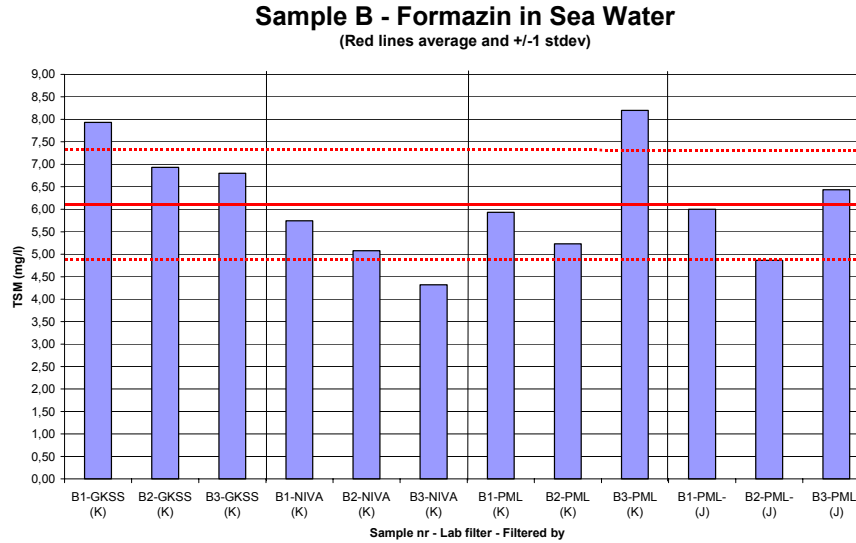
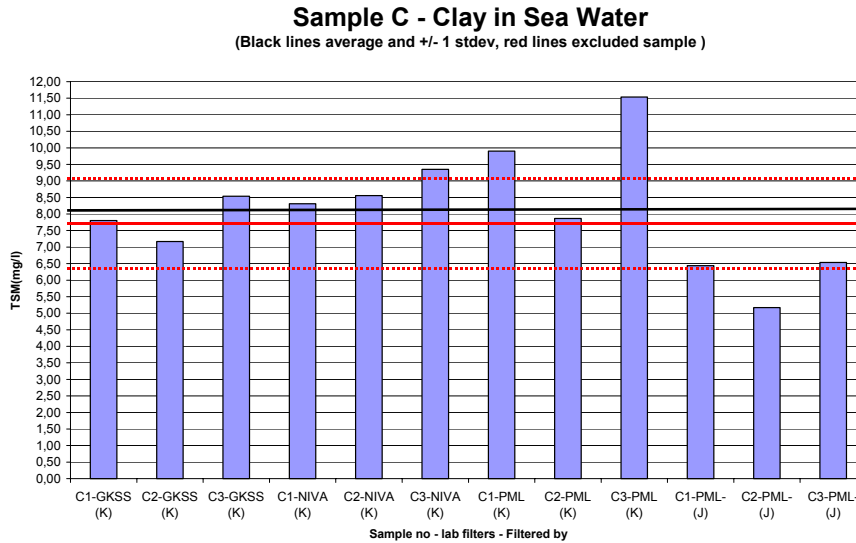


Figure 32. Total suspended matter of Clay in seawater.



Conclusions and recommendations

The inter-comparison indicates that the rinsing technique still may lead to discrepancies between laboratories. Further improvements of the rinsing technique are necessary which should include the rinsing of the filtration apparatus. For artificial water samples the error was < 10 % (5 % with triplicate samples), but for natural seawater samples the error was 15-20 % and up to 30% for samples below 1 mg of suspended material per filter. Due to the fact that the error of salt in the filters is the main problem in accurate determination of TSM concentrations, it is not possible to discriminate the other errors caused by analytical differences between the labs.

To discriminate between random and systematic errors in such an inter-comparison we recommend the same methods used in the MAVT chlorophyll-a inter-comparison (Sørensen et al. 2003). Formazin in water can be used as standard for quality procedures in determining TSM concentrations.