Joint European Research Infrastructure network for Coastal Observatories

Uncertainty estimation for temperature, salinity & chlorophyll-a

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2. Executive summary

This document constitutes Deliverable 5.5 of the JERICO project. It is intended to furnish members of the JERICO community with a basic understanding of how to proceed when attempting to establish measurement uncertainty for marine temperature, salinity and chlorophyll-a sensors. The document presents descriptions of the three measurands from a metrological standpoint, and discusses the approaches that could be taken to prepare uncertainty budgets for relevant sensors with some suitable examples and useful advice.

3. Introduction

The estimation of the uncertainty associated with the results of a measurement is an objective way to numerically depict the trustworthiness of those results. It is, therefore, a crucial part of the measuring process.

Any measured value can be considered complete only if accompanied by a relative estimate of uncertainty. However, the latter characteristic is rarely discussed in marine observing circles and in the marine data management community despite its intimate link to sensor performance, data quality and data usability issues. This disregard arises from ignorance concerning the rigor required of modern measuring activity and the complexity of the underlying metrological system supporting it.

There is a pressing need to begin to address this state of affairs, and the present publication, intended as a guidance document for members of the JERICO community, is a first step. The document deals with outlining a possible approach to determining uncertainty for sensor measurements of seawater temperature, salinity and chlorophyll-a. The approach is based on the generally accepted methodology for uncertainty evaluations given in the BIPM (Bureau International des Poids et Mesures) publication “Evaluation of measurement data - Guide to the expression of uncertainty in measurement”, commonly referred to as the GUM (2008).

In all three cases, the conceived blueprint for action is based on the following topical cornerstones: the specification of the measurand, the descriptions of the realized quantity and the relative reference value, and finally, the identification of the uncertainty components and the quantification of the uncertainty.

The present document is intended to be used in conjunction with the GUM, which continues to remain the master reference document for the evaluation of uncertainty in measurement at this time.

4. Main Report

4.1 Determining uncertainty: general considerations

A proper assessment of uncertainty can only be performed in relation to a clearly defined measurand and an ascertainable realized quantity, which implicitly entails operating in a controllable environment such as a suitably-equipped laboratory. Generally speaking, the infrastructure and operating environment required for uncertainty assessments are very similar to those that are needed for sensor calibrations. With the resources on hand, a series of stable measurement set-points covering the device's operational range are generated. At each set-point, sensor and reference readings are taken and confronted. The total uncertainty inherent in the reference measurements must be sufficiently low with respect to that associated with the sensor readings (established experimentally or on the basis of the sensor's declared specifications) to permit an unambiguous comparison, and therefore, a successful assessment. All known influence quantities must be measured and, if necessary, accounted for in the final uncertainty estimation. The possible effect of any significant adjustment employed to correct the sensor measurement results on the uncertainty must also be handled. All the relevant information must be presented in an "uncertainty budget", a conventionally-used tabular form of expression of the results of uncertainty estimations. Uncertainty budgets can be very elaborate. The level of detail will depend on the number of sources necessitating attention to achieve a final estimate of the uncertainty that satisfies the requirements of the sensor evaluation and can be experimentally verified under repeatability conditions.

4.2 Determining uncertainty: temperature

4.2.1 The measurand

The present definition of measured temperature is based on the International Temperature Scale of 1990 (ITS-90), currently the best available approximation to thermodynamic temperature (T). The unit of measure is the Kelvin, (K), specified as the fraction 1/273.16 of the thermodynamic temperature of the Triple Point of Water (TPW). However, it is common practice to report seawater temperature according to the Celsius scale (t), with the unit of "degree Celsius" (°C); t = T - 273.15. The TPW (0.0100 °C) is the most critical ITS-90 fixed point in resistance thermometry, the reference measuring technique most frequently employed in the range of seawater temperature measurements. The other relevant ITS-90 fixed points are the Triple Point of Mercury (TPHg = - 38.8344), the Melting Point of Gallium (MPGa = 29.7646) and the Freezing Point of Indium (FPIn = 156.5985). The TPW and the MPGa are the two main ITS-90 temperature reference points in the temperature range 0 °C - 30 °C.

4.2.2 The realized quantity and the reference value

The sensor to be evaluated is immersed in a thermostatic temperature calibration bath filled with seawater in a climate-controlled laboratory or facility. The bath is cycled down through the complete seawater temperature range in step changes from high to low temperatures in order to provide measurement set-points where sensor readings and comparable reference temperature values are acquired (Figure 1).

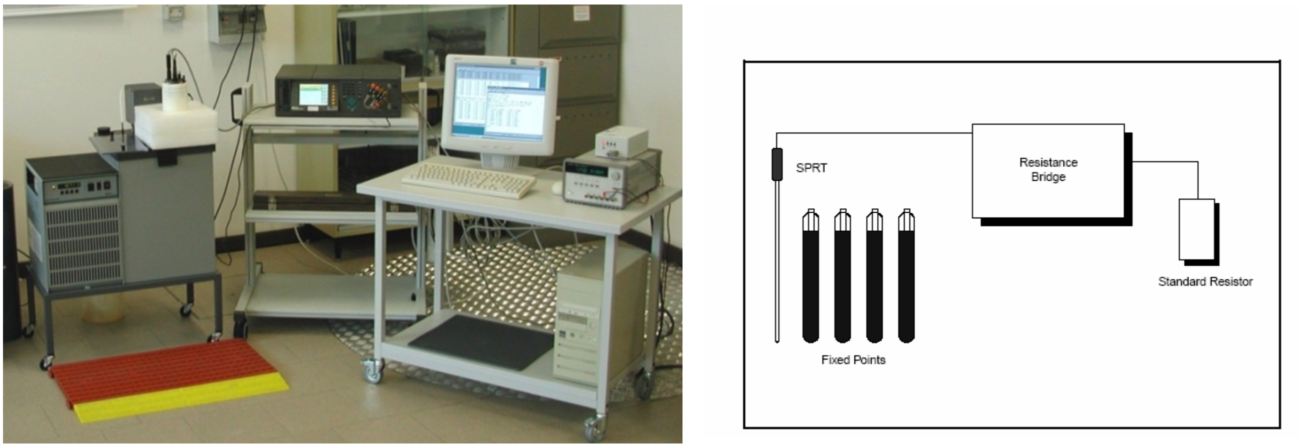
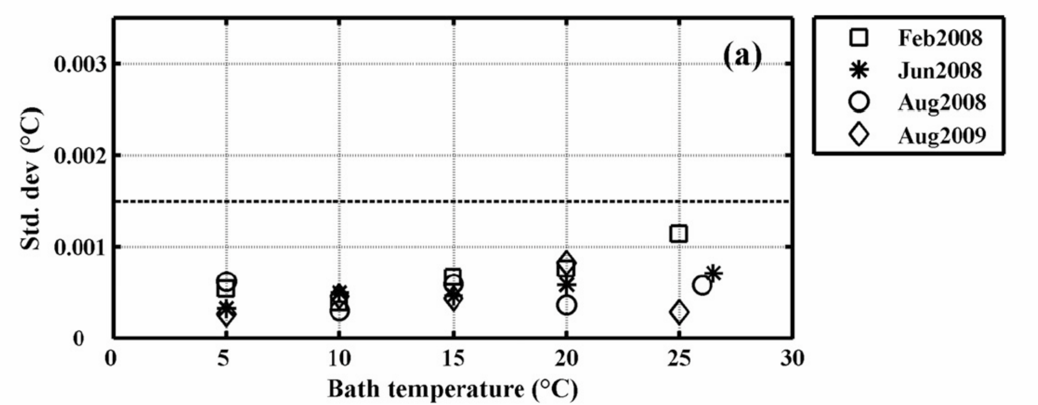


Figure 1. An example of a setup for uncertainty assessments of a temperature sensor consisting of a thermostatic bath and a reference measurement system (left); scheme of a temperature reference system using ITS-90 fixed points (right).

The repeatability and reproducibility of the calibration bath (Figure 2) and the SPRT (not shown) must be well-established *a priori*.



Source: Medeot, et. al., 2011.

Figure 2. Plot showing the variability (reported as standard deviations) of a commercial temperature calibration bath at different set-point temperatures over a 19 month period between February 2008 and August 2009; the dashed line indicates the combined standard uncertainty of the temperature measurements, which were made with a reference Standard Platinum Resistance Thermometer.

At each temperature set-point, a reference temperature value is estimated from a set of readings made using a calibrated Standard Platinum Resistance Thermometer (SPRT), the only acknowledged ITS-90 interpolating instrument, coupled with an AC or DC precision thermometry bridge. In principle, reference temperature measurements could be acquired using internal transfer standards (for example, another temperature sensor) in lieu of a SPRT, provided traceability to appropriate ITS-90 primary standards has been established and the quality of readings are compatible with the degree of uncertainty required for the assessment of the sensor in question. The temperature calibration bath should be allowed to settle at a measurement set-point for a sufficient period of time (an hour or more) before sampling is initiated. During the sampling interval, the stability of the bath should be continuously monitored and ambient temperature, barometric pressure and humidity must be recorded.

4.2.3 The uncertainty budget

A very straightforward uncertainty budget for a reference SPRT is presented in Table 1, below.

Temperature (ITS-90)				
Uncertainty sources	**Manufacturer's specification**	**Assumed probability distribution**	**Observed**	**Standard Uncertainty**
Temperature bath stability	0.002 °C	Triangular	---	0.0008 °C
Temperature bath uniformity	0.002 °C	Triangular	---	0.0008 °C
SPRT stability (at the Triple Point of Water)	---	---	0.0005 °C/year (2003 - 2010)	0.0005 °C
Precision Digital Thermometer accuracy	0.0015 °C	Rectangular	---	0.0009 °C
Combined standard uncertainty				0.0015 °C
Expanded Uncertainty (k = 2)				0.0030 °C

Source: Medeot, et. al., 2011.

Table 1. A simple uncertainty budget for reference calibration bath temperature measurements obtained with a Standard Platinum Reference Thermometer (SPRT).

A more detailed budget of an SPRT fixed-point calibration could look like the one shown in Table 2.

			TPAr	MPHg	TPW	FPSn	FPZn
Uncertainty sources	**Type**	**Distribution**	**mK**	**mK**	**mK**	**mK**	**mK**
Process variability	A	Normal	0.30	0.20	0.20	0.30	0.50
Measurement precision	A	Normal	0.02	0.02	0.02	0.04	0.06
Fixed-point cell temperature	B	Normal	0.087	0.110	0.035	0.250	0.300
Self-heating correction	B	Rectangular	0.006	0.006	0.006	0.012	0.012
Hydrostatic head correction	B	Normal	0.021	0.021	0.006	0.006	0.008
Non-ideal immersion	B	Normal	0.087	0.009	0.000	0.002	0.014
RTPW error propagation	B	Normal	0.021	0.085	0.000	0.189	0.257
Shunt losses	B	Rectangular	0.000	0.000	0.000	0.000	0.000
1595A linearity	B	Normal	0.008	0.018	0.008	0.041	0.059
Reference resistor stability	B	Rectangular	0.003	0.012	0.014	0.029	0.042
Total (k=2):			0.65	0.49	0.41	0.88	1.29

Source: Fluke Calibration,

Table 2. An elaborate uncertainty budget of a Standard Platinum Reference Thermometer (SPRT) fixed-point calibration; “RTPW” denotes the resistance at the Triple Point of Water and “1595A linearity” refers to the linearity of the resistance bridge apparatus used with the SPRT to make the temperature measurements.

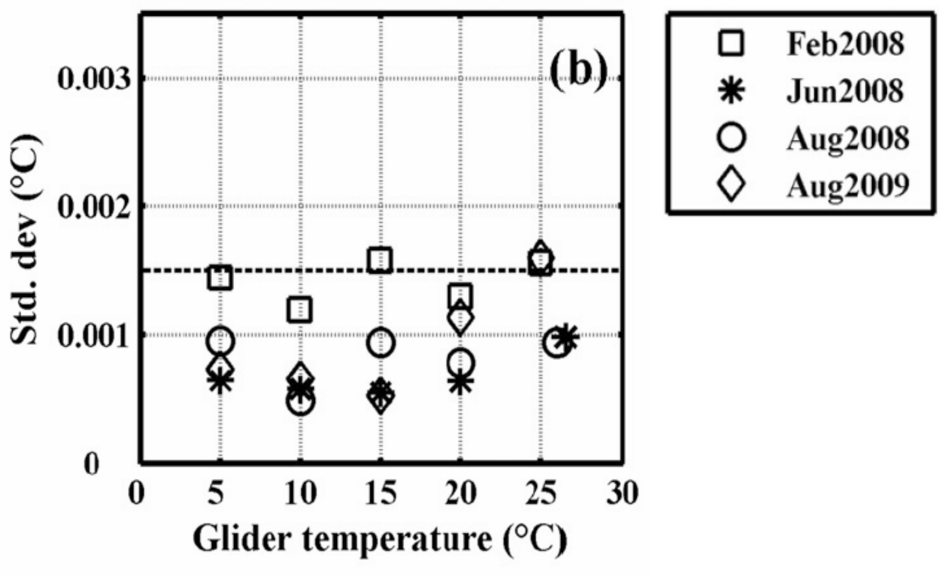
Table 3 provides an example of an uncertainty budget for a temperature sensor.

Table 3. An exhaustive uncertainty budget for a temperature sensor; “UUT” stands for Unit under Test, i.e., the sensor in question, and “SPRT” indicates the Standard Platinum Resistance Thermometer used for making the reference temperature measurements.

			-80 °C	-40 °C	0 °C	100 °C	200 °C
Uncertainty sources	**Type**	**Distribution**	**mK**	**mK**	**mK**	**mK**	**mK**
Process variability	A	Normal	1.8	1.3	1.0	2.2	2.6
UUT precision	A	Normal	0.3	0.3	0.3	0.3	0.3
Reference SPRT precision	A	Normal	0.3	0.3	0.3	0.3	0.3
Reference SPRT calibration	B	Normal	0.5	0.4	0.3	0.6	0.8
Reference SPRT drift	B	Rectangular	0.5	0.7	0.9	1.2	1.6
Measurement of SPRT	B	Normal	0.1	0.1	0.1	0.1	0.2
Measurement of UUT	B	Normal	0.4	0.5	0.6	0.9	1.2
Bath uniformity	B	Rectangular	1.2	1.2	0.9	1.2	1.2
Immersion error – SPRT	B	Rectangular	0.0	0.0	0.0	0.0	0.0
Immersion error – UUT	B	Rectangular	0.0	0.0	0.0	0.0	0.0
Repeatability of the UUT	B	Rectangular	0.8	3.7	4.3	6.0	8.2
Total (k=2):			**4.9**	**8.4**	**9.4**	**13.5**	**18.0**

Source: Fluke Calibration,

Figure 3 graphically depicts the standard uncertainties associated with a glider temperature sensor over consecutive evaluations at different temperature set-points between 0 °C and 30 °C.



Source: Medeot. et. al.. 2011.

Figure 3. Type A standard uncertainties characterizing a glider temperature sensor at different measurement set-points over a 19 month period between February 2008 and August 2009; the dashed line indicates the combined standard uncertainty of the reference temperature measurements, which were made with a Standard Platinum Resistance Thermometer (SPRT) coupled with a precision thermometry bridge.

4.3 Determining uncertainty: salinity

4.3.1 The measurand

Salinity is presently characterized as “Absolute Salinity”, a precisely defined measure of the absolute salinity with units of g kg^{-1} (i.e., a true mass fraction). The use of Absolute Salinity (capitalized), denoted by S_A, is in force since the recent adoption of the Thermodynamic Equation of Seawater - 2010 (TEOS-10). Numerically, the S_A of a seawater sample represents, to the best available accuracy (and with certain caveats), the mass fraction of dissolved solute in so-called Standard Seawater with the same density as that of the sample. Standard Seawater (or SSW) is seawater with a distinct composition, obtained from a reference material (IAPSO Standard Seawater) by adding pure water or removing pure water by evaporation.

Routine measurements of salinity are referred to SSW and, despite the transition to TEOS-10, will continue to be reported on the Practical Salinity Scale of 1978 (PSS-78). In the formulation of PSS-78, “the Practical Salinity, symbol S, of a sample of seawater, is defined in terms of the ratio K_{15} of the electrical conductivity of the seawater sample at the temperature of 15 °C and the pressure of one standard atmosphere, to that of a potassium chloride (KCl) solution, in which the mass fraction is 32.4356×10^{-3}, at the same temperature and pressure. The K_{15} value exactly equal to 1 corresponds, by definition, to a Practical Salinity exactly equal to 35” (Unesco 1981). In TEOS-10, the Practical Salinity S is denoted by S_P, and is related to S_A through another salinity variable, S_R, called the Reference-Composition Salinity (or Reference Salinity, for short), according to the simple formulas:

$$S_R = (35.16504/35)\ \mathrm{g\ kg}^{-1} \times S_P;$$

$$S_A = S_R + \delta S_A \text{ (where } \delta S_A \text{ is a correction factor).}$$

4.3.2 The realized quantity and the reference value

Generally, instruments measuring salinity do so by deriving them from in situ readings of conductivity, temperature and pressure, and report resulting values on the PSS-78. The experimental setup for assessing the uncertainty in salinity measurements made with such devices is similar to the one shown in Figure 1 in the previous section. As before, the sensor to be evaluated is immersed in a thermostatic temperature calibration bath filled with seawater in a climate-controlled laboratory or facility. The bath is brought to some convenient constant temperature and allowed to settle. Temperature, conductivity and, if pertinent, pressure readings are made with the unit under test in concomitance with a reference temperature measurement. A corresponding reference conductivity value is obtained by inverting the measured salinity from a bath water sample collected immediately after the reference and instrument recordings are completed. The salinity determination is usually carried out using a Laboratory Salinometer, standardized with IAPSO Standard Seawater.

The procedure can be repeated more than once, and for different salinities. The salinity (or salinities) of the seawater used in the bath for an assessment should be adequately representative of the range of values encountered by the instrument for the parameter when it is being used. During a sampling interval, the stability of the bath should be continuously monitored and ambient temperature, barometric pressure and humidity must be recorded.

4.3.3 The uncertainty budget

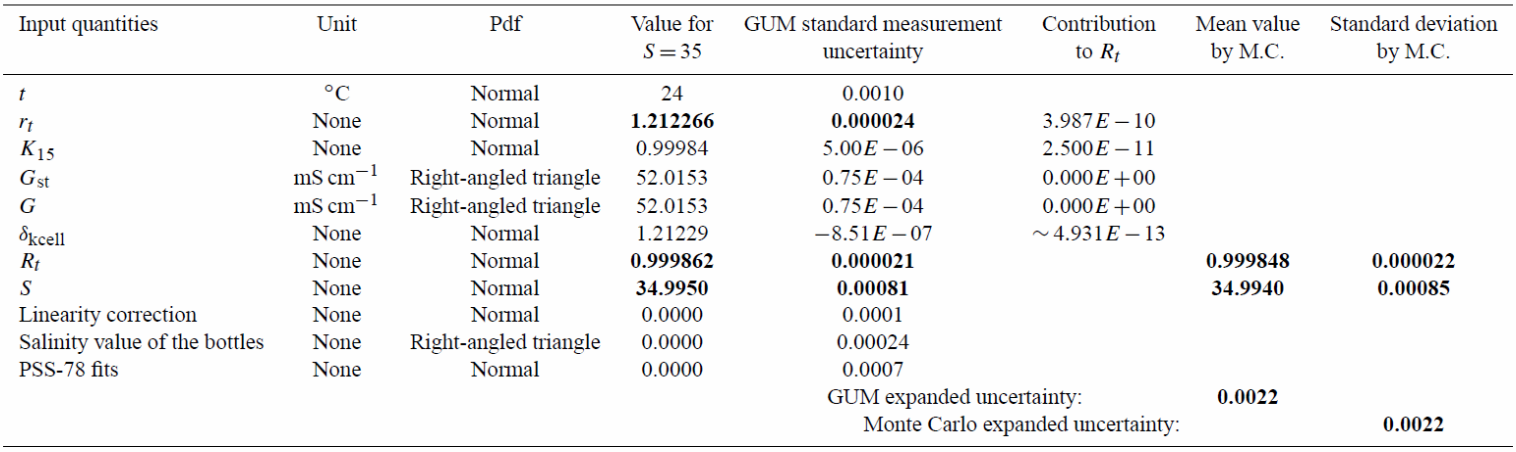
A very straightforward uncertainty budget for a reference salinity determination is presented in Table 4, below.

Conductivity				
Uncertainty sources	**Manufacturer's specification**	**Assumed probability distribution**	**Estimated**	**Standard Uncertainty**
Salinometer accuracy	0.002 (PSS)	Triangular	---	0.0008 (PSS)
Reference temperature measurement	---	---	0.0015 °C	0.0015 °C
Combined standard uncertainty				0.00017 Sm^{-1}
Expanded Uncertainty (k = 2)				0.00034 Sm^{-1}

Source: Medeot, et. al., 2011.

Table 4. A simple uncertainty budget for reference salinity measurements obtained with a Guildline 8400B “Autosal” Laboratory Salinometer.

A more detailed budget for reference salinity measurements could look like the one shown in Table 5.

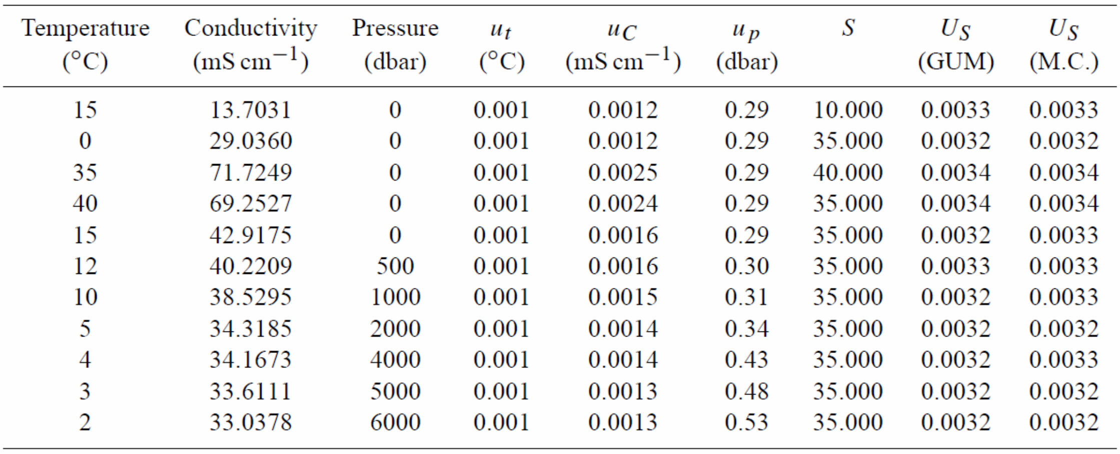


Input quantities	Unit	Pdf	Value for $S=35$	GUM standard measurement uncertainty	Contribution to R_t	Mean value by M.C.	Standard deviation by M.C.
t	°C	Normal	24	0.0010			
r_t	None	Normal	**1.212266**	**0.000024**	$3.987E-10$		
K_{15}	None	Normal	0.99984	$5.00E-06$	$2.500E-11$		
G_{st}	$\mathrm{mS\,cm^{-1}}$	Right-angled triangle	52.0153	$0.75E-04$	$0.000E+00$		
G	$\mathrm{mS\,cm^{-1}}$	Right-angled triangle	52.0153	$0.75E-04$	$0.000E+00$		
δ_{kcell}	None	Normal	1.21229	$-8.51E-07$	$\sim 4.931E-13$		
R_t	None	Normal	**0.999862**	**0.000021**		**0.999848**	**0.000022**
S	None	Normal	**34.9950**	**0.00081**		**34.9940**	**0.00085**
Linearity correction	None	Normal	0.0000	0.0001			
Salinity value of the bottles	None	Right-angled triangle	0.0000	0.00024			
PSS-78 fits	None	Normal	0.0000	0.0007			
				GUM expanded uncertainty:		**0.0022**	
					Monte Carlo expanded uncertainty:		**0.0022**

Source: Le Menn,

Table 5. An elaborate uncertainty budget for reference salinity measurements made with a Guildline Portasal Salinometer at S (PSS) = 35, showing the expanded uncertainty (k = 2) estimated using the GUM (“Guide to the expression of uncertainty in measurement”) and M.C (Monte Carlo) methods.

Table 6 indicates the kind of uncertainties that could be associated with salinity observations obtained from measurements of temperature, conductivity and pressure sensors.

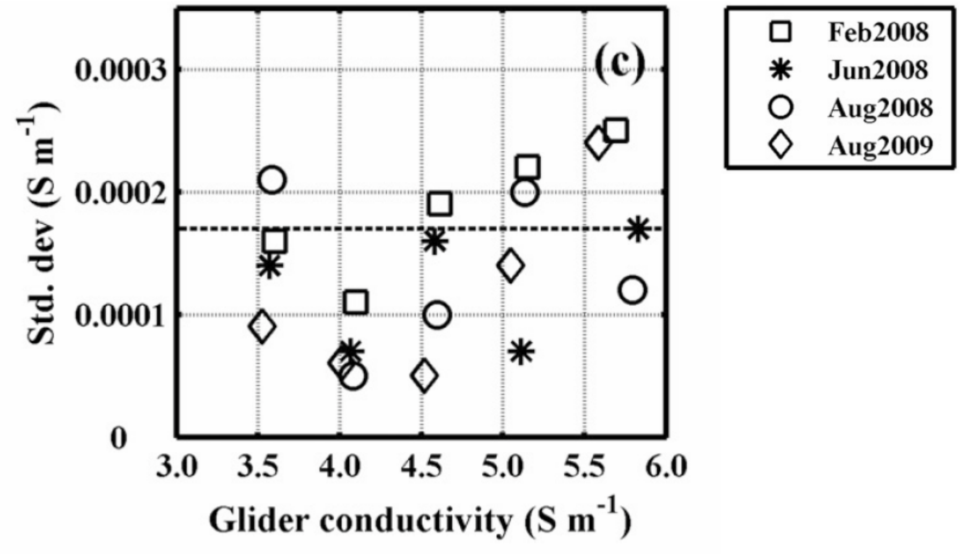


Temperature (°C)	Conductivity (mS cm^{-1})	Pressure (dbar)	u_t (°C)	u_C (mS cm^{-1})	u_p (dbar)	S	U_S (GUM)	U_S (M.C.)
15	13.7031	0	0.001	0.0012	0.29	10.000	0.0033	0.0033
0	29.0360	0	0.001	0.0012	0.29	35.000	0.0032	0.0032
35	71.7249	0	0.001	0.0025	0.29	40.000	0.0034	0.0034
40	69.2527	0	0.001	0.0024	0.29	35.000	0.0034	0.0034
15	42.9175	0	0.001	0.0016	0.29	35.000	0.0032	0.0033
12	40.2209	500	0.001	0.0016	0.30	35.000	0.0033	0.0033
10	38.5295	1000	0.001	0.0015	0.31	35.000	0.0032	0.0033
5	34.3185	2000	0.001	0.0014	0.34	35.000	0.0032	0.0032
4	34.1673	4000	0.001	0.0014	0.43	35.000	0.0032	0.0033
3	33.6111	5000	0.001	0.0013	0.48	35.000	0.0032	0.0032
2	33.0378	6000	0.001	0.0013	0.53	35.000	0.0032	0.0032

Source: Le Menn, 2011.

Table 6. An example showing the expanded combined uncertainties (k = 2) for salinity estimated using the GUM ("Guide to the expression of uncertainty in measurement") and M.C (Monte Carlo) methods, computed with representative values of temperature, conductivity and pressure and their combined standard uncertainties.

Figure 4 graphically depicts the standard uncertainties associated with a glider conductivity sensor over consecutive evaluations at different conductivity set-points between 3.0 S m^{-1} and 6.0 S m^{-1}.



Source: Medeot, et. al., 2011.

Figure 4. Type A standard uncertainties characterizing a glider conductivity sensor at different measurement set-points over a 19 month period between February 2008 and August 2009; the dashed line indicates the combined standard uncertainty of the reference conductivity values, which were obtained from salinity measurements made with a Guildline 8400B "Autosal" Laboratory Salinometer.

4.4 Determining uncertainty: chlorophyll a

4.4.1 The measurand

Presently, the most widely-employed measuring technique used in field sensors of chlorophyll a (Chl-a) is based on fluorescence determinations. Chl-a naturally absorbs blue light (peak absorption at ~438 nm) and emits, or fluoresces, red light (at around 685 nm). Generally, the intensity of this fluorescence ($F_{Chl\text{-}a}$) is directly proportional to the concentration of the pigment, which is utilized as an indicator of phytoplankton biomass.

Unfortunately, the relationship between $F_{Chl\text{-}a}$ and analytically measured Chl-a is not unequivocal. The former can be affected by many factors. Some of these factors are inherent to the biochemistry and physiology of phytoplankton at the cellular level, and others are related to their communal and ecological characteristics during measurement.

Furthermore, the measurement of $F_{Chl\text{-}a}$ is a comparative one. Sensor readings can be reported as output voltages (of the detector), counts (after analog-to-digital conversion of output signals) or units like RFU (Relative Fluorescence Units) and AU (Arbitrary Units), depending on the way the output is scaled. Some sensors give values in $\mu g\ L^{-1}$, but this is merely an expression of their outputs in terms of the concentration scale imposed during factory calibrations using some specific fluorophore.

Thus, $F_{Chl\text{-}a}$ is a hard measurand to define, making it a difficult variable to handle from a metrological perspective.

4.4.2 The realized quantity and the reference value

Experimental setups for uncertainty determinations of fluorescence-based Chl-a sensors can be modelled on their laboratory calibration schemes. However, it must be noted that such schemes can vary greatly from operator to operator (for examples, see Figure 5) as internationally-accepted standard protocols have still not been redacted for this activity.

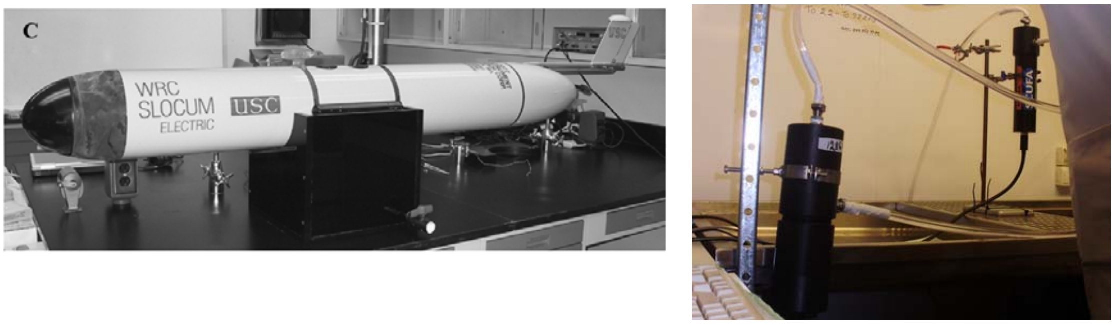


Figure 5. Two calibration setups for chlorophyll-a (fluorescence) sensors.

4.4.3 The uncertainty budget

The ambiguity of the variable, the diversity of possible evaluation setups, the lack of standardized procedures, and the extensive sensor-to-sensor differences encountered, make uncertainty determinations of $F_{Chl\text{-}a}$ sensors an arduous task. Any uncertainty budget that is formulated will be specific to the conditions and particularities of the assessment itself. Therefore, the conditions and method used to generate the fluorescence signal during the uncertainty evaluation must be clearly described, and all significant influence quantities must be carefully identified and accounted for. Similarly, the method used to obtain the reference readings must be specified, and the associated uncertainty established and documented. Some of the main factors whose effects need to be considered in uncertainty assessments of $F_{Chl\text{-}a}$ sensors are listed in table 7.

Factors		
Instrumental	**Matrix-related**	**Analyte-related**
Temperature	Temperature	Quenching
Calibration	Turbidity	Photochemical decay
Linearity	pH	Stability
Sensitivity	Stability	
Specificity		

Table 7. Some significant factors that can affect uncertainty assessments of $F_{Chl\text{-}a}$ sensors.

5. Conclusion

This report addresses uncertainty estimations as they relate to sensors used for measuring the following seawater variables: temperature, salinity and chlorophyll-a. Sensors for the first two variables are comparatively easy to handle. Sensors for chlorophyll-a, on the other hand, are more difficult to deal with, and it is hard to present detailed uncertainty budgets for them at the present time.

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