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## **SUBMITTED VERSION (PREPRINT):**

### **Uncertainty evaluation of CTD measurements: a metrological approach to water-column coastal parameters in the Gulf of La Spezia area**

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#### **Abstract**

The ENEA Marine Environment Research Centre of S. Teresa has been involved since the '70s in monitoring, analysis and comprehension of physical, chemical and biological processes in marine environment. The purpose of this work is to describe the recently-implemented metrological approach aimed at evaluating the uncertainty associated with measurements performed by a Conductivity-Temperature-Depth profiler (CTD) during routine coastal campaigns in the Eastern Ligurian Sea, close to the Gulf of La Spezia. Main effort of this work is focused on applying, to each involved parameter, the standard framework for uncertainty evaluation as prescribed by the Guide to the expression of uncertainty in measurement. To this aim, an appropriate uncertainty evaluation is performed by combining type A and B contributions, evaluated from experimental data obtained in reproducibility conditions and from calibration certificates periodically supplied by manufacturer, respectively. Concerning *in situ* measured practical salinity, probability density functions modelling water pressure, temperature and conductivity, from which salinity depends, are propagated by application of the Monte Carlo method for propagation of distributions, hence obtaining the salinity uncertainty.

*Keywords:* CTD probe, coastal monitoring, water-column parameters, uncertainty analysis

## 1. Introduction

The monitoring of chemical-physical parameters in coastal and marine areas is the prerequisite to achieve a Good Environmental Status (GES) [1] and a sustainable and integrated management of environmental resources, in line with both the objectives defined by the Marine Strategy Framework Directive in Europe [2] and the technical guidelines of Intergovernmental Oceanographic Commission in a global perspective [3,4]. Sea monitoring is especially essential in a climate change context: the analysis of long-term physical and chemical time series is the first step to support forecast models studying climate changes. To achieve this goal and study medium and long-term variability of marine ecosystems, it is imperative to evaluate the uncertainty associated with measurements performed in the sea, in order to assess their reliability. In this sense, a systematic metrological approach to marine measurements would be advantageous to develop a common database on which the marine observing system can be based. Actually, such approach needs a constant and effective cooperation between several actors, such as oceanographers, metrologists and instrument producers, each of them owning a specific expertise to be shared. Purpose of this work is the description of the metrological approach, recently implemented at the ENEA Marine Environment Research Centre of S. Teresa, aimed at evaluating the uncertainty associated with measurement results obtained by a well-characterized Conductivity-Temperature-Depth profiler [5] (in the following indicated as CTD, where the quantity depth is derived from the measured pressure), during routine coastal campaigns in the Eastern Ligurian Sea, close to the Gulf of La Spezia area (Fig. 1).

The monitored zone starts at the exit of La Spezia harbour and ranges from coastal areas under the influence of Magra River, at East, up to Cinque Terre National Park, at West, then extending to areas more similar to open sea (about 20 km off shore), for an overall surface of about 400 km<sup>2</sup>. Black dots in Fig. 1 indicate typical measurement stations where CTD profiler is lowered in order to perform a rapid, high-resolution vertical sampling on the water column, down to about 65 m water depth. Some views of both the probe and the experimental activity in field performed at ENEA Centre are shown in Fig. 2.

In this work, particular attention is paid to post-processing of the acquired data, i.e. the assessment of data reliability by evaluation of their combined standard uncertainty. As described in the following, the main effort is focused on applying, to each involved parameter, the standard framework for uncertainty evaluation as prescribed by the Guide to the expression of uncertainty in measurement [6]. To this aim, a typical table is elaborated and provided as a summary of all the uncertainty components contributing to the standard uncertainty of each quantity directly measured by the CTD probe. Type A and B contributions are evaluated from experimental data, measured in reproducibility conditions, and from calibration certificates, periodically supplied by the manufacturer, respectively. They are listed in the table together with the corresponding sensitivity coefficients, necessary for the output uncertainty calculation according to the law of uncertainty propagation. The combined standard uncertainty is then calculated and associated with the value of each quantity, together with the relevant degrees of freedom; hence, a corresponding expanded uncertainty can be also derived, encompassing a large fraction of the distribution of values reasonably

attributable to the measurand. As the last step, the standard uncertainty associated with the derived, *in situ* measured, practical salinity is calculated. In this case, since it is difficult to provide the partial derivatives of the non-linear model by which practical salinity derives from pressure, temperature and conductivity, its uncertainty is obtained as a by-product of the propagation of the probability distributions modelling pressure, temperature and conductivity, according to the Monte Carlo method for propagation of distributions described by [7].

## 2. Materials and Methods

In the following, an overview of CTD main features and uncertainty analysis method is described.

### 2.1. CTD profiler: main features

A CTD probe is a well-known, widespread and reliable multi-parameter instrument used to measure water-column quantities. Starting from direct measurements of (electrical) conductivity ( $C$ ), temperature ( $t$ ) and pressure ( $p$ ), to which depth ( $d$ ) is related, CTD profiler allows the determination of derived and relevant quantities like *in situ* measured practical salinity ( $S_p$ ). All these quantities, usually reported as profiles versus  $d$ , are of fundamental interest for oceanographers, forming the basis to study, interpret and modelling the interleaving and mixing processes along the water-column [5]. Main features of the CTD profiler currently used at ENEA are listed in the following, referring to proper huge literature [8-14] for a more detailed description of each transducer forming the multi-parameter probe:

- manufacturer: Sea-Bird Electronics (SBE),
- model: SBE 19plus SeaCAT Profiler,
- maximum deployment depth: 350 m,
- sampling rate of  $p$ ,  $t$  and  $C$  measures: 4 Hz,
- lowering speed from the ship: about 0.35 m/s.

CTD probe uses three independent channels to digitize  $p$ ,  $t$  and  $C$  concurrently: each channel converts the corresponding input analog signal into an output digital signal following a proper calibration curve pre-stored in the signal-conditioning unit installed on-board. Moreover, CTD is equipped with a proper TC-duct and pump that provide a constant flow rate through both the sensors (regardless of descent rate) in order to ensure that the measurement of  $t$  and  $C$  are made on the same parcel of water (so reducing spikes in the derived  $S_p$  due to the fact that  $t$  and  $C$  sensors are physically separated and characterized by different time responses). Main metrological features of  $p$ ,  $t$  and  $C$  transducers can be summarized as in Table 1 (where FSR indicates the full scale range of the instrument output). Profiles of  $t$  and  $C$  versus  $d$ , measured at each

station while CTD is descending, are firstly managed in accordance with the well-consolidated procedure of processing and quality control indicated by specific standards for analysis and validation of oceanographic data [3,15,16]: raw measures are therefore preliminarily processed by applying a five-points median low-pass filter to eliminate spikes and then  $t$  and  $C$  values are aligned in time relatively to  $p$  (or, equivalently, to  $d$ ). Finally, conductivity values are corrected for the cell thermal mass effect and upcast profiles, together with travelling backwards due to ship roll, are removed. Pre-processed data are then characterized in terms of their uncertainty in accordance with the current international metrological standard for the expression of uncertainty in measurement [6]: this type of analysis, that is the object of the next section, is applied to ENEA experimental direct measures of  $p$ ,  $t$  and  $C$  which vary typically in the following ranges: (0 to 65) dbar, (12 to 28) °C and (20 to 60) mS/cm, respectively. Corresponding values for *in situ* derived, dimensionless  $S_p$  are included in the interval (15.0 to 38.6) units on the practical salinity scale PSS-78 (for convenience here indicated as the well-known Practical Salinity Unit PSU [17]): the lowest limit of  $S_p$  values is associated to monitoring campaigns performed next to Magra River estuary.

## 2.2. Evaluation of uncertainty associated with CTD direct measurements of $p$ , $t$ and $C$

The standard uncertainty for  $p$  (and consequently  $d$ ),  $t$  and  $C$  quantities has been evaluated by compiling a corresponding uncertainty table where evidence is given to each uncertainty contribution, as prescribed by [6]. Analysis takes into account in a proper way both the uncertainty contributions declared (and periodically verified) by the manufacturer and those related to values measured on the field in repeatability conditions (with CTD profiler maintained at fixed depths for about 25 s for each measurement acquisition). Compiled tables for each involved quantity are reported in section 3 (Tables 2-4), where symbols have the following meaning:

- $X_i$ :  $i$ -th independent input quantity,
- $x_i$ : estimate of the  $i$ -th input quantity,
- SD: standard deviation,
- $u_A$ : type A standard uncertainty, i.e. estimated standard deviation evaluated from the statistical distribution of a series of measurement results,
- $u_B$ : type B standard uncertainty, i.e. the standard deviation of an assumed (*a-priori*) probability distribution, determined from calibration certificate data, experience or other information (in the present analysis, uniform distributions were typically assigned to those input quantities varying within ranges declared by the certificates),
- $\nu_i$ : degrees of freedom (DOF) of input uncertainty components (the value of 100 DOF is used when the quality of the information is considered “very funded”). If equal to infinity, the information has been obtained by datasheet or calibration certificate and consequently considered as very reliable,
- $u^2(x_i)$ : estimated variance (squared uncertainty) associated with input estimate  $x_i$ ,

- $c_i$ : sensitivity coefficients obtained from the mathematical model relating the output quantity to the input quantities,
- $c_i^2 \cdot u^2(x_i)$ : contribution to the output variance associated with the  $i$ -th input quantity,
- $u^4(y)/v_i$ :  $i$ -th contribution in the Welch-Satterthwaite formula, used to estimate the actual DOF of the output quantity  $y$ ,
- $u_c^2(y)$ : combined variance of the output quantity  $y$ ,
- $u_c(y)$ : combined standard uncertainty of the output quantity  $y$ ,
- $k$ : coverage factor calculated by the Student's  $t$ -distribution on the basis of both the chosen confidence level and the actual DOF,
- $U(y)$ : expanded uncertainty calculated as the product between  $k$  and  $u_c(y)$ .

In the following, specific considerations are provided for each involved quantity.

### 2.2.1. Pressure

With reference to Table 2, the total pressure  $p_{tot}$  measured by the CTD pressure sensor is by default corrected for the barometric offset  $p_{atm}$  of 14.7 psi (corresponding to about 1015 hPa); the correction is performed automatically by the CTD signal conditioning unit and should be verified by comparing the default value with the actual barometric value at sea level before deployment. In the evaluation of the uncertainty of  $p$ , the correctness of this offset has been verified by comparison with the historical atmospheric pressure mean  $p_{atm}$  acquired by a Vaisala-type analog barometer (mod. PTB101B) at ENEA S. Teresa Centre at an altitude of 49.5 m during the last 13 years (and normalized to sea level pressure by well-known formula [18]). The mean value of  $p_{atm}$  is  $(1015 \pm 7)$  hPa, being reasonably comparable with the default value implemented by SBE in the CTD unit. Further contributions to uncertainty connected to Vaisala barometer in measuring  $p_{atm}$  have been considered in Table 2. For both the input quantities  $p_{tot}$  and  $p_{atm}$  the uncertainty components due to calibration, stability, resolution and repeatability have been considered, respectively. For what concerns  $p_{atm}$  the components due to linearity, hysteresis and reproducibility have been taken into account, too.

### 2.2.2. Depth derived from pressure

The correct expression to calculate  $d$  as a function of  $p$  include some further terms [4], as follows:

$$d = f(p, Lat, \Psi, \Phi^0) \quad (1)$$

where  $Lat$ ,  $\Psi$  and  $\Phi^0$  are respectively the Latitude of the measuring station, the dynamic height anomaly ( $m^2 s^{-2}$ ) and the geopotential ( $m^2 s^{-2}$ ), both referred to zero sea pressure. Relationship (1) can be simplified by ignoring the two terms  $\Psi$  and  $\Phi^0$ : this approximation leads to a determination of  $d$  values affected by a relative standard uncertainty of about 0.1 %, as declared by [4]. The simplified formula here adopted to calculate  $d$  from  $p$  is the one reported in [11,17], valid for an ocean water column at 0 °C and with  $S_P$  equal to 35 PSU: ENEA data here analyzed (typically sampled at about 38 PSU and with higher values of  $t$ ) have

been verified to follow these conditions, belonging to the so-called "oceanographic funnel", as calculated by proper expression in [4]. Therefore, expression (1) can be simplified as follows:

$$d \approx f(p, Lat) = \alpha \cdot p \quad (2)$$

where  $\alpha \approx 0.992$  m/dbar is a correction factor determined by [17] where the Latitude value has been calculated at the centre of the typical ENEA sampling area (about 44.007°N). The  $\alpha$  factor can be considered as a constant for small depth profiles (as those considered in the present work, whose focus is actually on coastal monitoring campaign) up to 300 m (as reported in [5]).

In conclusion, taking into account the uncertainties of both  $p$  and  $\alpha$ , typical values of relative combined standard uncertainties for  $p$  and  $d$  are reported in the diagram in Fig. 5-a.

### 2.2.3. Temperature and conductivity

Differently from  $p$  and  $d$ , values of  $t$  and  $C$  are direct outputs of dedicated transducers in the CTD probe. Uncertainty evaluation, obtained following the scheme in Section 2.2, is reported in Tables 3 and 4, respectively; for both  $t$  and  $C$ , the uncertainty components due to calibration, stability, resolution and repeatability have been considered.

### 2.3. Evaluation of uncertainty associated with CTD indirect measurements: the case of *in situ* $S_P$

Although the recent adoption of absolute salinity [4], it is still strongly recommended that practical salinity  $S_P$  continues to be the salinity variable stored in data bases of research centres involved in sea monitoring, so maintaining the continuity with past measures as prescribed by PSS-78 [17,18]: this is due to the fact that  $S_P$  is considered as an (almost) directly measured quantity, closely related to measured values of *in situ* conductivity [19,20]. That said, practical salinity is defined as the conductivity ratio of the seawater sample at  $t_{68} = 15$  °C (where  $t_{68} = 1.00024 t$ , being  $t_{68}$  and  $t$  temperatures expressed following IPTS-68 and ITS-90 standards, respectively [13]) and  $p = 0$  dbar versus a standard potassium chloride (KCl) solution at the same temperature and pressure: this solution, characterized by a mass fraction of KCl equal to  $32.4356 \cdot 10^{-3}$  and a conductivity value  $C_0 = 42.914$  mS/cm, has a practical salinity value equal to 35 PSU by definition [4].

The calculation of  $S_P$  at oceanographic temperature and pressure is obtained by the following well-known expression [4,21], valid for  $2 < S_P < 42$ , where  $(p, t_{68}, C)$  are measured respectively in dbar, °C and mS/cm:

$$R = \frac{C(S_P, t_{68}, p)}{C(35, 15, 0)} = \frac{C}{C_0} = \frac{C(S_P, t_{68}, p)}{C(S_P, t_{68}, 0)} \frac{C(S_P, t_{68}, 0)}{C(35, t_{68}, 0)} \frac{C(35, t_{68}, 0)}{C(35, 15, 0)} = R_p R_t r_t. \quad (3)$$

Quantities  $R_p$ ,  $R_t$  and  $r_t$  have been fitted to experimental data according to the following polynomials in  $t_{68}$ :

$$r_t = \sum_{i=0}^4 c_i t_{68}^i, \quad (4)$$

$$R_p = 1 + \frac{p(e_1 + e_2 p + e_3 p^2)}{1 + d_1 t_{68} + d_2 t_{68}^2 + (d_3 + d_4 t_{68})R} \quad (5)$$

$$R_t = \frac{R}{R_p r_t}. \quad (6)$$

Finally, practical salinity is given by the following function of  $R_t$ , where constant  $k = 0.0162$  [4]:

$$S_p = \sum_{i=0}^5 a_i (R_t)^{i/2} + \frac{(t_{68} - 15)}{(1 + k(t_{68} - 15))} \sum_{i=0}^5 b_i (R_t)^{i/2}. \quad (7)$$

Numerical values of the 24 coefficients in Eq. (3-7) are reported in Appendix E in [4]. As it can be easily seen, the application of the usual expression for uncertainty propagation on  $S_p$  is not a trivial exercise, mainly due to the fact that input quantities  $p$ ,  $t$ , and  $C$  are not linearly involved in Eq. (7). As a solution, a proper application of a Monte Carlo method [7] can be adopted to calculate  $u_c(S_p)$ , as addressed in [22]. First of all, as described in the next section, an experimental evaluation of the correlations between the  $p$ ,  $t$ , and  $C$  has been performed, to be later used as an input in the Monte Carlo method.

### 2.3.1. Experimental evaluation of correlations between $p$ , $t$ and $C$

In the period from May to November 2017, during 34 campaigns of coastal water monitoring within ENEA S. Teresa experimental activity [23], the CTD probe has been deployed on the sea bottom at about 1.5 m depth for a whole duration of about 10 hours of data acquisition (position: 9.882°E, 44.081°N). The number of 1404 data set, each made of 100 triads ( $p$ ,  $t$ ,  $C$ ) acquired in 25 s (the sea water composition *considered* by the CTD probe can be supposed reasonably constant during the acquisition) was taken as a robust statistical sample to assess mutual correlation between  $p$ ,  $t$  and  $C$ . Obtained results are: no correlation between  $p$  and  $t$  (that can be considered as two independent quantities), no correlation between  $p$  and  $C$  and a very strong correlation between  $t$  and  $C$  (as can be deduced from Fig. 3, where mean trends of temperature and conductivity are reported vs. time). Experimental calculation of correlation coefficients  $r$  has confirmed the values reported in literature [22]: median values of the corresponding distributions for  $r(p, t)$ ,  $r(p, C)$  and  $r(t, C)$  are in fact equal to 0.001, -0.008 and 0.992, respectively (as shown in Fig. 4).



### 2.3.2. Monte Carlo method used to calculate $u_c(S_P)$

As already done for  $p$ ,  $t$  and  $C$ , a standard evaluation approach, according to the law of uncertainty propagation [6], could be applied to practical salinity, as made in [22], but it would result in a multi-step procedure requiring to evaluate the uncertainty associated with the output quantities of models (3) to (7) in cascade. It would also require to estimate several correlation coefficients between the involved input quantities, such as  $R$ ,  $R_p$  and  $r_t$ . On the other hand, nesting models from (3) to (7) leads to an overall model for practical salinity  $S_P$  according to which  $S_P$  ultimately depends on the “primordial”  $p$ ,  $t$  and  $C$ . In this framework, the Monte Carlo method for propagation of distributions described in [7] allows to directly recovering a numerical approximation of the probability density function (pdf) for the measurand ( $S_P$ ) starting just from an appropriate joint pdf modelling  $p$ ,  $t$  and  $C$ . From the output/measurand pdf, every summary of interest for the measurand can be obtained, in principle, such as the standard deviation, to be taken as its uncertainty, and a coverage interval at a desired coverage probability. Depending on the available information about the input quantities, document [7] provides guidance on the assignment of the pdf that can appropriately model them. When just an estimate and an uncertainty are provided for the input quantities, a Gaussian distribution with mean and standard deviation equal to these values, respectively, has to be assigned. Moreover, if there is correlation between any couple of input quantities, a corresponding multivariate Gaussian should be used. Therefore, for the present simulation, at each specific measured value of pressure, temperature and conductivity, a (univariate) Gaussian pdf was assigned to  $p$ , with mean equal to the measured value and standard deviation equal to the associated uncertainty, whereas a bivariate Gaussian pdf was assigned to  $t$  and  $C$ , having correlation coefficient equal to 0.992 (i.e. the median of the experimental  $r(t, C)$  values, as reported in Section 2.3.1). A number  $M = 10^6$  of triads ( $p, t, C$ ) were randomly drawn from such pdfs and processed into the nested combination of models (3) - (7), hence yielding to a set of  $M$  corresponding values  $S_{P_{MC}}$  for  $S_P$ . The simulation was performed in R ambient, by application of the “mvtnorm” package [24], which implements numerical computation of multivariate normal and Student’s  $t$ -distributions. From the pdf obtained for  $S_P$  via Monte Carlo method, the associated uncertainty was taken as the standard deviation  $SD(S_{P_{MC}})$  of the distribution, summed in quadrature with a term  $u_{PSS} = 0.0015$  which is the uncertainty contribution of the PSS-78 fits for  $R_p$  values different from 1 [22,25]. Therefore, the combined uncertainty associated to the  $S_P$  value was calculated according to:

$$u_c(S_P) = \sqrt{SD^2(S_{P_{MC}}) + u_{PSS}^2}. \quad (8)$$

### 3. Results

Tables for uncertainty assessment associated with the involved quantities are reported in the following. Asterisk indicates the calibration contribution to uncertainty due to calibration curve whose coefficients are directly memorized in the CTD unit; these coefficients are properly verified or renewed by means of periodic metrological tests performed at the manufacturer laboratory. The combined standard uncertainty of  $p$  (where  $p = p_{tot} - p_{atm}$ ) has been evaluated as equal to 0.24 dbar, the major contribution being the calibration effect (Table 2). With reference to Fig. 5-a, it can be noted that relative standard uncertainty of  $d$  is less than 1 % for depth greater than about 30 m. Combined standard uncertainty evaluated in Table 3 and Table 4 leads, respectively for  $t$  and  $C$ , to values equal to 0.023 °C and 0.032 mS/cm. The main uncertainty contribution for both  $t$  and  $C$  is due to the measurement repeatability. This term may in general be different at different depths; anyway, to be conservative, the largest of the repeatability values experienced along the water column during ENEA routine monitoring campaigns is reported. Moreover, it has been observed a negligible change in repeatability at different depths for a time period so brief (25 s), during which CTD probe is operated in quasi-static conditions.

In Fig. 5-b-c-d typical profiles for  $t$ ,  $C$  and  $S_p$  are shown, taking into account uncertainties on both axis; typical value of combined standard uncertainty associated with practical salinity is about 0.009 PSU.

Considering the effects of both  $t$  and  $C$  alignment and the correction of the cell thermal mass is very important to assess the quality of practical salinity profile. For the test case described in the present work, routine quality checks have allowed to verify that the differences between downcast and upcast profiles can be reasonably considered as negligible in formula (8). In the current case shown in Fig. 5d, practical salinity differences have a mean value of about 0.001 PSU (with a standard deviation of about 0.002 PSU): therefore these values are about one order of magnitude lower than the calculated standard uncertainty.

#### 3.1 Example of application: temperature comparison of model data vs experimental data

Uncertainty evaluation described so far allows the construction of a reliable experimental database to which model data can be compared in order to validate dedicated forecast systems. As an example of a possible application, daily mean model data of temperature profiles are compared with ENEA S.Teresa experimental data acquired by CTD close to the Gulf of La Spezia, during the monitoring campaign performed on the 10<sup>th</sup> of March 2016. Model data have the following features [26]:

- model: Copernicus Mediterranean Forecasting System,
- identifier: MEDSEA\_ANALYSIS\_FORECAST\_PHYS 006 001,
- horizontal grid resolution:  $1/16^\circ$  (about 5 km and 7 km for Longitude and Latitude, respectively),
- depths: 72 unevenly spaced levels.

Uncertainty assessment allows to compare model data vs experimental data both qualitatively and quantitatively, as shown in Fig. 6 [27]. Model data show in fact a trend that is confirmed by experimental data, that is to say a generalized warming ranging from the coast towards open sea. Moreover, both measures can now be effectively compared in terms of absolute values: at 5 m depth, in the station indicated by the squared dot in Fig. 6, CTD profiler measured a value of  $t$  equal to  $(13.786 \pm 0.023)$  °C, while model data provided a measure of  $(13.68 \pm 0.50)$  °C (temperature accuracy for model data is indicated in [28]). It can be concluded that, in this specific case, model data are reasonably comparable with experimental data. A further validation can be drawn if a larger model database is compared with experimental CTD data in the region of interest in Fig. 6: as an example, considering again the 5 m depth and experimental measures in the period from March 2015 to March 2016, the mean difference obtained between model data and CTD data is equal to  $(-0.14 \pm 0.48)$  °C, reasonably comparable with the value, reported in literature [28], of  $(-0.06 \pm 0.50)$  °C in the layer (0-10) m.

#### 4. Conclusions

Main results achieved by this work are underlined in the following list:

1. a more detailed knowledge of the nature of both measurand and measurement process for what concerns the direct measurement of  $p$ ,  $t$  and  $C$  profiles performed by CTD in the specific coastal zone of the Gulf of La Spezia. Up to now, these parameters can be measured with combined standard uncertainties of 0.24 dbar, 0.023 °C and 0.032 mS/cm in typical ranges of 0-65 dbar, 12-28 °C and 20-60 mS/cm, respectively;
2. uncertainty evaluation by means of the Monte Carlo method for propagation of distributions for the *in situ* measured practical salinity, for which a combined standard uncertainty of 0.009 PSU has been calculated (valid in a range of about 15-39 PSU);
3. CTD measures acquired and managed at ENEA Centre of S. Teresa, supplied by proper standard uncertainty bars, can now be used to draw metrological-founded conclusions about sea conditions in the coastal zone of interest (i.e. Empirical Orthogonal Functions analysis aimed at optimizing the

sampling campaigns, or data comparison with forecast algorithms as a support tool to calibrate/validate models);

4. realization of a well-consolidated framework for uncertainty evaluation, directly extensible to other relevant quantities derived by CTD measures (i.e. density) or measured by dedicated probes mounted together with CTD (i.e. dissolved oxygen concentration, turbidity or chlorophyll-a): uncertainty analysis of these quantities will be the subject of future works, taking into account at the same time the calibration capabilities already available at the ENEA Centre of S. Teresa in terms of internal reference standards (e.g. for dissolved oxygen concentration).

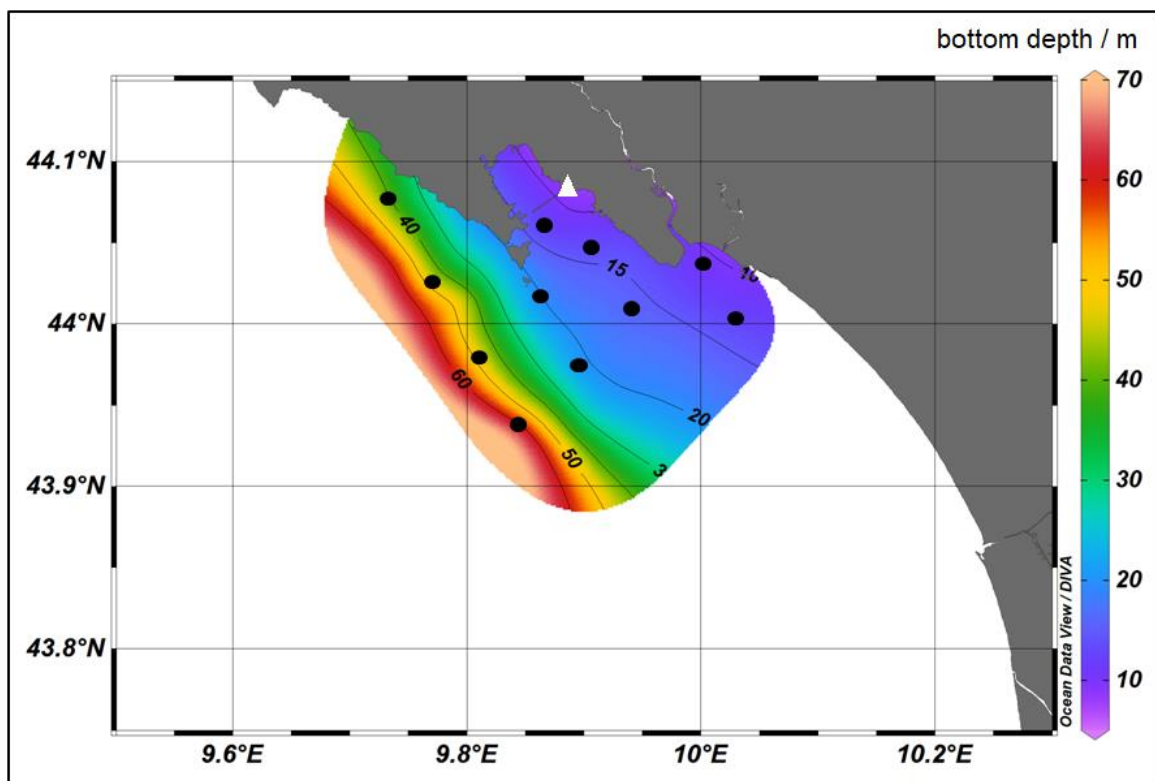
The uncertainty treatment method here proposed (not the corresponding resulting values *tout court*, of course) can be considered as generally applicable, provided that proper contributions related to specific conditions (i.e. sea, vessel, probes) are taken into account to customize input quantities accordingly.

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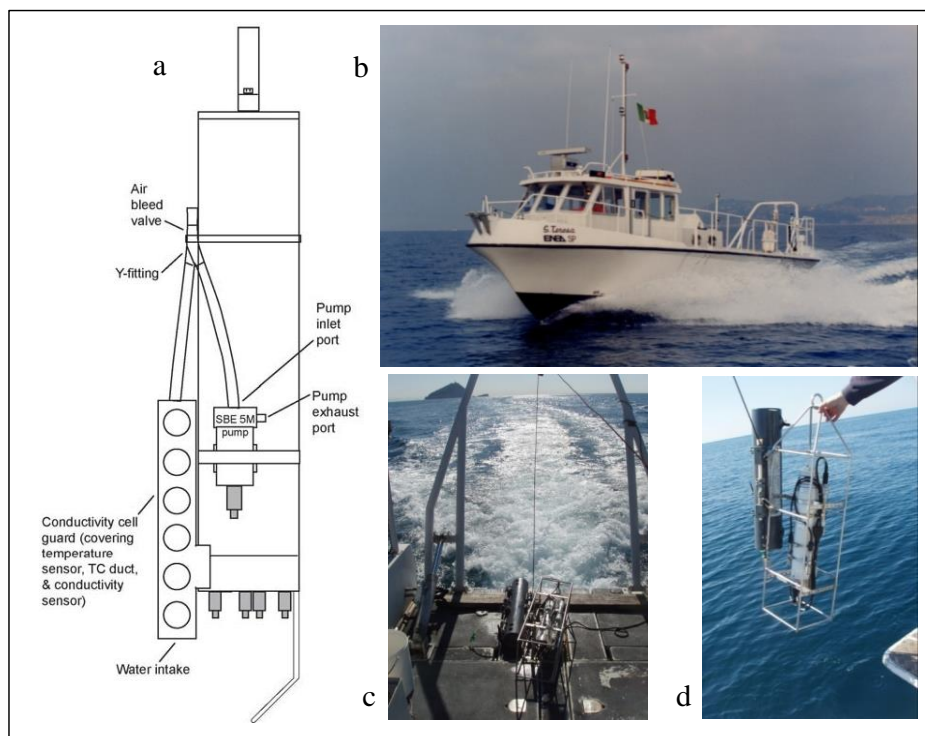
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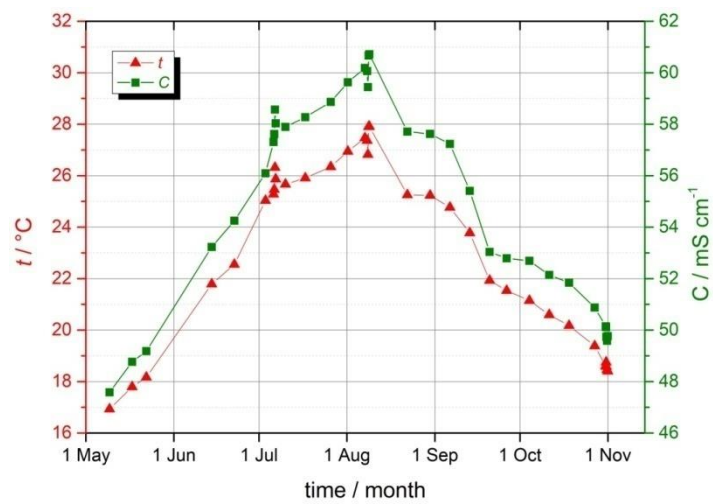
### Figures and figure captions



**Fig. 1.** Region of interest: bathymetry, position of the ENEA Centre (white triangle) and typical measurement stations where CTD is lowered (black dots).

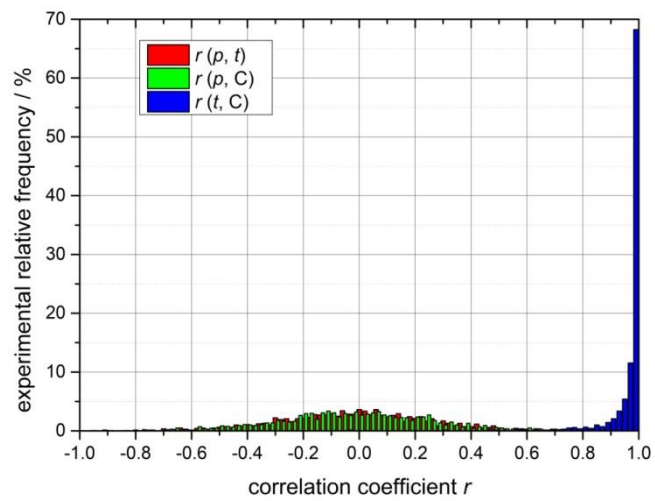


**Fig. 2.** a) Schematic view of the CTD probe, as supplied by the manufacturer. b) ENEA 12-m boat for coastal monitoring campaigns. c) CTD probe coupled with a Go-Flo bottle, during the transfer from one measurement station to another. d) CTD and Go-Flo bottle just before the profiling.

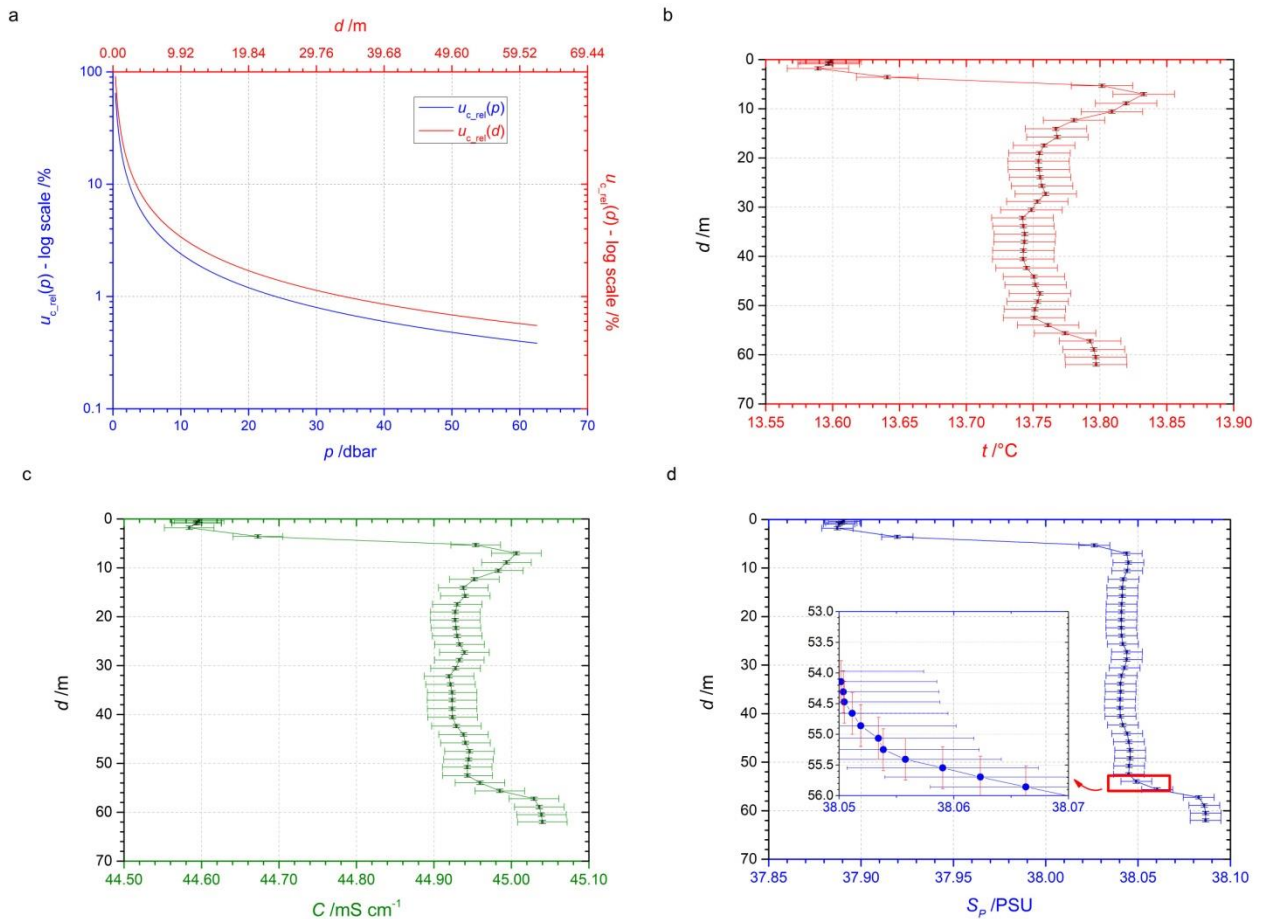


**Fig. 3.** Mean trends of temperature and conductivity acquired by CTD probe and used experimentally to calculate the correlation coefficients between  $p$ ,  $t$  and  $C$ .



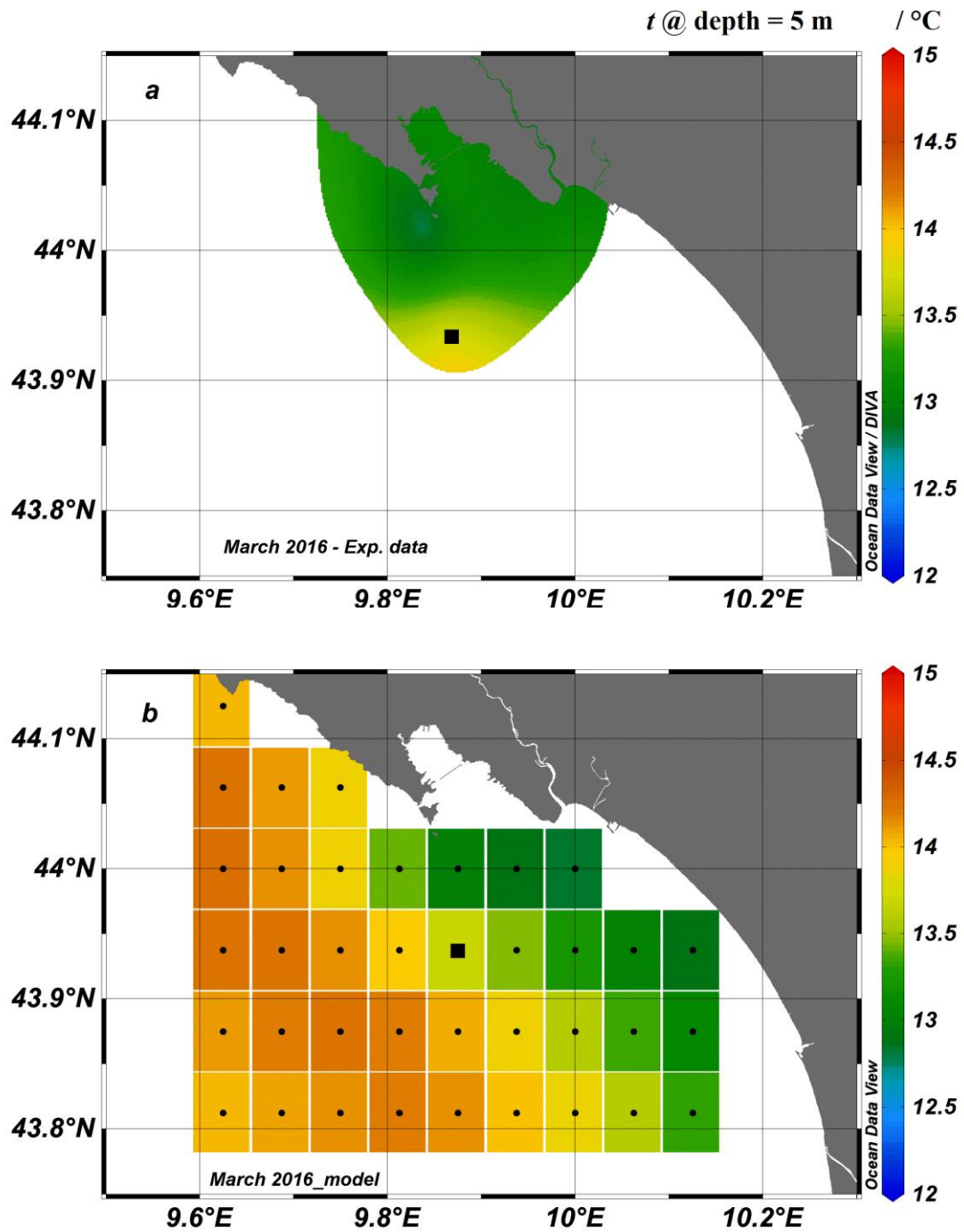


**Fig. 4.** Experimental distributions of correlation coefficients for pressure, temperature and conductivity measured by the CTD probe in repeatability conditions at a fixed depth.



**Fig. 5.** a) Values of relative combined standard uncertainty for pressure and depth (lower and upper line, respectively). b, c, d) Values of combined standard uncertainty in a typical profile (date of acquisition: 10<sup>th</sup> of March, 2016. Position: 9.847°E, 43.935°N): temperature, conductivity and practical salinity (with zoomed scales, too), respectively. Sub-sampling has been used just to plot data in a more readable way (data decimation in OriginPro).





**Fig. 6.** Temperature data of water column at a depth of 5 m on the 10<sup>th</sup> of March, 2016. **a)** Experimental data plotted in a continuous gridded field. **b)** Model data discretized at the spatial resolution of 1/16°. The square dot indicates respectively a downcast station where CTD has been deployed and the corresponding, nearest point in the model grid.

## Tables and table captions

Transducer	Quantities		
	$p$	$t$	$C$
Type	Micro-machined semiconductor strain gauge	Ultra-stable aged thermistor	Electrode cell sensor
M. R.	(0 to 350) dbar	(-5 to +35) °C	(0 to 90) mS/cm
I. A.	0.1 % FSR	0.005 °C	0.005 mS/cm
S. M.	0.004 % FSR	0.0002 °C	0.003 mS/cm
Res.	0.002 % FSR	0.0001 °C	0.001 mS/cm

**Table 1.** Main metrological features of the three transducers included in the CTD probe. Abbreviations indicate respectively: M. R. = measurement range, I. A. = initial accuracy, S. M. = stability per month, Res. = resolution.

Underwater pressure $p$ [dbar]	Standard uncertainty components for input quantities $X_i$				$u_A$	$u_B$	$\nu_i$	$u^2(x_i)$	$c_i = \partial f / \partial x_i$	$u^2_i(p) = c_i^2 \cdot u^2(x_i)$	$u^4_i(p) / \nu_i$	
	$X_i$	type	source	standard uncertainty estimated by	dbar	dbar		dbar <sup>2</sup>		dbar <sup>2</sup>	dbar <sup>4</sup>	
$p = f(X_i) = f(p_{tot}, p_{atm})$ $p = p_{tot} - p_{atm}$	$p_{tot}$	calibration	manufacturer's specifications*	range of variability (0.1 %FSR):		0.202	$\infty$	4.1E-02	1	4.1E-02	1.7E-05	
		stability	manufacturer's specifications	range of variability (0.004%FSR per month):		0.097	$\infty$	9.4E-03	1	9.4E-03	8.9E-07	
		resolution	manufacturer's specifications	range of variability (0.002%FSR):		0.004	$\infty$	1.6E-05	1	1.6E-05	2.7E-12	
		repeatability	repeated observations	SD (CTD fixed at various depth for about 25 s):		0.050		100	2.5E-03	1	2.5E-03	6.3E-08
	*verified by periodical calibration checks at manufacturer's calibration laboratories (once a year)											
	$p_{atm}$	linearity	manufacturer's specifications	SD, in the range [0 °C,+40 °C]:		0.007		$\infty$	4.6E-05	-1	4.6E-05	2.1E-11
		hysteresis	manufacturer's specifications	SD, in the range [0 °C,+40 °C]:		0.001		$\infty$	5.6E-07	-1	5.6E-07	3.2E-15
		repeatability	manufacturer's specifications	SD, in the range [0 °C,+40 °C]:		0.001		$\infty$	5.6E-07	-1	5.6E-07	3.2E-15
		calibration	manufacturer's specifications	SD, in the range [0 °C,+40 °C]:		0.002		$\infty$	5.1E-06	-1	5.1E-06	2.6E-13
		stability	manufacturer's specifications	range of variability (0.001 dbar per year):			0.007	$\infty$	5.2E-05	-1	5.2E-05	2.7E-11
		resolution	manufacturer's specifications	range of variability (0.001 dbar):			0.001	$\infty$	3.3E-07	-1	3.3E-07	1.1E-15
		reproducibility	repeated observations	SD of very long time series of data:		0.075		657362	5.6E-03	-1	5.6E-03	4.8E-11
											$u^2_c(p)$ [dbar <sup>2</sup> ]	5.8E-02
											$u_c(p)$ [dbar] and actual DOF	<b>0.24</b>
										coverage probability <i>prob</i>		0.95
										coverage factor $k = t(\text{prob}, \text{DOF})$		1.972
										expanded uncertainty $U(p)$ [dbar]		<b>0.48</b>

Table 2. Uncertainty evaluation for  $p$  measurement.

Water temperature $t$ [°C]	Standard uncertainty components for input quantities $X_i$				$u_A$	$u_B$	$\nu_i$	$u^2(x_i)$	$c_i = \partial f / \partial x_i$	$u^2_{f(t)} = c_i^2 \cdot u^2(x_i)$	$u^4_{f(t)} / \nu_i$
	$X_i$	type	source	standard uncertainty estimated by	°C	°C		°C <sup>2</sup>		°C <sup>2</sup>	°C <sup>4</sup>
direct measurement $t$	$t$	calibration	manufacturer's specifications*	range of variability (0.005 °C):		0.0029	$\infty$	8.3E-06	1	8.3E-06	6.9E-13
		stability	manufacturer's specifications	range of variability (0.0002 °C per month):		0.0014	$\infty$	1.9E-06	1	1.9E-06	3.7E-14
		resolution	manufacturer's specifications	range of variability (0.0001 °C):		0.0001	$\infty$	3.3E-09	1	3.3E-09	1.1E-19
		repeatability	repeated observations	SD (CTD fixed at various depth for about 25 s):	0.023		100	5.3E-04	1	5.3E-04	2.8E-09
		*verified by periodical calibration checks at manufacturer's calibration laboratories (once a year)									
								$u^2_c(t)$ [°C <sup>2</sup> ]		5.4E-04	
								$u_c(t)$ [°C] and actual DOF		<b>0.023</b>	104
								coverage probability <i>prob</i>			0.95
								coverage factor $k = t(\text{prob}, \text{DOF})$			1.983
								expanded uncertainty $U(t)$ [°C]			<b>0.046</b>

**Table 3.** Uncertainty evaluation for  $t$  measurement.

Water Conductivity C [mS/cm]	Standard uncertainty components for input quantities $X_i$				$u_A$	$u_B$	$\nu_i$	$u^2(x_i)$	$c_i = \partial f / \partial x_i$	$u^2_i(C) = c_i^2 \cdot u^2(x_i)$	$u^4_i(C) / \nu_i$
	$X_i$	type	source	standard uncertainty estimated by	mS/cm	mS/cm		(mS/cm) <sup>2</sup>		(mS/cm) <sup>2</sup>	(mS/cm) <sup>4</sup>
direct measurement C	C	calibration	manufacturer's specifications*	range of variability (0.005 mS/cm):		0.0029	$\infty$	8.3E-06	1	8.3E-06	6.9E-13
		stability	manufacturer's specifications	range of variability (0.003 mS/cm per month):		0.0208	$\infty$	4.3E-04	1	4.3E-04	1.9E-09
		resolution	manufacturer's specifications	range of variability (0.001 mS/cm):		0.0006	$\infty$	3.3E-07	1	3.3E-07	1.1E-15
		repeatability	repeated observations	SD (CTD fixed at various depth for about 25 s):	0.0247		100	6.1E-04	1	6.1E-04	3.7E-09
	*verified by periodical calibration checks at manufacturer's calibration laboratories (once a year)										
								$u^2_c(C)$ [(mS/cm) <sup>2</sup> ]		1.1E-03	
								$u_c(C)$ [mS/cm] and actual DOF		<b>0.032</b>	198
								coverage probability <i>prob</i>			0.95
								coverage factor $k = t(\text{prob}, \text{DOF})$			1.972
								expanded uncertainty $U(C)$ [mS/cm]			<b>0.064</b>

**Table 4.** Uncertainty evaluation for C measurement.