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TEST CASE IN A NEAR SHORE AREA (LIGURIAN SEA, LA SPEZIA GULF).

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Abstract

Total Suspended Solids (TSS) is considered a very important oceanographic quantity to describe the status of the seawater column. The ENEA Marine Environment Research Centre of S. Teresa, devoted since the '70s to the monitoring, analysis and comprehension of physical, chemical and biological processes in marine environment, has therefore developed an historical experience also in TSS measurement. Aim of the present work is to collect ENEA expertise and internal procedure related to experimental TSS measurement, formalizing in particular the assessment of TSS measurement uncertainty in accordance with reference guidelines and standards. The contribution of mass and volume in the laboratory-based gravimetric method to measure TSS (by filtering process) has been analysed, together with the effect due to repeatability proper of this type of experimental activity. TSS combined standard uncertainty has been finally evaluated, and just the repeatability contribution proved to be the most relevant one (about 10 % in terms of relative standard uncertainty). The link between TSS and Turbidity, continuously optically measured along the water column, is also discussed. Turbidity of a water sample can in fact be used to infer the mass of particles in suspension by means of a sort of a calibration curve that relates TSS to Turbidity itself. This relation can be reasonably approximated by a linear model, whose slope is sample-dependent: consequently, the conversion from a Turbidity profile to a TSS one has to be determined each time. Results prove that this consolidated approach can be applied in the near-shore area, where ENEA performs its monitoring campaigns.

The present technical report is intended to serve as a basis for developing procedures more and more compliant to international metrological standards, with the aim of further guaranteeing the metrological traceability of oceanographic quantities.

Keywords: *Total Suspended Solids; Column Water; Turbidity; Standard Uncertainty.*

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1. Introduction

Total Suspended Solids (*TSS* in the following) and Turbidity are two important quantities characterizing the seawater column, being in practice the most visible indicators of its quality (under the usual assumption that a clear water can be considered reasonably as a first clue of an healthy water). High levels of *TSS* and Turbidity can be considered generally as a symptom of some extraordinary or periodic phenomenon (e.g. soil erosion, river floods, anthropic pollution, algal blooms) and sometimes can be reason of concern for aquatic and human life (e.g. high *TSS* concentrations may in fact prevent sufficient oxygen transfer and result in the death of buried organisms, eggs, or macro-invertebrate larva).

By definition, *TSS* represents the undissolved material, composed of organic and inorganic fraction, present in suspension in a water sample, that can be separated through a membrane filter of standardized porosity and dimensions [1]. In practice, the filter to be used to obtain a separation of the totality of suspended solids (including colloids) must have pores with an average diameter of 0.45 μm: this dimension is considered the threshold that distinguishes a dissolved fraction from an undissolved one [2,3], so that all particles in the sample with a dimension larger than 0.45 μm are considered as suspended solids. *TSS* are mostly composed by inorganic material (e.g. sand, silt, clay), but also plankton, algae and even bacteria can play a role to *TSS* value, due to the fact that they also drift or float along the water column influencing its clarity.

TSS measurement requires the collection (in field) and, subsequently, the analysis (in laboratory) of water samples and therefore it is considered as a time-consuming activity: due to this fact, it is often combined with the measurement of Turbidity, for which different types of probes are available (e.g. turbidimeter based on optical, acoustic or laser technologies [1]). In particular, for what concerns the optical measurement of Turbidity, the measurand is the amount of light scattered by particles floating in the water column [4]; from this it follows that *TSS* and Turbidity are two closely related quantities whose correlation, highly dependent on characteristics of the suspended particles (e.g. diameter, composition, refractive index), has to be determined *ad hoc* by measurements in field and post-processing of data. It has to be underlined that these two quantities are not fully interchangeable. Turbidity can in fact be affected by substances whose dimensions are too small to be revealed as part of *TSS* concentration, like Colored Dissolved Organic Matter (CDOM). For this reason, differently from *TSS*, it can not be considered as a direct indicator of the total suspended material per volume of water. Consequently, the

experimental approach usually adopted in combining these two quantities during a routine monitoring campaign can be summarized as follows:

1. a representative number of seawater samples are taken along the water column (at different depths) and analysed in terms of *TSS* values;
2. along the same water column a profile of Turbidity measures is acquired simultaneously by means of a proper turbidimeter;
3. the conversion factor *TSS*/Turbidity is then calculated in correspondence of the *discrete TSS* samples: *TSS* can so be reconstructed along the entire water column as it was a *continuously* measured quantity.

In the following paragraphs, materials and methods followed by ENEA Marine Environment Research Centre of S.Teresa (from now on simply ENEA) to measure *TSS*, and its correlation with Turbidity, will be described. Main attention will be paid to the assessment of the standard measurement uncertainty associated with the involved quantities.

2. Materials and methods

Total Suspended Solids present in a seawater sample, whose volume is well-known, are collected by filtration on a special membrane filter and determined gravimetrically after drying the filter at a fixed temperature, up to constant weight. Equipment and procedure adopted by ENEA, and here briefly described, mainly refer to what is prescribed by national and international guidelines and standards [2,5]; some adaptations have been introduced, motivated by experience and experimental practice (e.g. drying temperature and duration lower and higher, respectively, to avoid possible filter damages). For what concerns Turbidity, on the other hand, continuous measures are acquired along the water column by a commercial turbidimeter.

In Fig. 1 a map of the stations where ENEA, in recent times, usually perform paired *TSS* and Turbidity profile measurements is shown.

2.1 Equipment for *TSS* measurement

During a standard monitoring campaign performed by ENEA [6], the following equipment is used to perform a *TSS* measurement at a given depth:

in-field equipment

- 12-meter length research vessel "S. Teresa", provided with a 400 m-cable winch;
- GO-FLO sampling bottles (5 and/or 30 liter volume, usually), deployed by using the winch of the research vessel at the mesurement depth;
- 5 liter tanks;

laboratory equipment

- Millipore HA filters (0.45 μm pore diameter, 4.5 cm diameter);
- oven, equipped with a thermostat capable of maintaining constant the temperature within ± 1 °C;
- dryer, equipped with a coloured indicator to check the degree of exhaustion of the drying agent;
- analytical balance (200 g full-scale), with a resolution of 0.1 mg;
- 2000 ml graduated measuring cylinder (Class B);
- laboratory glassware and tanks;
- vacuum filtration system (pump and tubing).

2.2 Procedure for *TSS* measurement

The procedure for *TSS* measurement can be summarized as follows:

- the day before the water sampling, membrane filters are placed in the oven (Fig. 2-a,b), inside the filter holder maintained open, at a temperature of 60 °C for at least one night;
- once the heat treatment is completed, the filter reaches again room temperature into the dryer and then is weighed on the balance. It is left in the filter holder in the dryer, ready to be used (Fig. 2-c);
- water samples are usually analysed in the afternoon/evening of the sampling day, in order to minimize the possibility of chemical, physical or biological variations during storage. The filtration system (Fig. 2-d) is composed of a 250 ml beaker for the sample (1), a metal clamp (2) and a filter holder (3), the latter is inserted in a support connected indirectly to a pump;
- after shaking the tank containing the seawater sampled by the GO-FLO bottle, a sample volume *V* (3 or 4 liters, usually) is measured by the graduated measuring

cylinder and transferred into 2 plastic bottles of 2 liters each. The first bottle (after shaking) is placed overturned on a station of the filtration system, where previously a filter has been mounted. The filtration can now be started by turning on the pump and opening the proper valve (Fig. 2-e): the filtration process can be performed on three different samples at the same time (two other samples can be filtered, if necessary, by adding other two bottles connected to a supplementary vacuum pump). In the overturned bottles it is possible to control the decrease in the level of the sample in order to replace the first with the second bottle as soon as it is empty, for each sample;

- when the sample filtration has been completed, the filter is washed with 10-15 ml of deionized water to dissolve any salt residue. The filter is then left to dry for a couple of minutes, by the action of the vacuum pump still running. Then, with the system off, each filter is transferred to the corresponding filter holder and placed in the oven at about 60 °C for the next night (Fig. 2-f);
- the next morning, both filter holders and filters are placed in the dryer or left for a couple of hours in the oven off (as the day before) to reach room temperature. Filters are finally re-weighed on the analytical balance.

Finally, for each filter (i.e. for each water sample), *TSS* value (in mg l^{-1}) is calculated as follows:

$$TSS = \frac{(m_2 - m_1)}{V} = \frac{\Delta m}{V} \quad (1)$$

where:

- m_1: mass of filter after first drying (mg);
- m_2: mass of filter and residue after filtration and second drying (mg);
- V: volume of the seawater sample (l) filtered for each filter, usually equal to 3 or 4 litres, obtained by summing two sub-volumes (V_1 and V_2) measured by means of the graduated cylinder.

2.3 Equipment for Turbidity measurement

Optical turbidimeter measure the cloudiness of water by analysing the effect suspended particles have on a light beam passing through them [4,7]. Two main phenomena can occur: light absorption (causing an intensity reduction of the transmitted beam, in

comparison with that of the incident ray) and light scattering (due to reflection and refraction phenomena). Depending on the size of the suspended particles, this or that effect may prevail but, in any case, both optical phenomena usually coexist. Turbidity can therefore be determined by measuring the absorption on the incident beam (measurement is performed in the same direction as the incident ray: turbidimetric method) or by quantifying the amount of scattered light (measured by a photodetector placed at a 90° angle with respect to the direction of the incident beam: nephelometric method). Turbidity is usually measured in Nephelometric Turbidity Unit (NTU), referenced to a proper turbidity standard.

At ENEA, Turbidity measurements are performed by using a nephelometric turbidimeter; in particular, since May 2015 a Turner Designs one (mod. Cyclops-7F) is used, whose main features are as follows (Fig. 3):

- minimum detection limit: 0.05 NTU;
- linear range:0-1500 NTU;
- depth range: 600 m;
- led-source: 850 nm wavelength.

At the moment, this probe is not calibrated periodically, not being used for absolute Turbidity measurements but to convert a continuous Turbidity profile into a *TSS* profile, as explained in the following paragraphs. Anyway, at the time of writing this document, ENEA is proceeding with the purchase of some NTU reference standards, so that in the future also Turbidity measures will be traceable.

2.4 Procedure for Turbidity measurement

Turbidimeter is connected to a CTD probe (mod. SBE19plus). For each profile, the CTD is deployed at well-known depths together with the GO-FLO bottle (for *TSS* samples) by using the winch of the research vessel (see Fig. 2 in [6]). Turbidity measures are acquired at a sampling rate of 4 Hz and stored in the internal buffer of the CTD, ready to be downloaded for post-processing. In Fig. 4 Turbidity profiles measured during ENEA routine monitoring campaigns since May 2015 are shown all together. Turbidity values range up to about 80 NTU, but the main part of measures is below 20 NTU.

2.5. Correlation between *TSS* and Turbidity

Since the optical properties of matter suspended in a sample of water are determined not only by the quantity of suspended particles, but also by their shape, size, mass density and refractive index, it is not possible to establish a direct correlation of general significance between *TSS* and Turbidity; the latter can be more properly considered as a relative measure of the weight concentration of suspended solids in the sample. However, if for each Turbidity profile some *TSS* samples are measured, then a contextual linear relationship between these two quantities can reasonably be derived, even if strictly valid only for the analyzed profile [8,9]:

$$TSS = a + b \times \text{Turbidity} \quad (2)$$

where the intercept *a* takes into account the non-complete overlapping between the two quantities, while the slope *b* is related to particular conditions of suspended solids in the considered profile, and consequently can vary significantly in time and space. Attention should be paid to the fact that a not negligible presence of air bubbles or organic material not detectable by a *TSS* measurement can lead Eq.(2) to be inconsistent (e.g. when Turbidity values are greater than 40 NTU for nephelometric method, the *TSS* vs Turbidity relationship becomes non-linear and Eq.(2) can not be applied [9]).

2.6 Procedure for *TSS* standard uncertainty evaluation

Standard uncertainty associated with a *TSS* estimate can be evaluated by compiling proper uncertainty budget where evidence is given to each uncertainty contribution, as prescribed by [10]. Analysis takes into account both the uncertainty contributions declared by the manufacturer and those related to the measurements in the field under repeatability conditions. Uncertainty budgets for each involved quantity are reported in Tables 1-4, where symbols have generally the following meaning, as prescribed by [10] (sometimes, similar symbols prescribed by specific standards are used, instead, as in the case of Tables 1-2):

- X_i: *i*-th 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 are typically assigned to those input quantities varying within ranges declared by the certificates);
- ν_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 coefficient obtained from the mathematical model relating the output quantity to the input quantities;
- $c^2_i \cdot u^2(x_i)$: contribution to the output variance associated with the *i*-the input quantity;
- $u^4_i(y)/\nu_i$: *i*-th contribution in the Welch-Satterthwaite formula, used to estimate the actual DOF of the output quantity *y*;
- $u^2_c(y)$: 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 of *k* and $u_c(y)$.

3. Uncertainty assessment

In the following, the steps performed at ENEA to evaluate *TSS* standard uncertainty are described, with the final aim of quantifying all uncertainty contributions. Then, for a given test case, the conversion curve to transform a Turbidity profile into a *TSS* profile is calculated.

3.1 Standard uncertainty of mass measures

The balance used to weigh *TSS* filtered out from a seawater sample is periodically calibrated (once a year, internally at ENEA) by using a set of reference masses [11]. The

calibration, performed following international and national standards [12-14], mainly consists in:

- application of test loads on the balance under specified conditions;
- determination of measurement errors (also indicated as variation of the indication *I*);
- evaluation of the standard uncertainty to be attributed to the weighing result.

In particular, the following uncertainty contributions due to balance itself are evaluated:

- resolution at null load;
- resolution under load;
- repeatability under the same load;
- eccentricity.

For what concerns the uncertainty contributions due to reference masses, the following are taken into account:

- standard uncertainty as declared by the calibration certificate of the mass set;
- buoyancy;
- time drift;
- convection;
- room temperature.

Calibration are usually performed both on full-scale (200 g) and on the minimum scale (10 mg). More quantitative details are shown in Appendices A and B, respectively. Tables 1-2 report final evaluation, in accordance with [12], of balance measurement error and its associated standard (and expanded) uncertainty on both scales (these tables represent the 6th, final step of the elaboration shown in Appendices). The easiest way to visualize mass error values and trends (together with their associated standard uncertainties) is shown in Fig. 5 (red curve), where the error on mass measure $E(m)$ is plotted and fitted as a function of m itself by means of the following linear model (with null intercept):

$$E(m) = c \times m \tag{3}$$

By the fact that the correct mass values m_1 and m_2 in Eq.(1) are calculated by subtracting the errors $E(m_1)$ and $E(m_2)$ to the respective reading mass values, their composed

standard uncertainties are by definition equal to $u(E(m_1))$ and $u(E(m_2))$, where (Fig. 5, blue curve):

$$u(m) = u(E(m)) = d \times m \quad (4)$$

The slopes *c* and *d* in Eq.(3-4), whose values are respectively equal to 1.03E-5 g g^{-1} and 1.05E-5 g g^{-1}, are reasonably considered without standard uncertainty (i.e. the uncertainty contributions due to fit are equal to some percent, therefore considered as a negligible second order correction). After correction for $E(m)$, the value Δm in Eq.(1) can finally be calculated and its combined standard uncertainty can be expressed as follows:

$$u(\Delta m) = \sqrt{u^2(m_1) + u^2(m_2)} \quad (5)$$

3.2 Standard uncertainty of volume measures

The volume *V* of the filtered seawater sample is measured by summing two sub-volumes (V_1 and V_2), usually equal to 2 l and 1 l (or 2 l) respectively. The graduated, type 1a, class B measuring cylinder has a tall form with spouted neck, with a nominal capacity of 2000 ml. Volume measurements are performed checking the meniscus is set so that the plane of the top edge of the graduation line is horizontally tangential to the lowest point of the meniscus, the line of sight being in the same plane. Uncertainty evaluation of volume measurement is obtained by referring to [10,15]; results are shown in Table 3. The composed standard uncertainty on a typical volume measure of a seawater sample is equal to 16 ml.

3.3. *TSS* repeatability

An *ad-hoc* campaign aimed to evaluate *TSS* measurement repeatability was performed on June 24, 2021. The large GO-FLO bottle (30 l capacity) was deployed at 08:10 UTC in position 9.849400 °E - 44.030717 °N (bottom depth 28 m), at a mean depth of about 23.6 m, to collect a unique sample of water. The bottle was well shaken and the water content was tapped into 2 tanks of 20 l. Once arrived in the laboratory, in the early afternoon, the water sample, well mixed again, was divided into 9 sub-samples of 3 liters, each subjected to the procedure for *TSS* measurement described in Sec. 2.2. Results are shown in Table 4. The relative standard uncertainty of about 8 % can be associated to ENEA *TSS* measurement.

3.4 Combined standard uncertainty of *TSS* measures: an example

Standard uncertainties on mass, volume and repeatability measures can now be used to calculate the combined standard uncertainty $u_c(TSS)$. In the following, for demonstration purposes, the steps to calculate $u_c(TSS)$ are applied to the following specific *TSS* measurement (that represents approximately the lower limit of ENEA *TSS* measurement capability, Fig. 4):

- date and time: June 24, 2021 - 10:02 UTC
- station position: 9.846767 °E - 44.030967 °N
- bottom depth: 28 m
- seawater sample taken at depth: 15 m.

TSS combined standard uncertainty assessment can be divided into the following steps:

1. **contribution due to mass measures**: mass pre- and post-filtering (m_1 and m_2) are equal to 8.8512 g and 8.8538 g, respectively. By applying Eq.(3-5), the following corrected values are obtained:
    - m_1 = (8.8511 ± 0.0001) g;
    - m_2 = (8.8537 ± 0.0001) g;
    - Δm = (2.60 ± 0.13) mg;
    - $u_{c,\,rel}(\Delta m)$ = 5.1 %;
2. **contribution due to volume measure**: in accordance with Table 3:
    - V = (2000 + 1000) ml
    - $u_c(V)$ = 16 ml;
    - $u_{c,\,rel}(V)$ = 0.5 %;
3. **contribution due to *TSS* repeatability**: in accordance with Table 4:
    - $u_{rep}(TSS)$ = 8.4 %;
4. **combination of relative standard uncertainties**: in accordance with [10] and Eq.(1):

$$u_{c,rel}(TSS) = \sqrt{u_{c,rel}^2(\Delta m) + u_{c,rel}^2(V) + u_{rep}^2(TSS)} \cong 10\ \%$$

5. **final result**: in the specific case, *TSS* measure is equal to (0.867 ± 0.087) mg l^{-1}.

It can be noted that the greatest contribution to the standard uncertainty is attributable to repeatability measures.

3.5 *TSS* vs Turbidity: experimental determination for a single profile

To illustrate a typical example of how a Turbidity profile (measured continuously in the field) is converted into one of *TSS* (discretely sampled and measured in the laboratory), the results for the following measurement station are shown:

- date and time: August 29, 2017 - five repeated CTD profiles (at different depths), from 13:15 UTC to 14:13 UTC;
- station position: 9.849717 °E - 44.03285 °N
- bottom depth: 27 m
- seawater sample taken at five depths: 24.4 m, 21.3 m, 19.0 m, 17.6 m, 14.1 m.

In Fig. 6 continuous Turbidity profiles and corresponding discrete *TSS* measures are reported. The water samples for *TSS* measurement are taken 50 cm higher than the position occupied by the turbidimeter mounted on the CTD probe: by the fact that the length of the GO-FLO (5 l capacity) is equal to 70 cm , the Turbidity values to be paired to *TSS* measures are mediated from (depth_max minus 85 cm) to (depth_max minus 15 cm) and their dispersion (calculated as SD) is taken into account. In accordance with Eq.(2), and with $u(TSS)$ calculated as in Sec. 3.4, the linear relation of *TSS* vs Turbidity for this test case is shown by diagram in Fig. 7.

In the end, by applying Eq.(2) in this particular case (to the average of all Turbidity profiles) a continuous *TSS* profile can be obtained as shown in Fig. 8, paired with experimental *TSS* discrete measures.

4. Conclusions and notes

The purpose of this work is the formalization of ENEA internal procedures for the measurement of *TSS* quantity and the assessment of its standard uncertainty, taking into account the contributions related to the measurements of mass, volume and in-field repeatability (which proved to be the most relevant contribution). Linear relation between *TSS* and Turbidity has been shown to be effective in converting *TSS* measurements from discrete to continuous. These "best practices", based on historical ENEA background, are obviously always subject to improvements and/or adjustments (e.g. more refined statistical data processing) that are more in line with international standards and able to follow the most advanced metrological traceability needs. Precisely in this context, this work aims to be a basis for future developments within the collaborations expected in the recently

started MINKE project (Metrology for Integrated marine maNagement and Knowledge-transfer nEtwork, H2020-INFRAIA-2020-1, site: https://minke.eu/).
Authors want to underline in particular the importance of the oceanographic internal database of the ENEA Center of S. Teresa, without which works like this could hardly be done.

Figures

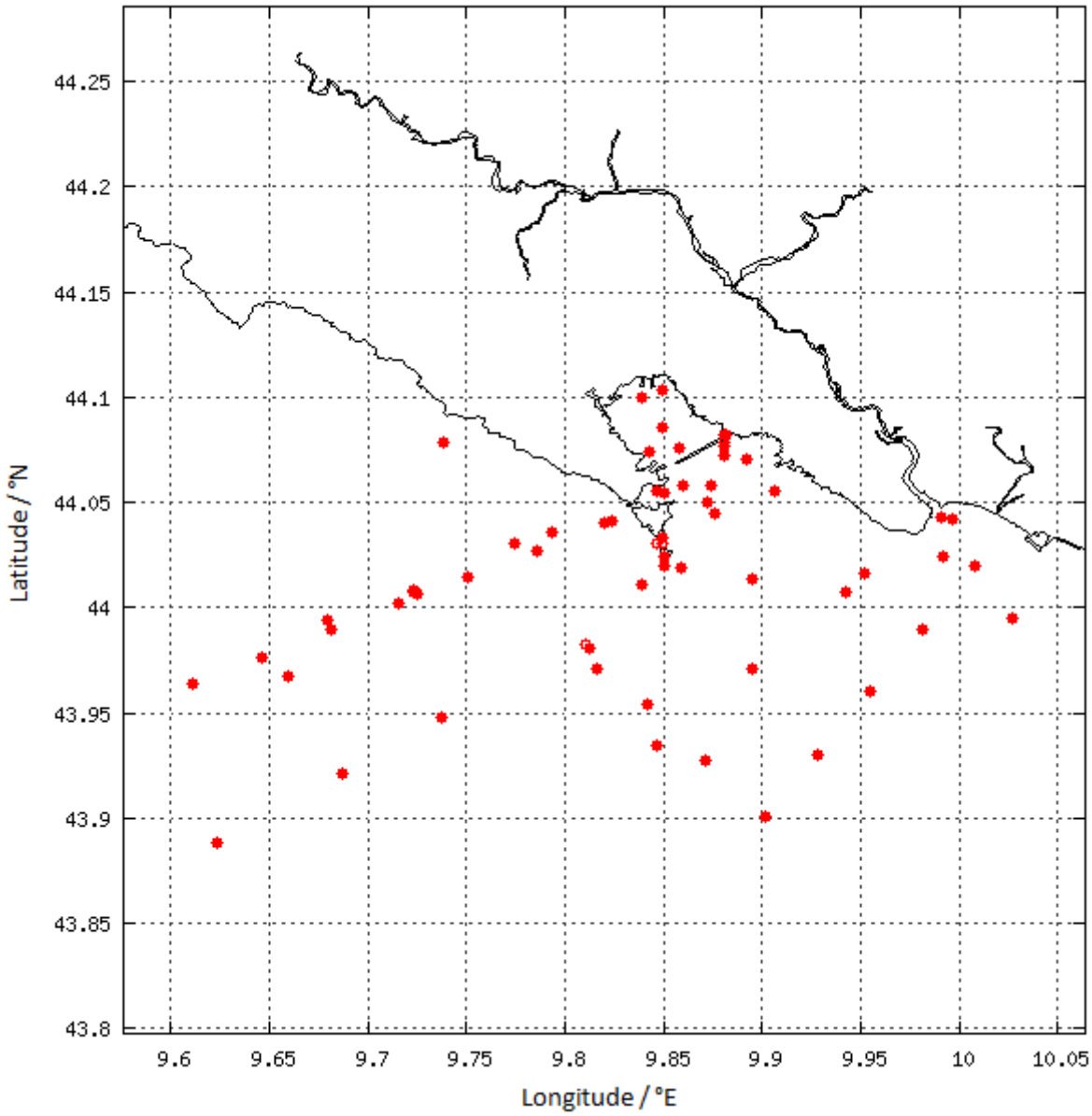

Fig. 1 - Area of interest. Red dots indicate the stations where ENEA, starting from May 2015, usually perform paired *TSS* and Turbidity profile measurements. Stations are periodically repeated during routine monitoring campaigns.

Fig. 2 - (a) Membrane filters before first drying; (b) filters during the first heat treatment in the oven; (c) filters in the dryer and analytical balance; (d) assembly of the filtration system; (e) measurement of the sampling volume and filtration; (f) filters after the filtration (the deposit of the suspended material collected is evident), ready for the second heat treatment and, in the end, weighing.

Fig. 3 - Nephelometric turbidimeter used at ENEA in the last years.

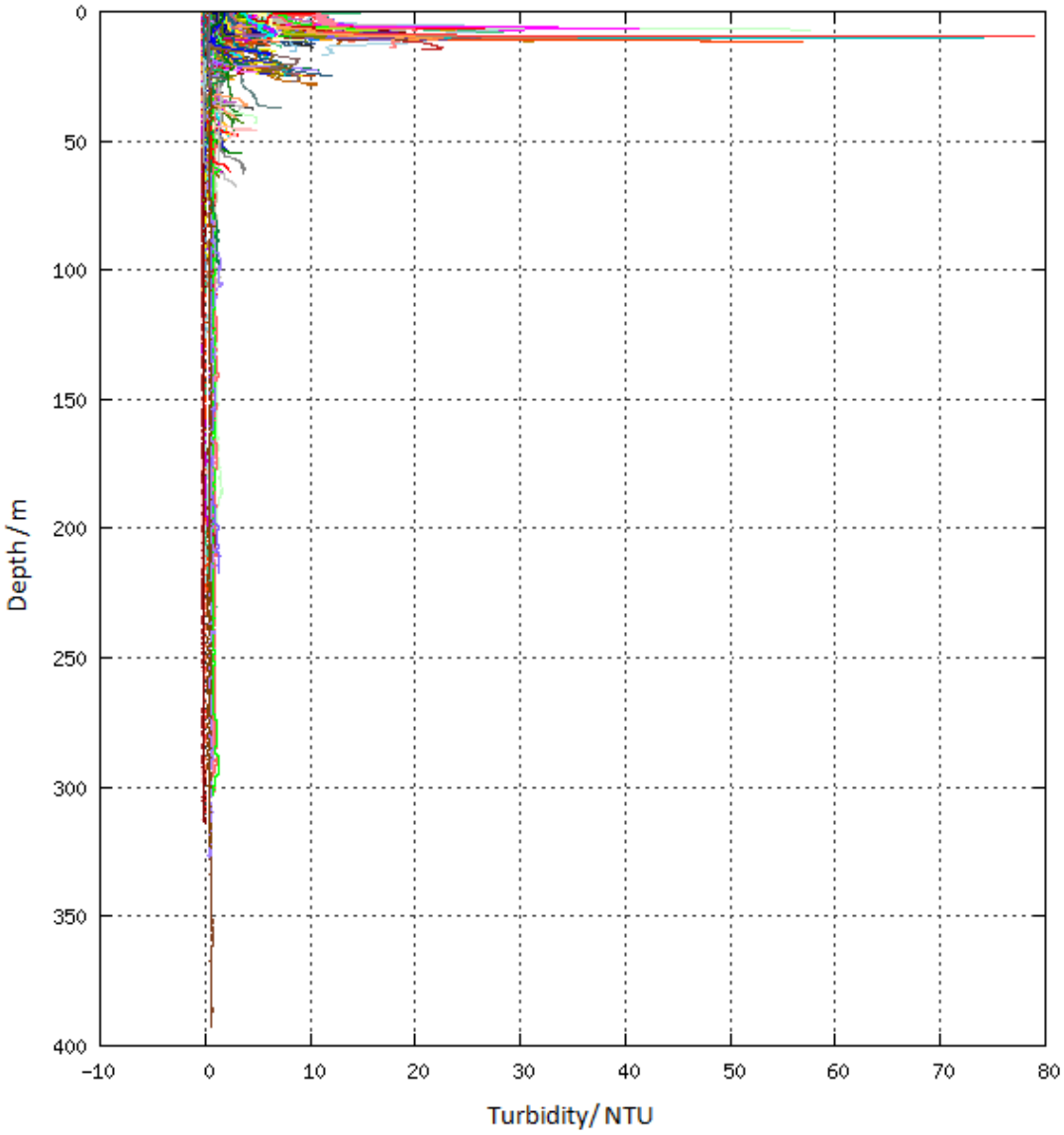

Fig. 4 - Overview of typical Turbidity profiles in the area of interest, since May 2015, as measured by Cyclops-7F nephelometric turbidimeter.

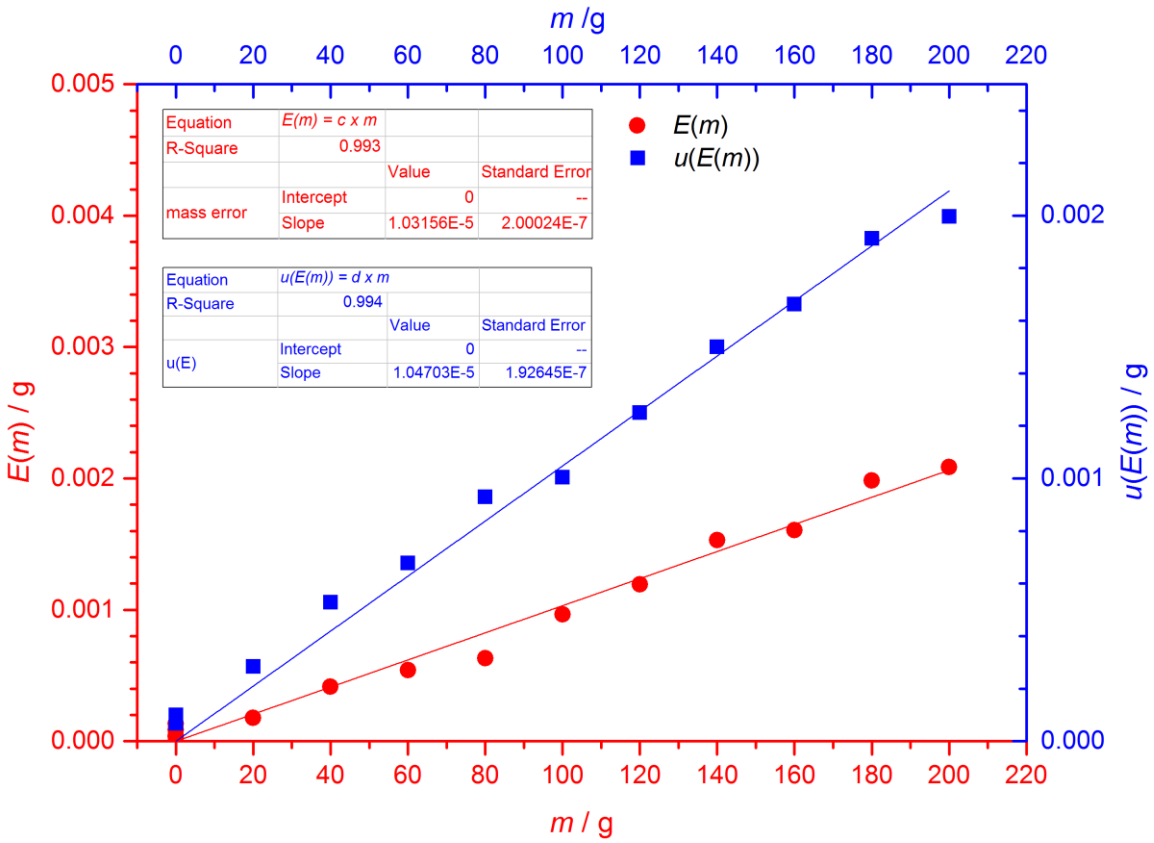

Fig. 5 - Errors by which mass values read by the balance have to be corrected (and standard uncertainties).

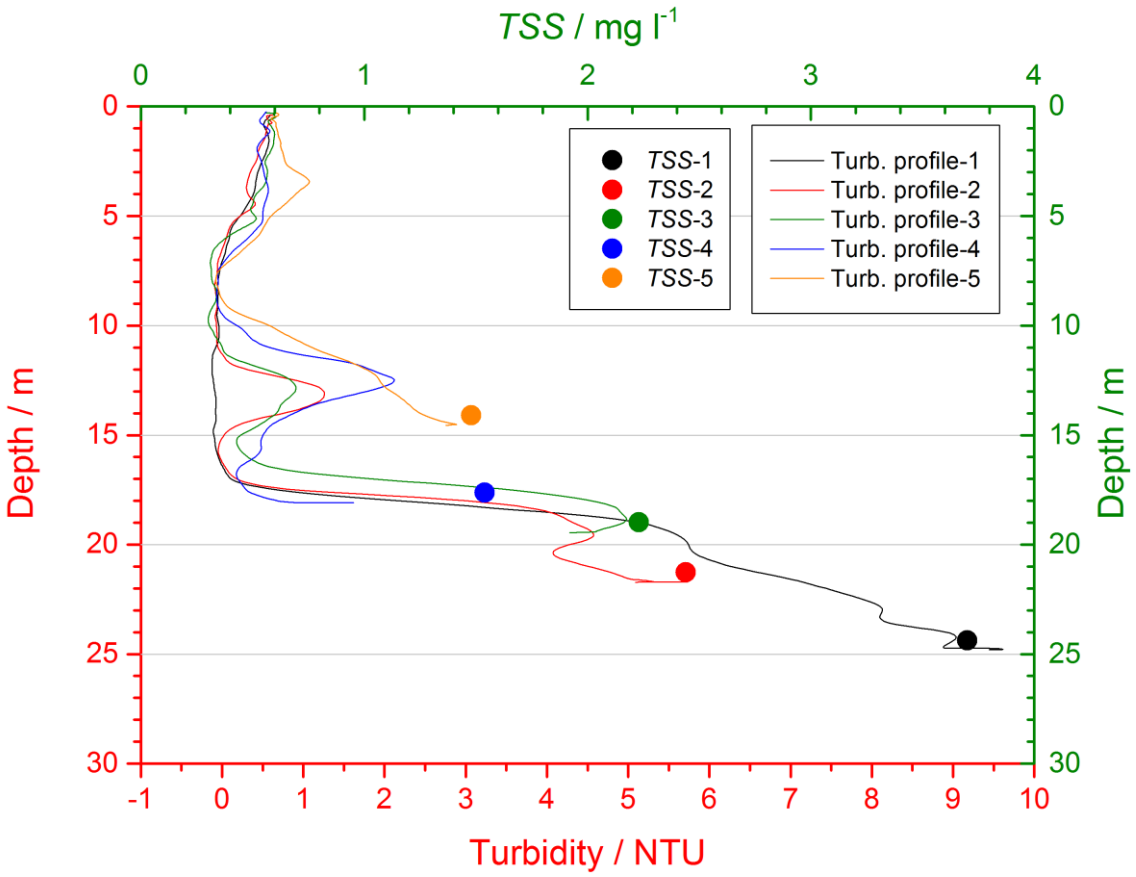

Fig. 6 - Repeated Turbidity profiles and corresponding *TSS* measures.

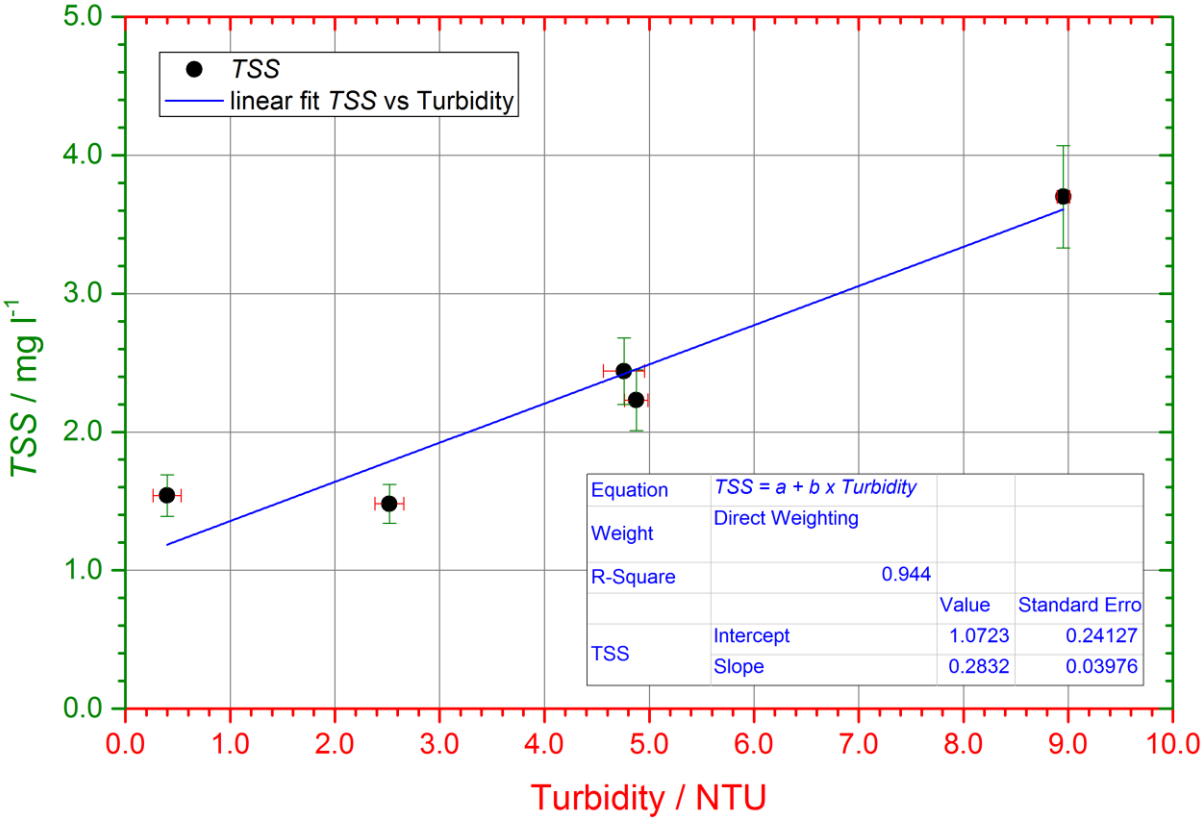

Fig. 7 - Linear relation between *TSS* and Turbidity.

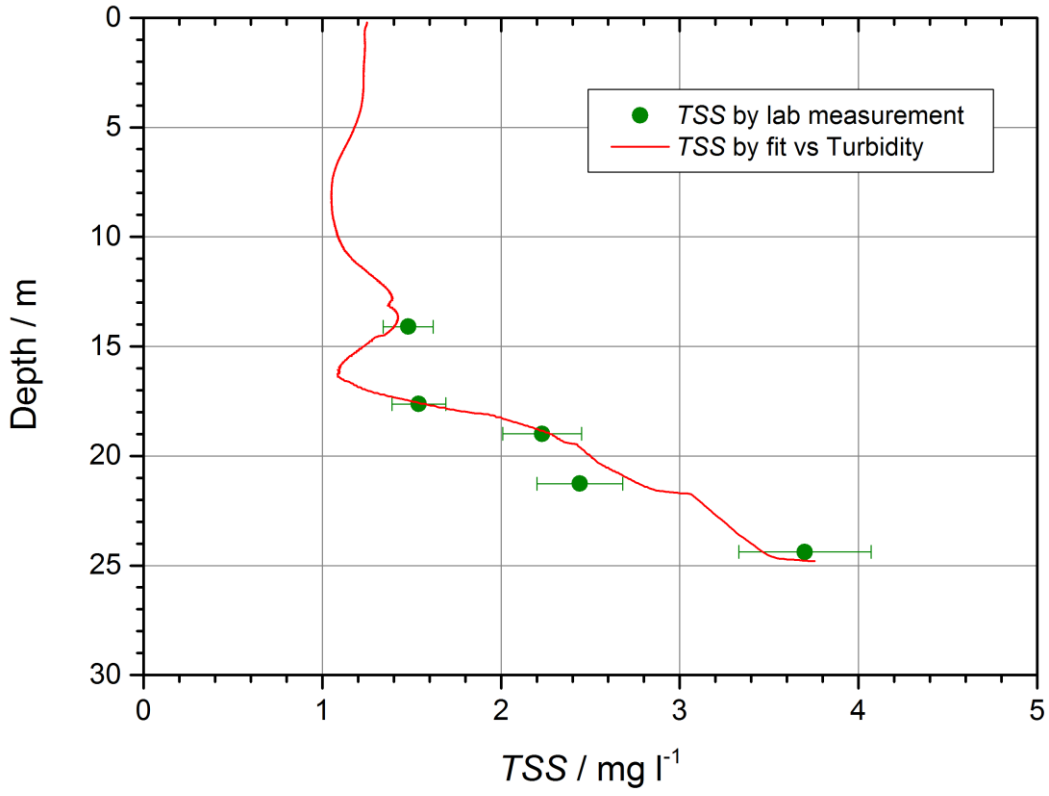

Fig. 8 - *TSS* discrete measures and continuous profile obtained by *TSS* vs Turbidity relation.

Tables

6 • Standard uncertainty of balance error

		symbol	u.m.											Distribution/ source	DOF
	Nominal load	L	g	20	40	60	80	100	120	140	160	180	200		
	Load composition	L	g	20	20+20°	50+10	50+20+10	100	100+20	100+20+20°	100+50+10	100+50+20+10	200		
	Error	$E(m)$	g	0.00018	0.00041	0.00054	0.00063	0.00097	0.00119	0.00153	0.00161	0.00198	0.00209		
Balance standard uncertainty	Standard uncertainty of resolution at null load	$u(\delta l_{dig0})$	g					0.00003						rectangular	∞
	Standard uncertainty of resolution under load	$u(\delta l_{digL})$	g					0.00003						rectangular	∞
	Repeatability standard uncertainty	$u(\delta l_{rep})$	g					0.00011						normal	9
	Eccentricity standard uncertainty	$u(\delta l_{ecc})$	g	0.00003	0.00007	0.00010	0.00014	0.00017	0.00021	0.00024	0.00028	0.00031	0.00035	rectangular	∞
Reference mass standard uncertainty	Mass standard uncertainty	$u(\delta m_c)$	g	0.00002	0.00004	0.00004	0.00006	0.00003	0.00005	0.00007	0.00007	0.00009	0.00004	cal. certificate	∞
	Standard uncertainty due to buoyancy	$u(\delta m_b)$	g	0.00021	0.00042	0.00059	0.00080	0.00094	0.00115	0.00136	0.00153	0.00174	0.00188	ref. standard	∞
	Standard uncertainty due to time drift of m_c	$u(\delta m_D)$	g	0.00014	0.00029	0.00029	0.00043	0.00029	0.00043	0.00058	0.00058	0.00072	0.00058	rectangular	∞
	Standard uncertainty due to convection	$u(\delta m_{conv})$	g	negligible (having respected the thermal stabilization period between masses and balance)										---	---
	Standard uncertainty due to room temperature	$u(\delta m_{\Delta T})$	g	0.00003										rectangular	∞
	Standard uncertainty of the error	$u_c(E(m))$	g	**0.00028**	**0.00053**	**0.00068**	**0.00093**	**0.00100**	**0.00125**	**0.00150**	**0.00166**	**0.00191**	**0.00200**		
	Effective degrees of freedom	ν_{eff}	---	438	5248	14240	50448	68543	164705	341314	516225	903683	1072357		
	Coverage factor (95 %)	k_{eff}	---	1.965	1.960	1.960	1.960	1.960	1.960	1.960	1.960	1.960	1.960		
	Expanded uncertainty	$U(E(m))$	---	0.00056	0.00104	0.00133	0.00182	0.00197	0.00245	0.00294	0.00326	0.00375	0.00391		

Table 1 - Measurement errors and associated uncertainties as obtained by full scale balance calibration.

6 • Standard uncertainty of balance error

		symbol	u.m.											Distribution/ source	DOF
	Nominal load	L	g	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008	0.009	0.010		
	Load composition	L	g	0.001	0.002	0.001+0.002	0.002+0.002*	0.005	0.005+0.001	0.005+0.002	0.005+0.002+0.001	0.005+0.002+0.002*	0.010		
	Error	$E(m)$	g	0.00004	0.00004	0.00004	0.00009	0.00000	0.00004	-0.00006	0.00003	0.00013	-0.00006		
Balance standard uncertainty	Standard uncertainty of resolution at null load	$u(\delta I_{dig\,0})$	g	0.00003										rectangular	∞
	Standard uncertainty of resolution under load	$u(\delta I_{dig\,I})$	g	0.00003										rectangular	∞
	Repeatability standard uncertainty	$u(\delta I_{rep})$	g	0.00005										normal	9
	Eccentricity standard uncertainty	$u(\delta I_{ecc})$	g	0.00001	0.00001	0.00002	0.00002	0.00003	0.00003	0.00004	0.00005	0.00005	0.00006	rectangular	∞
Reference mass standard uncertainty	Mass standard uncertainty	$u(\delta m_{cl})$	g	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	cal. certificate	∞
	Standard uncertainty due to buoyancy	$u(\delta m_B)$	g	0.00001	0.00001	0.00002	0.00003	0.00001	0.00002	0.00002	0.00002	0.00004	0.00001	ref. standard	∞
	Standard uncertainty due to time drift of m_c	$u(\delta m_D)$	g	0.00001	0.00001	0.00002	0.00002	0.00001	0.00002	0.00002	0.00003	0.00003	0.00001	rectangular	∞
	Standard uncertainty due to convection	$u(\delta m_{conv})$	g	negligible (having respected the thermal stabilization period between masses and balance)									---	---	
	Standard uncertainty due to room temperature	$u(\delta m_{\Delta T})$	g	0.00000										rectangular	∞
	Standard uncertainty of the error	$u_c(E(m))$	g	0.00007	0.00007	0.00007	0.00008	0.00007	0.00008	0.00008	0.00009	0.00010	0.00009		
	Effective degrees of freedom	ν_{eff}	---	26	27	36	50	35	48	55	82	116	76		
	Coverage factor (95 %)	k_{eff}	---	2.060	2.056	2.030	2.010	2.032	2.011	2.004	1.990	1.981	1.992		
	Expanded uncertainty	$U(E(m))$	---	0.00014	0.00014	0.00015	0.00016	0.00015	0.00016	0.00017	0.00018	0.00020	0.00018		

Table 2 - Measurement errors and associated uncertainties as obtained by balance calibration up to 10 mg.

Volume of filtered seawater V	Standard uncertainty components for input quantities X_i				u_A	u_B	ν_i	$u^2(x_i)$	$c_i = \partial f/\partial x_i$	$u^2_i(V)=c^2_i \cdot u^2(x_i)$	$u^4_i(V)/\nu_i$
	X_i	type	source	standard uncertainty by	ml	ml		ml^2		ml^2	ml^4
direct measurement $V = f(V_i) = V_1 + V_2$	V_1	calibration	manufacturer's specifications	mpe* (± 20 ml)		12	∞	1.3E+02	1	1.3E+02	0.0E+00
		resolution	operator's estimate of meniscus position**	1/10 of subdivision (20 ml)		1	100	3.3E-01	1	3.3E-01	1.1E-03
	V_2	calibration	manufacturer's specifications	mpe (± 20 ml)		12	∞	1.3E+02	1	1.3E+02	0.0E+00
		resolution	operator's estimate of meniscus position	1/10 of subdivision (20 ml)		1	100	3.3E-01	1	3.3E-01	1.1E-03
* maximum permissible error - ** the quality of the information is considered "very funded"									$u^2_c(V)$ [ml^2]	2.7E+02	
									$u_c(V)$ [ml] and actual DOF	16	32160200
									coverage probability *prob*		0.95
									coverage factor $k = t$ (*prob* , DOF)		1.960
									expanded uncertainty $U(V)$ [ml]		32

Table 3 - Standard uncertainty of volume measure.

***TSS* repeatability**

V	Δm	*TSS*
l	mg	mg l^{-1}
3	5.7	**1.90**
3	6.4	**2.13**
3	5.8	**1.93**
3	6.0	**2.00**
3	5.1	**1.70**
3	5.6	**1.87**
3	6.1	**2.03**
3	6.8	**2.27**
3	5.6	**1.87**

mean *TSS*	**1.97**	mg l^{-1}
SD	**0.17**	mg l^{-1}
$u_{rep}(TSS)$	**8.4**	%

Table 4 - Evaluation of *TSS* repeatability.

Appendices

In the following, details on balance calibration procedure and results are supplied.

A- Balance Calibration: full scale (200 g)

Balance calibration carried out internally to ENEA on 2021-06-28

Reference standards

- ACCREDIA DT-06-DT, rev.00 (25 Giugno 2013): Guida per la taratura di strumenti per pesare a funzionamento non automatico
- Euramet Calibration Guide No. 18, Version 4.0 (11/2015): Guidelines on the Calibration of Non-Automatic Weighing Instruments
- OIML R 111-1, Edition 2004 (E), INTERNATIONAL RECOMMENDATION, Weights of classes E1, E2, F1, F2, M1, M1–2, M2, M2–3 and M3

Steps 1 - 5

1 Balance type

• Manufacturer:	OHAUS Corp.		
• Model:	PA214 C		
• Serial number:	8730022552		
Metrological features			
• Maximum load:	210	g	
• Resolution:	0.0001	g	
Other			
• Start and end time of calibration:	09:00 / 10:00		
• Temperature:	23.0 / 23.2	°C	
• Eccentricity load:	50	g	5 position of measurement
• Repeatability load:	200	g	10 repeated measurements
• Linearity test:	10 loads	(10 % max load)	increasing and decreasing loads

- Acclimatization time of calibration masses near the balance: >12 h
- Before the load is applied, the balance is reset to zero

2 Standard masses used for balance calibration

- CIBE weight set from 1 mg to 200 g, inox steel, s.n. B11036
- Calibration certificate: LAT 117 18/1112, date: 2018-03-29 (five-year validity)

m_N	m_c	$U(m_c)$	$u(m_c)$	OIML Class	mpe
g	g	mg	g		mg
10	10.000067	0.041	0.000021	**F1**	0.20
20	20.000073	0.042	0.000021	**F1**	0.25
20°	20.000063	0.042	0.000021	**F1**	0.25
50	50.000092	0.044	0.000022	**F1**	0.3
100	100.000134	0.058	0.000029	**F1**	0.5
200	200.000214	0.081	0.000041	**F1**	1.0

3 • Eccentricity test

nominal load used: 50 g

Position	I_i	$\Delta I_{ecc,i}$	$\lvert\Delta I_{ecc,i}\rvert$
	g	g	g
1	50.0004	---	---
2	50.0003	-0.0001	0.0001
3	50.0004	0.0000	0.0000
4	50.0007	0.0003	0.0003
5	50.0006	0.0002	0.0002

eccentricity error:

ΔI_{ecc} 0.0003 g

4 ● **Repeatability test**

nominal load used: 200 g

n.	I_i g
1	200.0021
2	200.0022
3	200.0022
4	200.0021
5	200.0020
6	200.0020
7	200.0020
8	200.0019
9	200.0020
10	200.0019

balance standard deviation:

s_L 0.0001 g

5 ● **Linearity test with increasing and decreasing loads**

			increasing load			decreasing load		
			indication	error		indication	error	
n.	m_N g	m_c g	I_i g	I_i-m_c g	n.	I_i g	I_i-m_c g	mean error g
0	0	0	0.0000	0.0000	21	0.0000	0.0000	0.0000
1	20	20.000073	20.0003	0.0002	20	20.0002	0.0001	0.0002
2	40	40.000136	40.0007	0.0006	19	40.0004	0.0003	0.0004
3	60	60.000159	60.0007	0.0005	18	60.0007	0.0005	0.0005
4	80	80.000232	80.0009	0.0007	17	80.0008	0.0006	0.0006
5	100	100.000134	100.0011	0.0010	16	100.0011	0.0010	0.0010
6	120	120.000207	120.0014	0.0012	15	120.0014	0.0012	0.0012
7	140	140.000270	140.0019	0.0016	14	140.0017	0.0014	0.0015
8	160	160.000293	160.0021	0.0018	13	160.0017	0.0014	0.0016
9	180	180.000366	180.0025	0.0021	12	180.0022	0.0018	0.0020
10	200	200.000214	200.0023	0.0021	11	200.0023	0.0021	0.0021

B- Balance Calibration: minimum scale (10 mg)

Balance calibration carried out internally to ENEA on 2021-06-28

Reference standards

● ACCREDIA DT-06-DT, rev.00 (25 Giugno 2013): Guida per la taratura di strumenti per pesare a funzionamento non automatico

● Euramet Calibration Guide No. 18, Version 4.0 (11/2015): Guidelines on the Calibration of Non-Automatic Weighing Instruments

● OIML R 111-1, Edition 2004 (E), INTERNATIONAL RECOMMENDATION, Weights of classes E1, E2, F1, F2, M1, M1–2, M2, M2–3 and M3

Steps 1 - 5 **1** **Balance type**

● Manufacturer:	OHAUS Corp.		
● Model:	PA214 C		
● Serial number:	8730022552		
Metrological features			
● Maximum load:	210	g	
● Resolution:	0.0001	g	
Other			
● Start and end time of calibration:	15:00 / 16:00		
● Temperature:	24.0 / 24.3	°C	
● Eccentricity load:	0.005	g	5 position of measurement
● Repeatability load:	0.010	g	10 repeated measurements
● Linearity test:	10 loads		increasing and decreasing loads

● Acclimatization time of calibration masses near the balance: >12 h

● Before the load is applied, the balance is reset to zero

2 Standard masses used for balance calibration

- CIBE weight set from 1 mg to 200 g, inox steel, s.n. B11036
- Calibration certificate: LAT 117 18/1112, date: 2018-03-29 (five-year validity)

m_N	m_c	$U(m_c)$	$u(m_c)$	OIML Class	mpe
mg	g	mg	g		mg
1	0.001006	0.0031	0.000002	**F1**	0.02
2	0.002006	0.0032	0.000002	**F1**	0.02
2°	0.002006	0.0032	0.000002	**F1**	0.02
5	0.005003	0.0030	0.000002	**F1**	0.02
10	0.010009	0.0032	0.000002	**F1**	0.025

3 ● Eccentricity test

nominal load used: 0.005 g

Posizione	I_i	$\Delta I_{ecc,i}$	$\lvert\Delta I_{ecc,i}\rvert$
	g	g	g
1	0.0050	---	---
2	0.0051	0.0001	0.0001
3	0.0050	0.0000	0.0000
4	0.0050	0.0000	0.0000
5	0.0049	-0.0001	0.0001

eccentricity error:

ΔI_{ecc} 0.0001 g

4 ● Repeatability test

nominal load used: 0.010 g

n.	I_i
	g
1	0.0099
2	0.0099
3	0.0100
4	0.0100
5	0.0100
6	0.0099
7	0.0100
8	0.0099
9	0.0099
10	0.0100

balance standard deviation:

s_L 0.0001 g

5 ● Linearity test with increasing and decreasing loads

			increasing load			decreasing load		
			indication	error		indication	error	
n.	m_N	m_c	I_i	I_i-m_c	n.	I_i	I_i-m_c	errore medio
	g	g	g	g		g	g	g
0	0	0	0.0000	0.0000	21	0.0000	0.0000	0.0000
1	0.001	0.001006	0.0010	0.0000	20	0.0011	0.0001	0.0000
2	0.002	0.002006	0.0020	0.0000	19	0.0021	0.0001	0.0000
3	0.003	0.003012	0.0031	0.0001	18	0.0030	0.0000	0.0000
4	0.004	0.004012	0.0040	0.0000	17	0.0042	0.0002	0.0001
5	0.005	0.005003	0.0050	0.0000	16	0.0050	0.0000	0.0000
6	0.006	0.006009	0.0060	0.0000	15	0.0061	0.0001	0.0000
7	0.007	0.007009	0.0069	-0.0001	14	0.0070	0.0000	-0.0001
8	0.008	0.008015	0.0080	0.0000	13	0.0081	0.0001	0.0000
9	0.009	0.009016	0.0091	0.0001	12	0.0092	0.0002	0.0001
10	0.010	0.010009	0.0099	-0.0001	11	0.0100	0.0000	-0.0001

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